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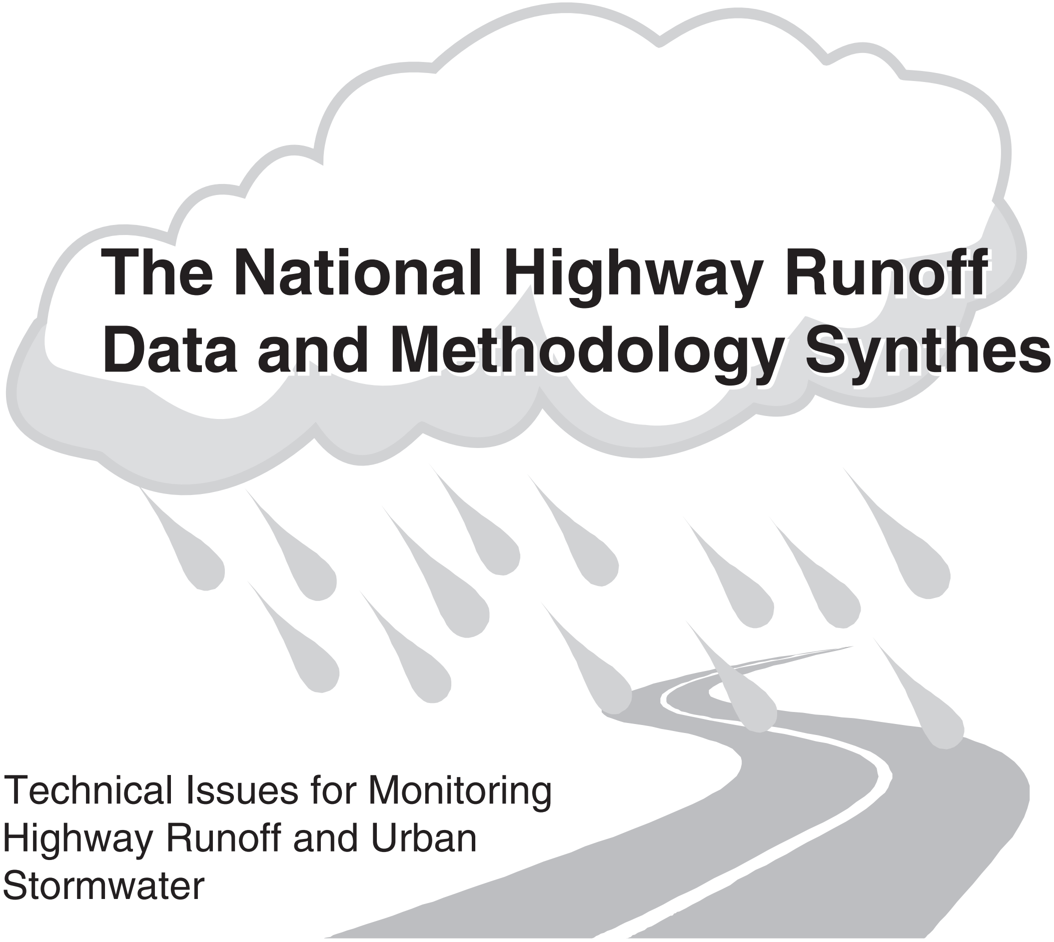

The National Highway Runoff Data and Methodology Synthesis

Volume I – Technical Issues for Monitoring Highway Runoff and Urban Stormwater

Office of Natural Environment
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16. Abstract

Knowledge of the characteristics of highway runoff (concentrations and loads of constituents and the physical and chemical processes that produce this runoff) is important for decision makers, planners, and highway engineers to assess and mitigate possible adverse impacts of highway runoff on the Nation's receiving waters. The Federal Highway Administration and the U.S. Geological Survey began the National Highway Runoff Data and Methodology Synthesis to provide a catalog of the pertinent information available; to define the necessary documentation to determine if data are valid (useful for intended purposes), current, and technically supportable; and to evaluate available sources in terms of current and foreseeable information needs.

This report is a compilation of "expert chapters" designed to address different technical issues for monitoring highway runoff and urban stormwater. These chapters include information about basic information and data quality; quality assurance and quality control practices; measurement of precipitation and runoff flow; the geochemistry of runoff; measurement of sediments, trace elements, and organic chemicals in runoff; assessment of the potential ecological effects of runoff; monitoring atmospheric deposition; and interpreting runoff data using appropriate statistical techniques. This paper is one volume in a three-volume series. The titles of these volumes are:

FHWA-EP-03-054	Volume I--Technical Issues for Monitoring Highway Runoff and Urban Stormwater
FHWA-EP-03-055	Volume II--Project Documentation
FHWA-EP-03-056	Volume III--Availability and documentation of published information for synthesis of regional or national highway-runoff quality data

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PREFACE

Knowledge of the characteristics of highway runoff (concentrations and loads of constituents and the physical and chemical processes which produce this runoff) is important for decision makers, planners, and highway engineers to assess and mitigate possible adverse-impacts of highway runoff on the Nation’s receiving waters. In October 1996, the Federal Highway Administration and the U.S. Geological Survey began the National Highway Runoff Data and Methodology Synthesis to provide a catalog of the pertinent information available; to define the necessary documentation to determine if data are valid (useful for intended purposes), current, and technically supportable; and to evaluate available sources in terms of current and foreseeable information needs. This paper is one contribution to the National Highway Runoff Data and Methodology Synthesis. More information about this project is available on the World Wide Web at http://ma.water.usgs.gov/fhwa/

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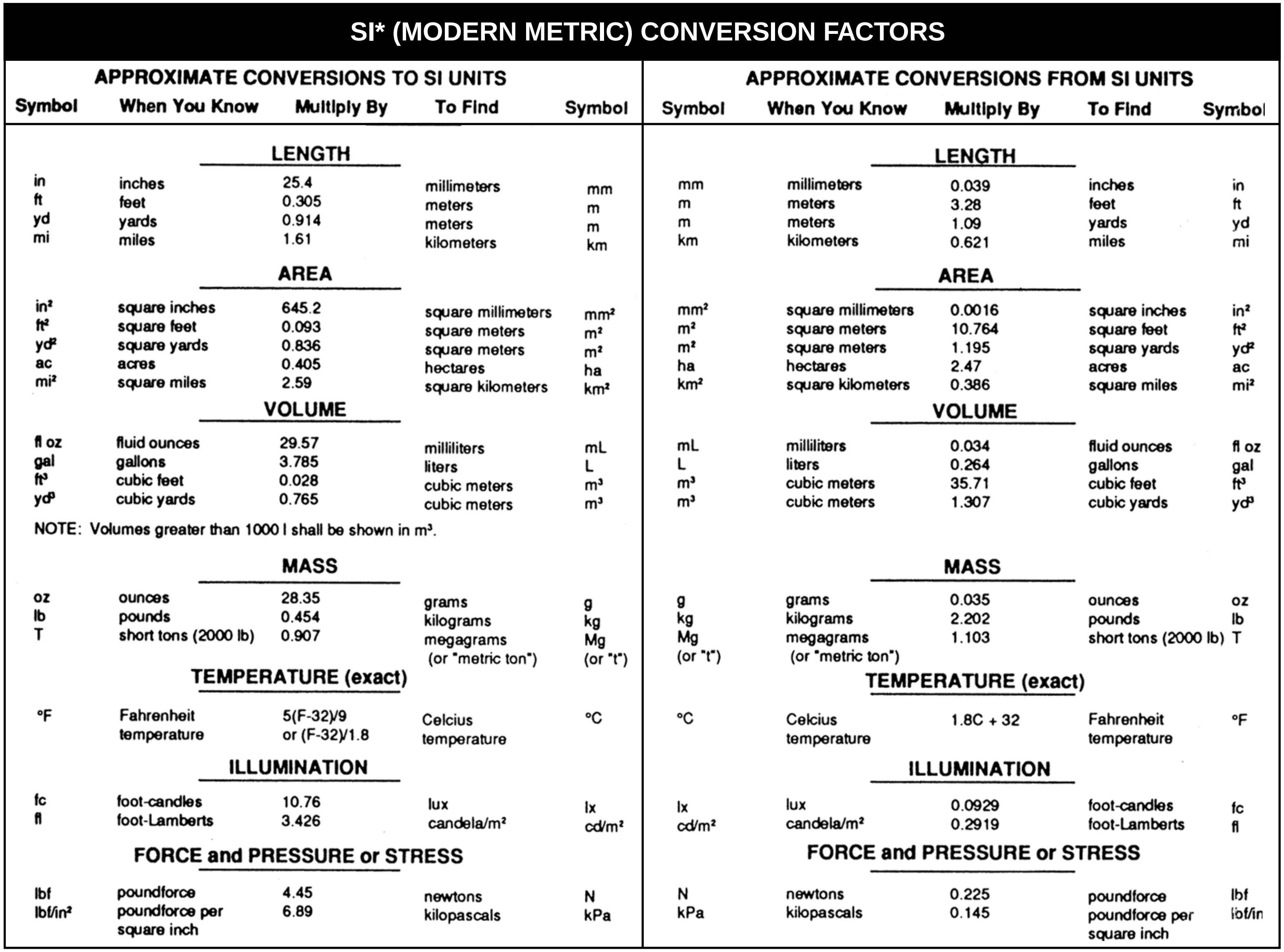

SI* (MODERN METRIC) CONVERSION FACTORS

APPROXIMATE CONVERSIONS TO SI UNITS

Symbol	When You Know	Multiply By	To Find	Symbol
		LENGTH		
in	inches	25.4	millimeters	mm
ft	feet	0.305	meters	m
yd	yards	0.914	meters	m
mi	miles	1.61	kilometers	km
		AREA		
in^2	square inches	645.2	square millimeters	mm^2
ft^2	square feet	0.093	square meters	m^2
yd^2	square yards	0.836	square meters	m^2
ac	acres	0.405	hectares	ha
mi^2	square miles	2.59	square kilometers	km^2
		VOLUME		
fl oz	fluid ounces	29.57	milliliters	mL
gal	gallons	3.785	liters	L
ft^3	cubic feet	0.028	cubic meters	m^3
yd^3	cubic yards	0.765	cubic meters	m^3
NOTE: Volumes greater than 1000 l shall be shown in m^3.				
		MASS		
oz	ounces	28.35	grams	g
lb	pounds	0.454	kilograms	kg
T	short tons (2000 lb)	0.907	megagrams (or "metric ton")	Mg (or "t")
		TEMPERATURE (exact)		
°F	Fahrenheit temperature	5(F-32)/9 or (F-32)/1.8	Celcius temperature	°C
		ILLUMINATION		
fc	foot-candles	10.76	lux	lx
fl	foot-Lamberts	3.426	candela/m^2	cd/m^2
		FORCE and PRESSURE or STRESS		
lbf	poundforce	4.45	newtons	N
lbf/in^2	poundforce per square inch	6.89	kilopascals	kPa

APPROXIMATE CONVERSIONS FROM SI UNITS

Symbol	When You Know	Multiply By	To Find	Symbol
		LENGTH		
mm	millimeters	0.039	inches	in
m	meters	3.28	feet	ft
m	meters	1.09	yards	yd
km	kilometers	0.621	miles	mi
		AREA		
mm^2	square millimeters	0.0016	square inches	in^2
m^2	square meters	10.764	square feet	ft^2
m^2	square meters	1.195	square yards	yd^2
ha	hectares	2.47	acres	ac
km^2	square kilometers	0.386	square miles	mi^2
		VOLUME		
mL	milliliters	0.034	fluid ounces	fl oz
L	liters	0.264	gallons	gal
m^3	cubic meters	35.71	cubic feet	ft^3
m^3	cubic meters	1.307	cubic yards	yd^3
		MASS		
g	grams	0.035	ounces	oz
kg	kilograms	2.202	pounds	lb
Mg (or "t")	megagrams (or "metric ton")	1.103	short tons (2000 lb)	T
		TEMPERATURE (exact)		
°C	Celcius temperature	1.8C + 32	Fahrenheit temperature	°F
		ILLUMINATION		
lx	lux	0.0929	foot-candles	fc
cd/m^2	candela/m^2	0.2919	foot-Lamberts	fl
		FORCE and PRESSURE or STRESS		
N	newtons	0.225	poundforce	lbf
kPa	kilopascals	0.145	poundforce per square inch	lbf/in

* SI is the symbol for the International System of Units. Appropriate rounding should be made to comply with Section 4 of ASTM E380.

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The National Highway Runoff Data and Methodology Synthesis—Volume 1. Technical Issues for Monitoring Highway Runoff and Urban Stormwater

By Gregory E. Granato, Chester Zenone, *and* Patricia A. Cazenas (editors)

INTRODUCTION

The Federal Highway Administration's (FHWA) mission is to improve the quality of our Nation's highway system and its intermodal connections by providing leadership, expertise, resources and information in cooperation with its partners to enhance the country's economic vitality, the quality of life and to protect and enhance the natural environment and communities potentially affected by highway transportation (FHWA, 2000). Among other information needs, sound water-quality data are needed to provide a basis for regional and national transportation policy decisions. Water-quality data also are needed for planning, design, construction, and operation of our Nation's transportation infrastructure and for implementing best management practices (BMPs) designed to minimize the effect of transportation on the environment. Decisionmakers need robust information on local, regional, and national-highway runoff and urban stormwater, including the magnitudes of flows, the concentrations and loads of chemical constituents and sediment, the potential effects on receiving waters, and the effectiveness of BMPs, as well as viable methods for interpretation of this information and data. The mission of the U.S. Geological Survey (USGS) is to assess the quantity and quality of the earth and biological resources of the Nation and to provide information that will assist resource managers and policymakers at Federal, State, and local levels in making sound decisions (USGS, 1999). In a merging of the mission and information needs of the FHWA and the mission of the USGS, the two agencies began the National Highway Runoff Data and Methodology Synthesis (NDAMS) to provide a catalog of the available information; to define the documentation necessary to determine if the available data are valid (useful for intended purposes), current, and technically supportable.

The NDAMS project includes an extensive literature search to catalog available reports in a centralized database, a metadata review program to evaluate available reports, and an interpretive effort to assess the results of the metadata review in terms of current and foreseeable regional or national runoff-quality information needs. Results of the synthesis are documented in a three-volume series of reports. These reports are designed to examine technical issues to establish the review criteria (this volume), to document the review process and results of this National synthesis (volume II), and to provide an interpretation of the availability and documentation of published information for use in regional or national highway-runoff quality studies (volume III).

This volume is organized into 10 "expert chapters," each designed to provide a focused synopsis of technical issues of concern for interpretation of highway and urban runoff data. A team of subject-matter experts was assembled to examine technical issues associated with the collection, processing, interpretation, and documentation of data that would be valid, current, comparable, and technically defensible for individual studies and for subsequent regional and (or) national synthesis of highway-runoff data. Experts from the USGS Water Resources and

Biological Resources Disciplines combined their input with that from State and Federal environmental and transportation agencies to establish key issues and data-evaluation criteria based upon the current state-of-the-art. Each chapter focuses on one aspect of highway-runoff-quality investigations that were used to produce the NDAMS program review sheets (Dionne and others, 1999). These "expert chapters" document criteria for monitoring the quality of runoff including: basic information and data quality; quality assurance and quality control; precipitation and runoff flow; the geochemistry of runoff; sediments in runoff; trace elements in runoff; organic chemicals in runoff; the potential ecological effects of runoff; monitoring atmospheric deposition; and the statistical interpretation of runoff data.

The "expert chapters" included in this volume may be viewed in two ways. They were designed to provide objective criteria for evaluation of existing reports. These "expert chapters" also provide information and perspectives, as well as a summary of concerns and research needs, with which to evaluate future efforts to characterize runoff quality, so that the information and data generated by runoff monitoring programs will be valuable for local, regional, and national needs.

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Chapter 1. Data Quality Objectives and Criteria for Basic Information, Acceptable Uncertainty, and Quality-Assurance and Quality-Control Documentation

By GREGORY E. GRANATO, FRED G. BANK, and
PATRICIA A. CAZENAS

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Data Quality Objectives and Criteria for Basic Information, Acceptable Uncertainty, and Quality-Assurance and Quality-Control Documentation

By Gregory E. Granato, Fred G. Bank, *and*
Patricia A. Cazenas

Abstract

The Federal Highway Administration and State transportation agencies have the responsibility of determining and minimizing the effects of highway runoff on water quality; therefore, they have been conducting an extensive program of water-quality monitoring and research during the last 25 years. The objectives and monitoring goals of highway runoff studies have been diverse, because the highway community must address many different questions about the characteristics and impacts of highway runoff. The Federal Highway Administration must establish that available data and procedures that are used to assess and predict pollutant loadings and impacts from highway stormwater runoff are valid, current, and technically supportable.

This report examines criteria for evaluating water-quality data and resultant interpretations. The criteria used to determine if data are valid (useful for intended purposes), current, and technically supportable are derived from published materials from the Federal Highway Administration, the U.S. Environmental Protection Agency, the Intergovernmental Task Force on Monitoring Water Quality, the U.S. Geological Survey and from technical experts throughout the U.S. Geological Survey.

Water-quality data that are documented to be meaningful, representative, complete, precise, accurate, comparable, and admissible as legal evidence will meet the scientific, engineering, and regulatory needs of highway agencies. Documentation of basic information, such as compatible monitoring objectives and program design features; metadata (when, where, and how data were collected as well as who collected and analyzed the data); ancillary information (explanatory variables and study-site characteristics); and legal requirements are needed to evaluate data. Documentation of sufficient quality-assurance and quality-control information to establish the quality and uncertainty in the data and interpretations also are needed to determine the comparability and utility of data sets for intended uses. The fact that a program's data may not meet screening criteria for a national synthesis does not mean that the data are not useful for meeting that program's objectives or that they could not be used for water-quality studies with different objectives.

INTRODUCTION

The Federal Highway Administration (FHWA) and State transportation agencies (STAs) are responsible for determining and minimizing the effects of highway runoff on the quality of receiving waters while planning, designing, building, operating, and maintaining the Nation's highway infrastructure. This responsibility is established by Federal and State legislation, including the National Environmental Policy Act, the Clean Water Act, the Safe Drinking Water Act, the Coastal Zone Management Act, and other legislation, as well as derivative rules, regulations, executive orders, and policies (FHWA, 1986; Young and others, 1996). Federal and State environmental agencies are increasing efforts to quantify and regulate sources of nonpoint-source pollution through mandatory monitoring programs and to establish best management practices (BMPs) to minimize the impact of these sources (FHWA, 1986; Young and others, 1996). As part of this effort, the FHWA has tried to supply valid, current, and defensible legal and technical information relating to the quality of highway runoff. In this report, the term "information" refers to the documentation of the characteristics of the study, the study site, and processes used to collect, analyze, interpret and validate the data collected. The term "data" refers to documented measurements made in the field, or to results of laboratory analysis of samples collected in the study.

The FHWA, in conjunction with many STAs, has conducted an extensive program of water-quality monitoring and research during the last 25 years (Smith and Lord, 1990). The objectives and monitoring goals of highway runoff have been diverse. Data from different highway runoff studies have been combined to

- Characterize various physical properties and chemical constituents in highway runoff;
- Determine pollutant loads for constituents in highway runoff;
- Assess the effects of highway stormwater discharges on receiving waters;
- Identify the sources and mechanisms that determine the quantity of pollutants in highway runoff;
- Develop information for the design and operation of BMPs;
- Respond to regulatory monitoring requirements and litigation; and
- Predict the impacts of highway runoff on surface- and ground-water quality for aquatic life, human consumption, and recreational and industrial uses.

Diverse study objectives and monitoring goals impose different data and information requirements. As study objectives and monitoring goals increase in complexity, the cost and data requirements increase and the level of acceptable uncertainty decreases. Preliminary monitoring at a single site may require only a few samples. However, complex scientific investigations designed to characterize physical and chemical processes, or to develop design or predictive methods may require thousands of samples over an extended period of time (Sonnen, 1983). To date, information and water-quality data from relatively few highway-runoff monitoring studies (fig. 1) have been available

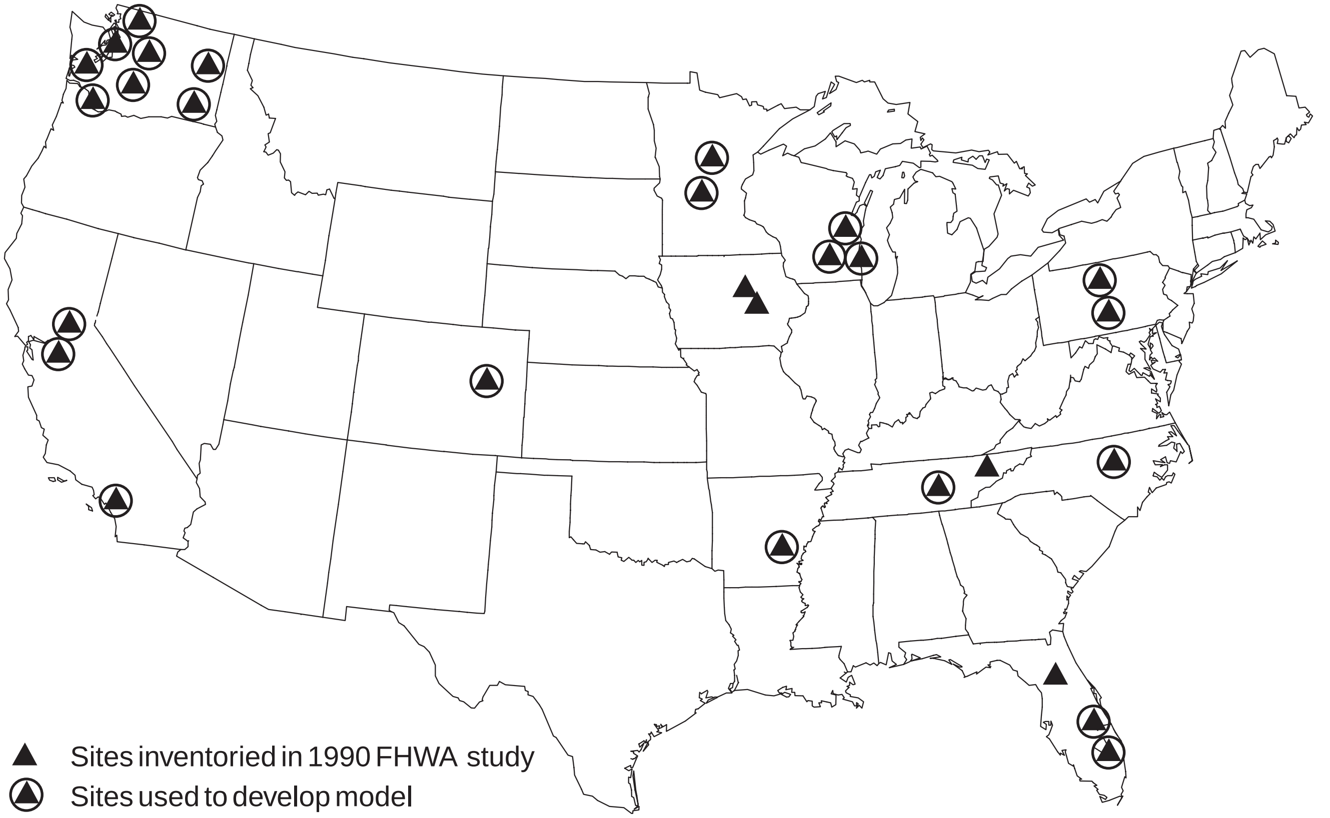

Figure 1. Locations of highway-runoff study sites inventoried during the 1990 study and sites used by the FHWA to develop the water-quality prediction model (modified from Driscoll and others, 1990, Volume III).

to support planning, design, construction, operation, and maintenance decisions for the Nation's highway infrastructure.

Problem

The FHWA must verify that available data and procedures used to support decisions concerning highway runoff are valid (useful for intended purposes), current, and technically supportable. The validity of historical data can be difficult to determine if documentation is not sufficient to substantiate the quality of the data. Also, continuing changes in sources of highway-runoff pollutants add increasing uncertainty as to the current validity and utility of historical data sources. Such changes include the disappearance of leaded fuels (Young and others, 1996); the development and use of new and potentially problematic fuel additives, such as Methyl*tert*-butyl ether (MTBE) (Delzer and others, 1996); and changes in materials used for automobiles (Helmers, 1996) and highway construction, such as pulverized rubber tires in pavement mixtures (Young and others, 1996).

To demonstrate that water-quality data are valid and technically supportable, sufficient documentation must be available to prove that the data are meaningful, representative, complete, precise, accurate, comparable, repeatable, and admissible as legal evidence (Alm and Messner, 1984; FHWA, 1986; ITFM, 1995a, 1995b; USEPA, 1997). These terms have operational definitions that are used to determine data-evaluation criteria for this investigation. Although the concepts intertwine, each is a distinctive part of the evaluation process. For data to be meaningful, they must be collected as part of a study designed to examine a typical highway site largely free from the influence of a unique contributing source. For example, the data set collected for the Washington State Department of Transportation during the eruption of Mount St. Helens may be representative, complete, precise, accurate, comparable, and admissible as legal evidence, but it can not be considered meaningful in characterizing typical highway-runoff quality (Driscoll and others, 1990b). A data set that is representative accurately and precisely characterizes a population, a process, and parameter variations at a study site. A data set that is complete contains enough representative information to characterize the uncertainties in the data and resultant interpreted values. For example, a data set may completely define water-quality characteristics for one storm, but a one-storm data set would not characterize differences from storm to storm, season to season, or year to year. To be considered complete, a data set from a monitoring study should characterize seasonality over more than 1 year because annual highway-runoff solute loads have been shown to vary from approximately 50 percent to 200 percent of the median from year to year over a 5-year period (Granato, 1996). Precision implies a high degree of repeatability for samples obtained under similar conditions. Accuracy implies a lack of bias (no systematic errors). Data that are comparable are taken from the same matrix, such as the water column, suspended solids, sediment, or biota by using documented sampling and analysis methods demonstrated to produce results with similar and acceptable levels of bias and variability. Data sets that are admissible as legal evidence must contain enough information to withstand any reasonable challenge to their quality and veracity.

The quality and quantity of environmental data required to support a decision can vary greatly depending on the nature and scope of the problem and the regulatory environment. However, a national synthesis requires robust data-evaluation criteria to ensure adequate representation of the different characteristics and natural settings of U.S. highways and maximum utility of data sets for scientific, engineering, and regulatory needs of highway agencies. The U.S. Environmental Protection Agency (USEPA) and the Intergovernmental Task Force on Monitoring Water Quality (ITFM) have established criteria for water-quality data to be included in national data bases (USEPA, 1994, 1996; ITFM, 1995a, 1995b). Review of data within the context of currently accepted environmental data-quality specifications and objectives for a national synthesis is necessary to establish the accuracy of available information. A well-defined data set is important because decision makers increasingly bear personal as well as institutional responsibility for the veracity of environmental monitoring information that is collected to meet regulatory purposes (Young and others, 1996).

Purpose and Scope

The purpose of this report is to evaluate data-quality criteria that are used to examine a sampling of the available highway-runoff data sets that were collected during the last 25 years. This report outlines the data quality objectives process, describes basic information requirements, assesses acceptable uncertainty, and provides an overview of necessary quality-assurance and quality-control information. These criteria are needed to demonstrate that existing information is valid, current, and technically supportable for current and future uses. The criteria were derived from published materials from the FHWA, USEPA, ITFM, and U.S. Geological Survey (USGS). Input from technical subject-matter experts throughout the USGS also were used to determine the evaluation criteria.

The choice of criteria for this national synthesis reflects the potential difficulties involved in combining data from diverse programs to develop a data base that covers broad geographical areas and catalogs consistent, technically sound water-quality data. The fact that a program's data may not meet these screening criteria does not mean that these data are not useful for meeting that program's objectives or that they could not be used for water-quality studies with objectives different from those stated herein. Some data sets may be disqualified because the required information for a particular study may not be sufficiently documented in available reports. A detailed investigation of each study would require on-site inspection, extensive interviews with program personnel, and a detailed examination of original records. Even if the appropriate people and original records were available, this type of effort would go far beyond the scope of this national synthesis.

DATA QUALITY OBJECTIVES

The data quality objectives (DQOs) process is designed to help weigh the costs of data acquisition against the consequences of a decision error caused by inadequate input data. The DQOs process also is intended to help weigh the costs and benefits of local short-term monitoring requirements against regional and national long-term information needs. Standards for quality assurance and quality control (QA/QC), comparability, and documentation must be higher for a national synthesis than for a local monitoring program to distinguish between real intersite differences and sampling artifacts. Strict national standards may add to monitoring costs on a case-by-case basis, but experience indicates that monitoring activities need to be improved and integrated to meet the full range of local, regional, and national information needs more effectively and economically (ITFM, 1995a).

The validity of data is, in some ways, a relative term. Data that are adequate for one purpose may be totally inadequate for another (Keith and others, 1983; USEPA, 1994). DQOs are used to define the degree to which experimental uncertainty in a data set must be controlled to achieve an acceptable level of confidence in a decision based on the data (USEPA, 1986, 1994, 1996; ITFM, 1995b). The concept of DQOs is meaningful only in relation to intended uses and risks of decision error. The quality of data that is required is dependent upon the problem at hand and local regulatory restrictions that can change with time. When problems pertaining to highway-runoff quality are evaluated, the DQO process can be used to determine the level of acceptable uncertainty and the resultant QA/QC needed to determine what data are appropriate for program objectives (USEPA, 1986, 1994). Once a problem is identified, the decision risks are evaluated, and resultant DQOs are defined, these criteria can be used to evaluate different program designs and (or) data sets (USEPA, 1994). DQOs also provide a standard for comparison for use in evaluating and combining different data sets for quantitative analysis (USEPA, 1996).

In the DQO process, decision errors are characterized as Type I or Type II errors. A Type I error occurs when a determination is made, on the basis of available data, that problems exist when they do not really exist. A Type II error occurs when real problems exist but the determination is made, on the basis of available data, that no problems exist. Substantially overestimating concentrations, loads, and the impacts of highway runoff pollutants—a Type I error—could intensify and lengthen regulatory processes, lead to changes in highway alignments, and force design changes and the adoption of additional BMPs. Therefore, a Type I error may increase costs for planning, design, construction, and maintenance of the Nation's highways. Substantially underestimating concentrations, loads, and the impacts of highway runoff pollutants—a Type II error—also can cause problems, incur high corrective costs, and negatively affect public perceptions about the veracity of environmental information provided by transportation agencies. Discovery of large prediction errors during the planning, design, and construction phases of a highway could increase costs. Type II errors discovered while monitoring runoff from a highway once it is in operation could result in regulatory actions, fines, and costs associated with additional BMPs.

The DQO process also applies to the interpretation of field data. The interpretive process, whether conceptual, statistical, or deterministic, is often the best means to synthesize available data into a form that will help determine the cause and effect relations that are used to support decisions. The financial and legal risks to decision makers and agencies for Type I or Type II errors will drive the selection of acceptable uncertainty levels for interpretive methods (USEPA, 1986, 1994). The interpretive process (including necessary simplifications and assumptions) propagates uncertainties generated in the data collection process. Once DQOs are established, however, the characteristics of the interpretive process can be used to determine the type, amount, and allowable uncertainty of data that are needed to support decisions (USEPA, 1994).

Information requirements for determining highway-runoff quality are diverse and vary from region to region, from state to state, and from situation to situation. Therefore, it is incumbent upon State, regional, and Federal decision makers and regulators to determine the DQOs necessary to address each issue. A single quantitative set of DQOs might either be too restrictive and disqualify a data set otherwise appropriate for a given use, or too vague and preclude useful predictive interpretations. Therefore, this study will evaluate a sample of available information to determine if existing reports sufficiently document the basic information, acceptable uncertainty, and QA/QC necessary to meet various DQOs that may be established by decisionmakers and regulators to evaluate a particular runoff issue.

BASIC INFORMATION REQUIREMENTS

To establish data quality and to ensure the usefulness of available water-quality information, basic information needed to evaluate the validity of the data and the methods of data collection and processing must be documented. For a national synthesis, data are useful only if collected and analyzed in a relatively consistent manner, because differences in methods commonly overshadow real variations caused by differences in the explanatory variables (ITFM, 1995a). The ITFM established metadata standards to describe the content, quality, and other characteristics that are needed to determine how useful a data set is for any particular application (ITFM, 1995a, 1995b). Basic data requirements include information about the monitoring objectives, sampling design, methods for collecting and handling samples, field and laboratory measurements, and data qualifiers.

In a review of water-quality data collected by Federal, State, and local water-quality monitoring entities, Hren and others (1987) defined five characteristics necessary to establish that data are useful. To be useful, data must be: (1) representative of the system under study; (2) available for public use as original data; (3) collected from a readily located sampling site (to assess data comparability and to interpret results of geographic/climatological variations); (4) associated with sufficient quality assurance (QA) information (to indicate the validity, reliability, and compatibility of data from different sources); and (5) available in useful computer files (to increase reliable compilation and manipulation of large volumes of data). These criteria were developed to screen data from diverse programs for inclusion in a database that could provide consistent, technically sound water-quality data representing broad geographic areas through time (Hren and others, 1987). A national synthesis of surface-water pesticide data concluded that quantitative synthesis may not be feasible when each study has unique objectives, sampling schedules, sampling and analysis methods, target analytes, detection limits, data presentation, and complete data sets that are not available in open literature (Larson and others, 1997).

Monitoring Objectives and Program Design

Study objectives and monitoring goals define where samples are collected, the frequency of collection, the timing and duration of sample collection, matrixes sampled, methods used, and properties and constituents that are analyzed (Hren and others, 1987; Larson and others, 1997). These characteristics can affect the applicability and availability of data for broad-scale studies. Data quality objectives determined by study objectives and monitoring goals define the maximum allowable errors consistent with the level of confidence in decisions made with data collected (USEPA, 1994). For example, in an analysis of urban-runoff monitoring requirements, Sonnen (1983) calculated that as few as 24 samples with about 6 analytes might be sufficient to provide information for BMP design equations at one site; whereas, 54,000 samples with about 100 analytes might be needed to determine physical and chemical processes and the environmental mechanisms that control concentrations of various stormwater constituents in a region. The purpose of many data-collection programs is to monitor problem sites; thus, data sets assembled from these programs are biased (Norris and others, 1990). Therefore, the study objectives and monitoring goals of a data-collection program may determine if results can be combined into a national synthesis without substantial qualifications on decisions made by using the assembled database.

Metadata Standards

Metadata standards established by the ITFM are designed to aid in the determination of data comparability among different monitoring programs. The ITFM defines comparability as the characteristics that allow data from multiple sources to be of such definable quality that the data can be used to address program objectives other than those for which the data were collected (ITFM, 1995b). To determine comparability, potential data users must be able to determine when, where, and how data were collected, as well as who collected and analyzed the data. The ITFM established the following minimum set of qualifiers to be documented with the sampling and analytical data:

- Parameter, property, constituent, or identifier evaluated;
- Sample matrix (the water column, suspended solids, sediment, atmospheric deposition, or biota);
- Methods for collection, handling, analysis, and interpretation;
- Type of data measured (concentration, population variable, or ratio);
- Location (latitude and longitude) of sampling point;
- Date and time of day sample was collected;
- Data collection and analyzing entities (who actually made the measurements);
- Data source (whose monitoring program); and
- Indication of data quality (including precision, bias, detection limits, and a defined QA/QC system).

Documentation of these basic criteria were evaluated and deemed essential in several reports written to examine the utility of data for regional or national water-quality assessment (U.S. General Accounting Office, 1981; Childress and others, 1987; Hren and others, 1987; Norris and others, 1990; Larson and others, 1997).

Ancillary Information

Ancillary information is also needed to evaluate available data for a national synthesis. Ancillary information about the characteristics of a study area may provide explanatory variables that can be used to standardize data to a common basis for comparison, or to account for some of the variability in the data (Norris and others, 1990). For example, flow data are needed for surface-water quality assessments because concentrations of many constituents are affected by changes in flow (Norris and others, 1990). In a study using a compiled database of approximately 2,800 storms measured at urban monitoring stations in metropolitan areas of 24 states, Driver and Tasker (1990) found that physical and climatic information, such as impervious area, land use, rainfall characteristics, and mean minimum January temperatures, were useful in determining loads and concentrations of stormwater constituents. Other characteristics, such as local geology, soil properties, and surrounding land and water use, also have been shown to be important characteristics for data evaluation. For example, Gupta and others (1981) indicated that a large percentage of highway runoff constituents are inorganic and are derived from local geologic materials.

Ancillary information also has proven useful in past evaluations of highway runoff pollution. Gupta and others (1981) determined that the concentrations and loads of constituents in highway runoff were affected by

- Highway design features;
- Traffic characteristics (speed, volume, braking, acceleration);
- Climatic conditions (amount, intensity, and form of precipitation);
- Maintenance policies (sweeping, mowing, repairing, deicing, and so forth);
- Surrounding land use (industrial, commercial, residential, or rural);
- Percentage of impervious area within the total drainage area;
- Type of pavement material;
- Average age of automobiles in the study area;

- Application of littering and vehicle emission laws;
- Use of additives in vehicular operation;
- Types of soils and vegetation along the highway right-of-way; and
- Local and regional atmospheric deposition.

Subsequent studies indicate that these characteristics, as well as the hardness of local waters, drainage system characteristics, and the implementation of BMPs influence the constituents in and effects of highway runoff (FHWA, 1986; Driscoll and others, 1990a; Young and others, 1996).

Legal Requirements

The FHWA and the STAs conduct most water-quality sampling for legal and scientific objectives. Data may be technically valid but not admissible in court. Consequently, sampling programs must be designed to produce legally admissible data (FHWA, 1986). In the regulatory and legal arena, the costs and penalties for submitting data and supporting information that are not deemed to be valid can be high for the responsible individuals and organizations (Mallan and others, 1993; Klodowski, 1996).

Data that are presented as legal evidence must meet three tests of admissibility; they must be shown to be (1) relevant (the data support a claim made in the case), (2) material (the claim addresses an issue in the case), and (3) competent (the data are valid, current and technically supportable). Relevance and materiality are highly case-specific, but competence can be controlled by using and documenting proper data-collection methods. Data sets that are admissible as legal evidence must contain enough information to withstand any reasonable challenge to their quality and veracity. To demonstrate competence, agencies must prove by documentation that data-collection methods are accepted by the scientific community and were performed properly, and that data were collected, verified, and interpreted by qualified personnel. For analytical data, documentation of the quality-control process and quality-assurance measurements should substantiate competence (Klodowski, 1996). The USEPA and FHWA require chain-of-custody information for authentication of water-quality samples to be admissible as legal evidence (FHWA, 1986).

The legal requirements for providing interpretive results are increasing as are the requirements for producing field and laboratory data (Haan and others, 1990). Defensible interpretations are increasingly dependent on the availability of information that documents the uncertainty and QA/QC practices that are used to develop, test, and verify interpretive models (Haan and others, 1990; Heijde, 1990; Water Science and Technology Board, 1990). For model results to be admissible in a technical or legal setting, it must be demonstrated that

- Underlying data are valid, unbiased, complete, and original or properly documented from a reliable source;
- The underlying theory of the model and modeling assumptions are correct;
- The computer programs properly implement the theory; and
- The programming and data processing were done accurately with sufficient safeguards against error.

Estimates of the uncertainty, the predictive accuracy, and the risks of an incorrect analysis are the determining factors when models and resultant interpretations are held to a legal standard of "truth" (Haan and others, 1990).

ACCEPTABLE UNCERTAINTY

Uncertainty is a measure of the errors and losses of information inherent in environmental studies that prevent the characterization of exact properties of the underlying distribution of that information (Ward and Loftis, 1983). The total uncertainty is the sum of uncertainty caused by natural variability, measurement errors, and interpretive generalizations. Environmental data collection always involves some error as an inherent characteristic of the hydrologic environment; sampling design; land-use history of the study area; and methods used for sample collection, sample analysis, and data interpretation (USEPA, 1986, 1994; Childress and others, 1987; Brown and others, 1991; Clark and Whitfield, 1993).

Rigorous uncertainty assessments are needed to determine if data are sufficiently valid and technically supportable, because the usefulness of water-quality data is inversely related to the amount of uncertainty in the data (Montgomery and Sanders, 1985). The acceptable uncertainty of data and interpretations for a given problem must be evaluated in terms of the regulatory objectives, the decisions to be made by using the data, and the possible consequences of making incorrect decisions (USEPA, 1986, 1994). The total uncertainty increases when data from different studies are combined because differences in analytical laboratories, methods, and the characteristics of pollutant sources through time are incorporated into the resultant data set. To support decisions, the level of total uncertainty from random and systematic error introduced into the different sampling processes must be less than the natural variability caused by differences from site to site and study to study.

Historically, inconsistent performance within and between analytical laboratories has been a constant and substantial source of uncertainty (U.S. General Accounting Office, 1981). Use of validated methods, reference laboratories, and experienced personnel does not ensure reliable analytical results (Keith and others, 1983). Participation in an interlaboratory comparison program is one component of good laboratory QA/QC practices. Results from a laboratory implementing good QA/QC practices should be more reliable than results from an uncontrolled analytical program.

Results of interlaboratory comparisons indicate that analytical uncertainties in data sets are larger than published values for the accuracy of standard methods. Different interlaboratory comparisons have documented consistent problems with accuracy, repeatability, and performance through time in the population of participating laboratories throughout the period of highway runoff research (General Accounting Office, 1981; Polvi and others, 1985; Farrar and Long, 1997). One study of analytical laboratories used for National Pollutant Discharge Elimination System (NPDES) compliance monitoring revealed that there was only a 32- to 42-percent chance that any given laboratory would measure all constituents within acceptable limits (Polvi and others, 1985).

An indication of analytical uncertainty in available data sets may be derived from examination of statistics for analytical results of natural-matrix reference samples from the USGS interlaboratory evaluation program (Farrar and Long, 1997). Interlaboratory statistics—for example the most probable value (MPV) of chromium concentrations and the estimated error of laboratory results—from the USGS program from 1989 through 1997 are shown in figure 2. The range of the MPV concentrations for these samples is within the ranges of measured concentrations for most metals reported as constituents in highway runoff (Smith and Lord, 1990). In the concentration ranges presented, percent accuracy increases with increasing concentration. The uncertainty for the “best” laboratories (those in the top 5 percent of the performance rating in the USGS interlaboratory evaluation program) ranged from plus or minus 100 to 3 percent of the MPV as concentration increased, but “most” laboratories (in the top 95 percent) ranged from plus or minus 400 to 12 percent of the MPV (fig. 2). The uncertainty range for the “best” laboratories probably indicates the magnitude of error expected for the analytical methods used. However, the uncertainty range for “most” laboratories indicates the effects of inadequate quality control in addition to expected method error. The range of uncertainty for “most” laboratories in these interlaboratory

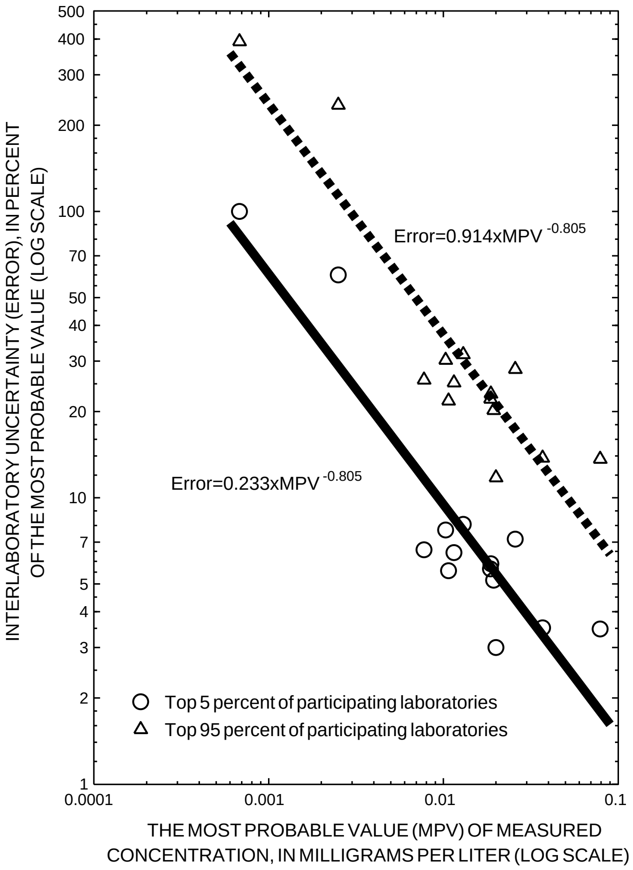

Figure 2. The analytical uncertainty of reported results from laboratories in the USGS interlaboratory evaluation program for the most probable value of chromium concentrations in natural-water matrix samples that were tested from 1989 through 1997.

studies is probably a conservative estimate of the uncertainties caused by combining data from different sources because it does not include outliers (the laboratories rated in the bottom 5 percent of the USGS interlaboratory evaluation program), or laboratories not participating in QA/QC programs. Combining analytical data from laboratories that have inadequate or undocumented QA/QC programs may introduce an unacceptable level of uncertainty.

Differences between methods and materials that are used for water-quality sampling and analysis in different studies (or changes within a single study over time) also are a substantial source of uncertainty that can impede aggregation of data from available sources (ITFM, 1995b). The uncertainty introduced by different methods can greatly overshadow real differences in constituent concentrations (Horowitz and others, 1994). Combining data from studies that were designed to collect concentrations of dissolved constituents (in filtered water) with data from studies that were designed to collect total concentrations (in water and suspended sediments) may obscure meaningful interpretations because the concentrations of metals and other contaminants in suspended sediments can be orders of magnitude higher than their concentrations in the dissolved fraction (Chapman and others, 1982; Horowitz, 1991).

Each step in the methods used to collect, process, and analyze water-quality samples can potentially change measured concentrations. Contamination that is introduced during sampling and analysis may substantially increase measured concentrations (Horowitz and others, 1992, 1994). Methods and materials that were designed to minimize contaminants that are introduced by the sampling process were shown to systematically decrease measured dissolved metal concentrations by up to an order of magnitude in an experiment using concurrent, side-by-side comparisons (Taylor and Shiller, 1995).

Alternatively, methods and materials that are used in the sample-collection, handling, and analysis process may artificially reduce measured concentrations by removing constituents from solution. For example, figure 3 demostrates that filter diameter, pore size, and the amount of water filtered can control measured constituent concentrations of dissolved constituents in filtered samples (Horowitz and others, 1992). The concentration of suspended sediment in the stream associated with the samples shown in figure 3 was relatively low [about 11 milligrams per liter (mg/L)] in relation to the range of suspended sediment concentrations (about 4 to 1,160 mg/L) reported for highway runoff (Smith and Lord, 1990). Therefore, a thorough understanding of the sampling and analysis methods that are used for each source is important if data from different sources are combined.

Unknown or variable detection limits are also a substantial source of uncertainty when combining available data (Larson and others, 1997). Statistical methods (Helsel and Cohn, 1988; Helsel, 1990) can be used to extrapolate data below detection limits, but not without introducing additional uncertainty. A comparison of results from Phase I (Gupta and others, 1981) and Phase II (Kobriger and Geinopolos, 1984) of FHWA water-quality studies along Interstate-81 (I-81) near Harrisburg, Pennsylvania, provides insight to possible sources of uncertainty. These two studies are presented because the laboratory that analyzed the samples, sample collection and processing methods, historical rainfall statistics, climatic conditions, and other geographic characteristics were similar for both studies.

The median, mean, and range of event mean concentrations (EMCs) of chromium measured along I-81 are plotted against the reported annual average daily traffic volume (ADT) in figure 4. The boxes indicate the measured range of the EMC populations with respect to the estimated range of ADT measurements, assuming an error bar of plus or minus 10 percent for ADT. The median and mean runoff volumes for monitored rain storms was 0.47 and 0.2 inch (per unit area), respectively, for Phase I, and 0.16 and 0.04 inch, respectively, for Phase II (Driscoll and others, 1990b). Despite the fact that Phase II had more than twice the traffic and about one-third the dilution, the minimum EMCs measured during Phase II were about 50 percent of the minimum EMCs measured during Phase I. Higher minimum chromium EMCs detected during the Phase I study may be an artifact of a lower laboratory detection limit in effect for samples analyzed during Phase II, contamination by field sample collection and processing during Phase I, or a background source of contaminants that did not influence EMCs during Phase II. The large differences in runoff volume statistics for these two studies conducted along I-81 in Pennsylvania raise questions about the comparability of data and also indicate that uncertainty may arise from inadequate characterization of the natural

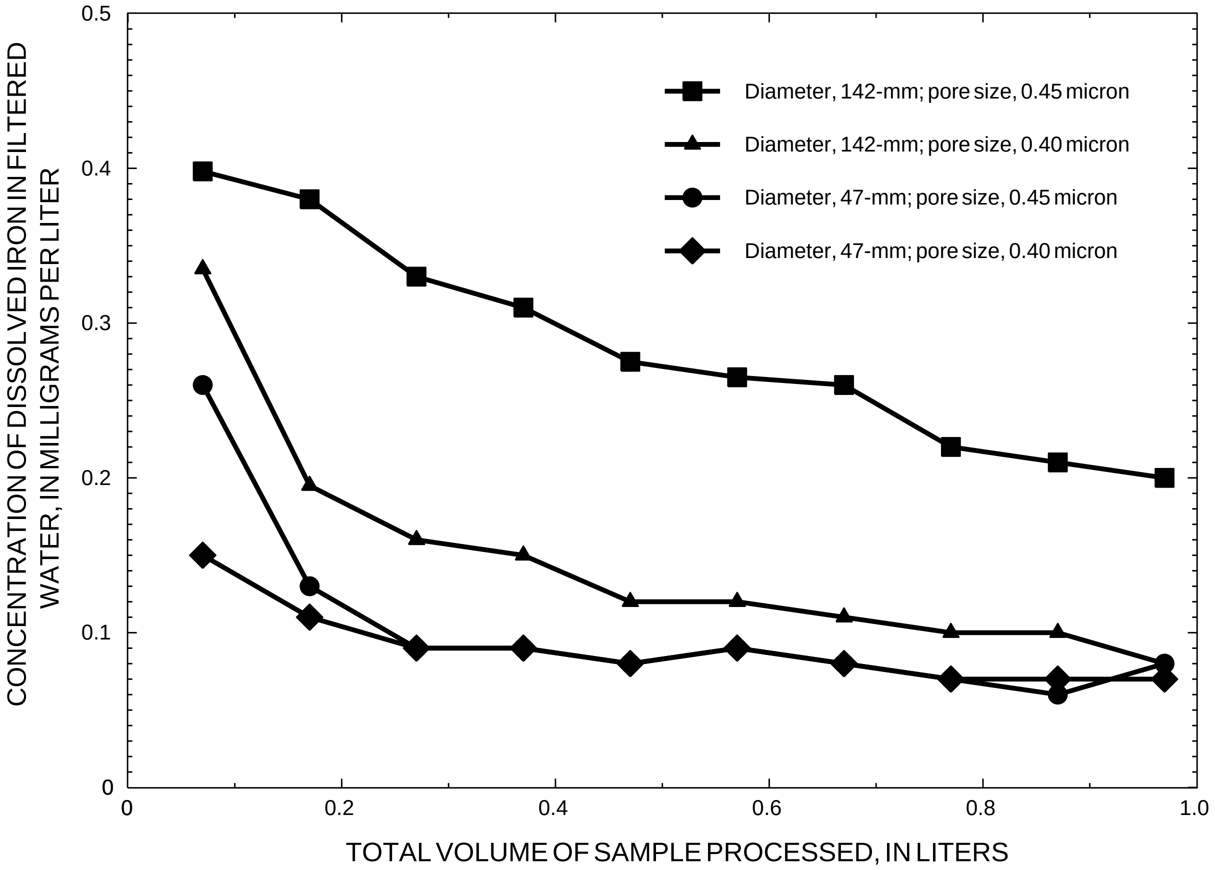

Figure 3. Effect of filter diameter and pore size and total volume of water processed, on measured concentrations of dissolved iron (from Horowitz and others, 1992).

variability in the amount and type of precipitation and runoff conditions at any given study site. In any case, these artifacts change population statistics of the combined data base and increase the uncertainty of predicted concentrations and loads from a model constructed by using the two data sets.

The uncertainty in model results is the sum of the uncertainty in the input data as well as the uncertainty incorporated by the modeling process (Young, 1983; Haan and others, 1990). Uncertainty in data from sampling programs that are used to characterize spatial and temporal water-quality processes will translate to uncertainties in model results (Montgomery and Sanders, 1985). The effects of large uncertainties in data that are used to construct or calibrate a model are popularly termed "garbage in, garbage out" (Haan and others, 1990). The modeling process can introduce uncertainty through interpretive errors, data-entry errors, and selection of the wrong model (Montgomery and Sanders, 1985). Proven success in one situation does not reduce the uncertainty in the application of a model to a new situation or to a different site because the true effect of one input condition can often be compensated by errors in values for other input conditions (Water Science and Technology Board, 1990).

Model uncertainties can be assessed by applying the model to data or to sites that were not used in the formulation of the model. When models are applied to data from sites or studies that were not used to create the model, the differences in site characteristics, data-collection methods, and source changes will be reflected in the measured uncertainty of model results. For example, an urban-runoff-quality model created by using data collected from about 100 storm events at 81 sites characterizing different land uses in 12 urban areas was shown to have an uncertainty of

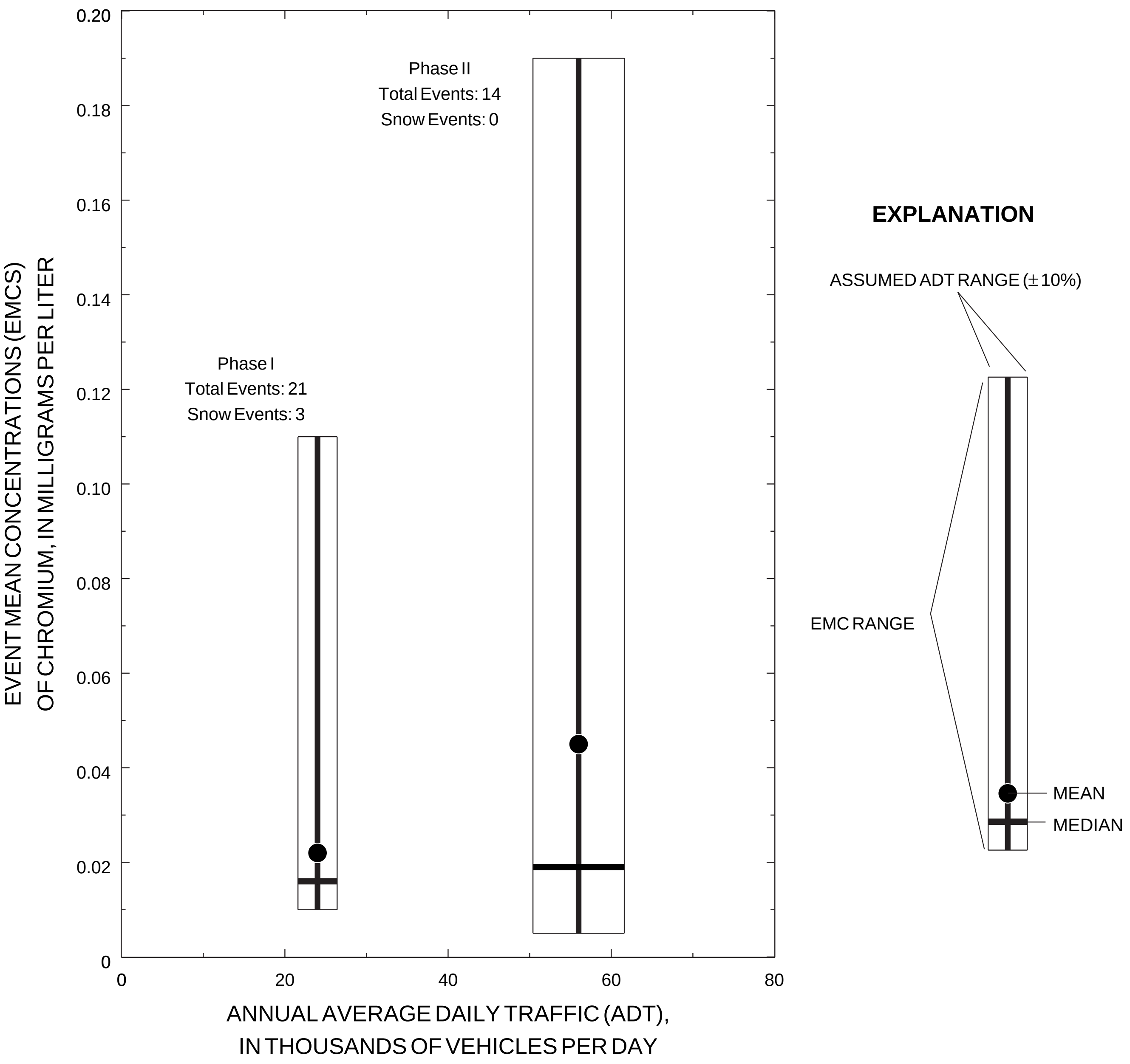

Figure 4. The median, mean, and range of event mean concentrations (EMC) of chromium and the average daily traffic (ADT) volume, with an assumed uncertainty of 10 percent, measured along I-81 in Pennsylvania during phase I (1976-1977) and phase II (1980-1981) of the FHWA water-quality studies (data from Driscoll and others, 1990, Volume III).

plus or minus an order of magnitude when tested against data from different watersheds in the same region (Marsalek and Schroeter, 1988). For another regional urban-runoff model (Driver and Tasker, 1990), statistical analysis indicated that the model could be used to estimate EMCs and loads of contaminants with an uncertainty of plus or minus 56 to 334 percent. However, when the Driver and Tasker (1990) model was applied to data collected in urban watersheds in Tennessee, large prediction errors (up to about 806,000 percent for lead) indicated that changes in pollutant sources, differences in site characteristics, and changes in data-collection methods limit the accuracy of the existing model without adjustments for these factors (Hoos and Patel, 1996).

Uncertainties in the input data sets caused by differences in field or laboratory methods and reporting limits between studies may obscure evidence for physical or chemical relations that can be used to frame predictive models. When data from different studies were combined (Driscoll and others, 1990b), quantitative relations between pollutant concentrations and traffic volume were weak. For example, if differences in the minimum EMCs indicated in figure 4 are an artifact of methods used, this may be a factor precluding formulation of a useful model for minimum EMCs based on ADT and the physical characteristics of the study sites. Results of studies using internally consistent methods (Shaheen and Boyd, 1975; Kobriger and others, 1981; Racin and others, 1982; Kerri and others, 1985), however, indicate relatively strong correlations between traffic volume estimators and measured pollutant concentrations and loads (Young and others, 1996).

Weak correlations between traffic volume and the magnitude of measured highway-runoff pollutants may reflect large uncertainties in historical traffic volume data estimators. ADT measurement and calculation methods have been standardized only recently and have not been consistent through time or from place to place (Wilkinson, 1994). Although ADT estimates from permanent counting stations are considered 95 percent accurate, estimates from 24- to 48-hour counts (typical for many sites) may deviate from actual ADT values by more than 100 percent if affected by special conditions such as inclement weather, seasonality, or a special event (Anthony Esteve, Office of Highway Information Management, FHWA, written commun., 1997).

The most recent predictive water-quality model developed by the FHWA (Driscoll and others, 1990a) used local and regional environmental characteristics correlated with the median of EMCs at each site to predict the environmental impact of highway runoff. While the use of EMC values is a practical approach for formulation of national regression equations, information is lost when populations of average values are combined (Schaeffer and Janardan, 1978). EMCs can be calculated from discrete measurements of concentration and flow (Driscoll and others, 1990a), but temporal variations within storms cannot be determined from EMC data. Although model predictions based on EMCs will tend toward the center of input parameter populations, data for individual sites or individual storms may deviate considerably from the normal range. Figure 4 indicates that individual EMCs at a given site can vary as much as an order of magnitude. Consequently, instantaneous concentrations may vary from the normal range by more than an order of magnitude. Providing model results without indicating that results are based upon central parameter values, and without indicating the uncertainty in the results, may be perceived as misleading (Haan and others, 1990).

Even when data distributions follow expected patterns, uncertainty in the data may preclude quantitative modeling. A cause- and-effect relation may be inferred logically, but problems with data may alter or obscure the true quantitative relation. For example, a relation between ADT and the maximum concentrations and therefore loads of constituents in runoff at a site is suggested by the data presented in figure 4, but this relation can be distinguished from variability caused by differences in sampling programs only if there is enough QA/QC to substantiate that results are otherwise comparable.

A documented uncertainty analysis is an important tool to assess the comparability of data and resultant interpretations. Organizations collecting data commonly use methods that are not comparable to obtain and interpret data. Also, continuing changes in the science and technology of environmental monitoring increase uncertainty in the comparability of data (ITFM, 1995a, 1995b). If, however, sufficient QA/QC information is collected, documented, and available, the uncertainty can be determined quantitatively. If this information is not available, a subjective determination of the uncertainty and resulting validity associated with existing environmental data must be derived (USEPA, 1986, 1994).

QUALITY ASSURANCE AND QUALITY CONTROL

Quality assurance and quality control (QA/QC) programs are used to detect and control errors and to maintain and document the reliability and uncertainty of results. Historically, QA/QC programs have been recognized as an essential component of laboratory analysis, but the usefulness of data for decision-making is affected by many external factors (Brown and others, 1991). QA/QC requirements to document that data from laboratory and field sampling activities are valid, current, and technically supportable have been increasing over the last two decades.

Data are no better than the weakest link in the data-collection processes. Without sufficient QA/QC, the effectiveness of validated methods, reference laboratories, and experienced personnel cannot be established conclusively (Keith and others, 1983). QA/QC programs must evaluate all aspects of a data-collection effort, including program design; sample collection, transport, and storage; chain of custody control; sample analysis; documentation; and data reporting (FHWA, 1986; Childress and others, 1987; Clark and Whitfield, 1993). The USEPA specified the application of quality assurance to all steps within environmental data-collection efforts as early as 1984, and suggested such practices as early as 1979 (Alm and Messner, 1984; Childress and others, 1987). QA/QC practices are required by many Federal agencies involved in water quality and have been encouraged in courses, meetings and publications supported by most professional water-quality organizations because documentation of QA/QC information has been deemed essential to ensure that data are reliable and legally defensible (Childress and others, 1987).

The FHWA recognizes the importance of QA/QC activities to demonstrate that data are valid, current, and technically supportable (FHWA, 1986). The FHWA has long encouraged the collection and publication of QA/QC information with highway runoff monitoring data, including

- A quality-assurance plan documenting methodologies and operating procedures, and specifying the accuracy and precision of field and laboratory methods, as well as specifying method detection limits;
- Interoffice quality-assurance reviews as specified in the QA/QC plan to examine and approve (1) site selection, (2) project documentation, (3) procedures and records for calibration and maintenance of instrumentation and equipment, (4) sample collection handling and preservation methods, and (5) availability of properly trained personnel;
- Appointment of a quality-assurance coordinator to ensure that QA/QC activities are actually being done and documented, and to review and approve final data before release;
- Selection, documentation, and adherence to proven methods;
- Selection of laboratories based on their ability to conduct the required analysis at a given detection limit, comply with accreditation requirements, and adhere to published QA/QC procedures;
- Sufficient personnel training and performance evaluation; and
- Sufficient analytical quality control to demonstrate that measured values represent actual environmental conditions within specified limits of accuracy, precision, completeness, and comparability between studies (FHWA, 1986).

The need for extensive QA/QC documentation is greatest when data from different studies are combined. Cause-and-effect relations may be indicated within a study as long as field and laboratory methods are consistent and control sites are used. When absolute values from individual studies are to be combined, however, the standards of data quality must be higher because differences in methods that were used to collect and analyze water-quality samples may obscure cause-and-effect relations (Childress and others, 1987; Hren and others, 1987). A synthesis of available data cannot be truly quantitative without adequate quality-assurance programs that quantify the precision, accuracy, and integrity of published data (Childress and others, 1987; ITFM, 1995b).

The ITFM has recently defined strict guidelines for the collection, analysis, and documentation of water-quality information. The issues involved in achieving data comparability are consistent with operating in a well-defined quality system for physical, chemical and biological measures in the field and in the laboratory (ITFM, 1995a, 1995b). The ITFM requires that sample-collection procedures and analysis methods need to be fully described, validated, and conducted by competent personnel. To document that data-collection information is internally reliable and comparable to results from other groups, performance needs to be evaluated against a reference (ITFM, 1995b). The USEPA recommends the use of quality-assurance plans within the scope of a data quality objectives process to document all activities needed to ensure that the data-collection program will produce the type and quality of data that will be sufficient to support decisions made using data collected (USEPA, 1986, 1994).

A QA/QC program to document and control data reduction, evaluation, and modeling as part of the interpretive process is as important as traditional QA/QC programs for data collection and analysis (Brown and others, 1991). When QA/QC issues in data interpretation activities are actively integrated into the QA/QC for data-collection activities, the feedback often results in better data and models for the intended purposes (Clark and Whitfield, 1993). Rigorous QA/QC procedures are required at all stages of a modeling effort

(Heijde, 1990). Interpretive errors arise from natural heterogeneity, measurement errors, and structural differences between the real world and the methods used for predictions; therefore, QA/QC programs must be designed to quantify these sources of uncertainty. However, QA/QC practices and sufficient peer reviews are not generally widespread in the application of many modeling efforts (Water Science and Technology Board, 1990).

A successful modeling process requires substantial QA/QC efforts with scientific and technical reviews at each stage of the process (Water Science and Technology Board, 1990). The QA/QC procedures for model development include verification of the structure and coding, model validation, record keeping, and software documentation. The QA/QC procedures for model application include selection and verification of input data, and documentation of the data-analysis procedures and modeling methodology. Documenting a calibration and sensitivity analysis—determining how input parameters control model output—is important to indicate how uncertainty in input values will affect uncertainty in calculated results. QA/QC procedures for a model also include a post audit to quantify how well the model works for the same system later in time, or for a different system with slightly different input parameters (Water Science and Technology Board, 1990).

SUMMARY

Transportation agencies face many different issues concerning the characteristics and effects of highway runoff. The FHWA and State transportation agencies need to determine what information is available and whether this information is valid (useful for intended purposes), current, and technically supportable. The types and urgency of various environmental concerns and regulatory issues vary among the States and regions of the Nation. These technical and regulatory complexities make it difficult to establish a uniform set of data quality objectives. It is important, however, to establish criteria that may be used in the data evaluation process.

Basic information requirements, information about the uncertainty of data sets, and documentation of quality-assurance and quality-control practices will indicate the potential utility of available water-quality information for any given purpose. Basic data requirements include information about the monitoring objectives, sample design, data qualifiers, and methods for sample collection, sample handling, and field and laboratory measurements. Study objectives and monitoring goals determine where samples are collected, the frequency of collection, the timing and duration of sample collection, the matrixes sampled, the methods used, and the properties and constituents that are analyzed. Ancillary information on characteristics of a study area often provides explanatory variables needed to standardize data to a common basis for comparison or to account for some of the variability in the data. Uncertainty analysis provides important information for the design and evaluation of data-collection programs. This examination of potential errors and losses of information inherent in environmental studies can be used to quantify and minimize risks associated with decision errors. Quality-assurance and quality-control activities throughout the sample collection, processing, analysis, and interpretive process establish that data are valid, current, and technically supportable by defining and controlling uncertainty and errors in the data collected. The fact that a program's data may not meet these screening criteria does not mean that the data are not useful for meeting that program's objectives or that they could not be used for water-quality studies with objectives different from those required for a national synthesis.

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Chapter 2. Principles and Practices for Quality Assurance and Quality Control

By BERWYN E. JONES

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Principles and Practices for Quality Assurance and Quality Control

By Berwyn E. Jones

Abstract

Quality assurance and quality control are vital parts of highway runoff water-quality monitoring projects. To be effective, project quality assurance must address all aspects of the project, including project management responsibilities and resources, data quality objectives, sampling and analysis plans, data- collection protocols, data quality-control plans, data-assessment procedures and requirements, and project outputs. Quality control ensures that the data quality objectives are achieved as planned. The historical development and current state of the art of quality assurance and quality control concepts described in this report can be applied to evaluation of data from prior projects.

INTRODUCTION

Water-quality monitoring is a resource-intensive activity. A rigorous quality-assurance and quality-control (QA/QC) program within each project ensures that government resources are responsibly expended, so that the results of water-quality monitoring projects satisfy the needs of State departments of transportation, the Federal Highway Administration (FHWA) and other customers such as regulatory agencies and property owners. QA/QC ensures that project conclusions are based on precisely drawn project goals, appropriate data, and technically defensible interpretations; that is to say, QA/QC documents that the information produced by water-quality monitoring projects is as accurate and precise as possible. No other kind is worth the cost! According to a statement by Clark and Whitfield (1993), "Bad data for half the price of good data is a fool's investment."

The FHWA and the U.S. Geological Survey (USGS) have undertaken the National Highway Runoff Data and Methodology Synthesis to catalog the pertinent available information, define the documentation that is needed to validate the data, and evaluate data sources for current and future information needs.

The concept of quality systems encompassing and managing QA and QC activities is not new to the transportation community. In 1963, the Public Roads Director of Research and Development appointed a task force to study the problem of quality systems in highway construction (McMahon and others, 1990). Federal, State, and local transportation agencies have long been expected to incorporate quality systems in planning, design, construction plans and specifications, construction activities, and maintenance of highway systems (Maslin and others, 1983). Just as responsible transportation agencies would not purchase materials or contract for construction without proper assurances of quality, they cannot responsibly purchase water-quality information without the same kinds of assurance. Many of the same principles that apply to quality assurance in construction also apply to quality assurance in environmental information. As stated in the FHWA water-quality training course student workbook (FHWA, 1986), "Quality assurance programs document field and laboratory methods used for a monitoring program, to ensure that the monitoring program will yield data that are [sic]:

- meaningful,
- representative,
- complete,
- precise,
- accurate,
- comparable, and
- admissible as legal evidence."

Data collected for regulatory purposes must be substantiated by documentation of QA and QC activities. For example, the U.S. Environmental Protection Agency (USEPA) (1984) requires that, "...environmental data collected by and on behalf of the agency be supported by a mandatory quality system...," including project quality assurance.

Although QA is a necessary part of any scientific research or data-gathering project, it is even more important in environmental sciences than in traditional laboratory sciences. In laboratory research, the experimental system is carefully isolated from its surroundings, and experimental conditions are carefully controlled and documented so that an independent experimenter can repeat the observations to verify them. In environmental sciences, conditions are observed and described as thoroughly as possible, but they seldom are subject to the experimenter's control, nor can they be reproduced at will. Even a complete description of the significant influences on the system may be difficult or impossible to achieve. Therefore, the best assurance that a researcher's data and interpretations are valid depends on the ability to document that (1) the project design was adequate to achieve the stated goal of the project, (2) valid protocols were used to collect and interpret data, and (3) the protocols were properly executed. Data obtained by the use of valid protocols provide a basis for making sound management decisions, whereas unvalidated data serve merely to cast suspicion and create argument. Well-documented protocols allow one to compare data collected at different times and places, in order to identify trends, similarities, and differences. In this way, scientists can generalize their observations and make predictions about the future behavior of systems, which is the goal of all science and the basis for sound management and engineering decisions.

Documented QA/QC data that validate protocols describe the bias and variability of the data, which allows the user to assess its statistical significance. Data of known bias and variability have validity not only for the current investigation, but for future investigations as well. Therefore the cost of providing QA/QC, which can be substantial, is more than repaid by the value added to the data as a result.

Purpose and Scope

This report describes the history and current state of QA/QC concepts and practices that are used in water-quality monitoring. It is intended to assist the user in evaluating data from prior highway runoff water-quality monitoring projects.

It is not possible to prescribe a single set of QA practices to be used in all projects. The QA issues are different for every activity, based on the risks of error associated with each activity of the project and the likelihood and consequences of each type of error. There are, however, consistent principles that apply to evaluating these risks and constructing a QA program that will minimize them in a cost-effective way. The currently accepted approach to project QA design is to

- Define project goals and the quality and quantity of data required to meet them,
- Design a set of data-collecting and data-analysis activities to generate the required data,
- Assess the data-quality risks associated with these activities, and
- Develop project-specific QA requirements that address the more significant risks.

This report describes the basic principles of QA for water-quality monitoring and provides guidelines for selecting appropriate practices for monitoring the specific quality risks identified in a project.

Terms Used to Describe Quality and Their Application to Water-Quality Monitoring

Terms that are used to describe quality are commonly confusing and must be carefully defined. The international authority for these definitions is the International Organization for Standardization (ISO). In the United States, ISO standards are sponsored by the American National Standards institute (ANSI), and published as American National Standards by the American Society for Quality (1998), formerly the American Society for Quality Control (ASQC). The appropriate standard for definitions in the field of quality is American National Standard A8402-1994, "Quality Management and Quality Assurance-Vocabulary" (American National Standards Institute and others, 1994).

The ISO definition of the word "quality" is as follows: "Quality is the totality of characteristics of an entity that bear on its ability to satisfy stated and implied needs." The assessment of quality in environmental data, then, depends on the ability to define the needs of the intended user(s) of project results. To determine these needs, it is necessary to define the goals of the project in some detail. Thus, environmental project planning begins with an exact description of the problem to be addressed, and an analysis of the specific quality, quantity, and types of data required to address the problem.

Quality assurance is defined (American National Standards Institute and others, 1994) as: "...all the planned and systematic activities implemented within the quality system, and demonstrated as needed, to provide adequate confidence that an entity will fulfill requirements for quality." Once the requirements for quality in environmental data have been defined, QA activities are implemented to provide confidence in the data to be collected. QA activities generally fall into three categories:

- Documentation of the project plans to produce quality (project QA plan),
- Records that demonstrate that the project quality plans have been followed (QA Records), and
- Audits by internal or external personnel to assure that the QA activities are being carried out according to the plan. (QA audits).

Confidence in the data and data interpretations depends on the availability and completeness of these kinds of QA information.

The purpose of QA is to demonstrate to the customer and other readers of project reports that valid data and justifiable conclusions have been produced during the project. The project manager and staff, however, are usually the greatest beneficiaries of their own project QA plan, because it provides a framework for rigorous planning for project activities. Frequently, the cost of QA is repaid by eliminating unnecessary activities in the project, the need to repeat imperfectly planned or executed activities, or the consequences of wrong management decisions based on incorrect information.

QA records consist of various logs certifying that project activities were conducted according to the project QA plan, and QC data that demonstrate that project activities were successfully performed. The requirement to maintain QA records is a deterrent to "cutting corners" when time is short or conditions in the field are unpleasant. It is less tempting to violate protocols when the scientist has to sign a log certifying that the job was done "by the book." QC data provide quantitative evidence that protocols were effective in producing useable results.

QA audits provide internal or external scrutiny of process execution, project planning documents, and QA records. Auditing the project plans ensures that they meet organizational standards, and auditing quality records ensures that the specified practices were performed during periods when no auditor was on-site. Auditing the way processes are actually carried out guards against "protocol drift," which occurs when instructions are miscommunicated or misunderstood, or when processes are incorrectly recalled as the project wears on.

Quality control is defined (American National Standards Institute and others, 1994) as: "...operational techniques and activities that are used to fulfill requirements for quality," with the following explanatory NOTE: "Quality control involves operational activities aimed both at monitoring a process and at eliminating causes of unsatisfactory performance at all stages of the quality loop in order to result in economic effectiveness." In environmental monitoring, the concept of 'economic effectiveness' is interpreted to mean confidence in the data and in data interpretation. Thus, environmental QC includes activities that (1) monitor the sampling processes, including equipment function and cleanliness, instrument test and calibration, and sample preservation, shipping and analysis, and (2) document that the data meet all requirements for quality. QC also is applied to data interpretation protocols, as well as data transmission, storage, and retrieval. Environmental QC also includes the corrective and preventive actions taken to eliminate causes of unsatisfactory performances that are identified by the monitoring activities. It should go without saying that all instances of corrective and preventive actions must be logged as part of the project's quality records.

Quality management (QM) is defined (American National Standards Institute and others, 1994) as "...all activities of the overall management function that determine the quality policy, objectives, and responsibilities, and implement them by means such as quality planning, quality control, quality assurance, and quality improvement, within the overall quality system." In water-quality monitoring work, quality management occurs above the project level and provides the framework within which the project manager works.

Taken together, QM, QA, and QC represent the quality system for a water-quality monitoring project. The essence of this system can be summarized in terse and simple terms as:

- Say what you are going to do.
- Do what you said you would.
- Prove that you did it.

The project planning activities covered by Granato and others (1998) represents the first item in this list. QM and QA plans describe how the second item is accomplished, and the third item is satisfied by QC data, QA records, and quality audits.

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DEVELOPMENT AND EVOLUTION OF ENVIRONMENTAL QUALITY ASSURANCE

Although quality control through product inspection existed earlier than this, the scientific study of quality is usually dated from the publication of "Economic control of quality of manufactured product" (Shewhart, 1931), in which statistical quality-control charts were first described. This book was the outgrowth of the 1926–31 experiments with statistical studies at the Western Electric Hawthorne Works, the manufacturing facility of the Bell Telephone System. From this beginning, the science of statistical quality control has gradually expanded into comprehensive quality systems, and has spread to many types of process-oriented work, including water-quality monitoring (Juran, 1995).

A decade or more after producers introduced quality control, customers of manufactured products developed the idea of quality assurance. The first kind of QA activity was "acceptance testing" of statistically sampled product, using a decision rule in which a cerNStain fraction defective product was considered acceptable. The U.S. Army's Rock Island (Ill.) Arsenal developed many of these concepts, culminating in the MIL-STD-105 series of acceptance sampling tables (Dodge and Romig, 1959). Much later, purchasers of manufactured goods realized that QA by inspection is wasteful, and gradually shifted to the present type of QA, which is based on ensuring quality by requiring that proper processes be used to make and quality control products. This methodology-based concept of QA, codified in the ISO 9000 series of international standard for QA (American National Standards Institute and American Society for Quality Control, 1994), has been carried over into non-manufacturing activities, including environmental monitoring.

The transfer of QA/QC concepts to environmental analytical laboratories was pioneered in 1965, when the USGS developed a system of interlaboratory QC that is based on Standard Reference Water Samples for its network of water-quality laboratories around the country (Skougstad and Fishman, 1974; Schroder and others, 1981). The USEPA was primarily responsible for extending the concepts of QA/QC nationwide into other environmental laboratories, and ultimately into all environmental monitoring activities (Kulkarni and Bertoni, 1996). In the 1970s, the USEPA required use of USEPA-approved methods in contract laboratories, and evaluated laboratory data quality on the basis of blind analyses of reference samples. In the 1980s, the USEPA added a requirement for Quality Assurance Project Plans (USEPA, 1980, 1984) that addressed both field and laboratory processes. About the same time, the American Chemical Society's Committee on Environmental Improvement published comprehensive guidelines for environmental project QA (American Chemical Society Committee on Environmental Improvement, 1980; Keith and others, 1983). Introduction in the 1990s of the concept of designing project QA around well-designed data quality objectives (DQO) (USEPA, 1994a) extended the QA concept by providing results to which specific confidence limits on decisions could be assigned, as described by Granato and others (1998).

The American National Standards Institute (ANSI) and the American Society for Quality Control extended the QA concept into an overarching quality system for environmental investigations and remediation (American National Standards Institute and American Society for Quality Control, 1994). The quality system includes organization-level quality management, project-level quality assurance, and quality control of environmental measurements. Together, these elements form an information product that is both reliable and self-improving over time. The quality system concept defines the current state-of-the-art in quality of environmental monitoring programs and projects.

THE QUALITY MANAGEMENT PLAN AND RELATED ACTIVITIES

The ANSI/ASQC comprehensive environmental quality system begins a quality management plan (QMP) that provides the project manager with a clear and reasonable set of expectations for quality, and the resources with which to meet them. In addition, it provides the organization with a means of managing the quality of multiple projects effectively. The QMP assures that the project will have personnel, equipment and supplies, and records and computer systems that meet stated quality standards, and a solid framework of documented and tested protocols for project activities. The QMP assures management that adequate information will emanate from the project to ensure that organizational standards are met. Thus, both parties have a common set of expectations and a system for achieving them. Responsibility for the QMP should reside with a quality manager who reports directly (and regularly) to top management. The QMP should be audited on a regular basis. Audits may be performed by first-party (in-house), second-party (customer) or third-party (outside expert) auditors. The values of external audits are manifold - they (1) provide a neutral, expert assessment of the QMP and its execution, which assures that sound management practices are in place and are being followed, (2) emphasize the importance that management gives to quality, and (3) are invariably learning experiences for all concerned. The QMP may be audited to certify compliance with ISO 9000 standards, if desired. Certification to ISO 9000 provides public confirmation of management's commitment to quality, to employees and customers, as well as to other information users such as regulators. The Quality Management Plan (QMP) covers the fundamental management responsibilities for quality, as defined by ANSI/ASQ Standard E-4 (1994b). Ten elements of a Quality Management Plan are required by that Standard:

- a quality policy for the organization,
- a quality system that ensures that the policy is implemented,
- a system to ensure the quality of equipment and supplies procured externally,
- personnel hiring and development systems to provide quality staff,
- documents and records systems to ensure that information is accurately preserved in a retrievable form,
- a quality system for computing systems,
- a systematic process for planning projects,
- a work-process documentation system,
- a system for assessing quality and responding to deficiencies, and
- a continuous improvement system.

The QMP represents management's responsibilities to provide the project chief with the resources required to produce a quality information product. Because this report is directed primarily toward project-level QA/QC, the interested reader is referred to ANSI/ASQC Standard E-4 for detail about preparation of the QMP.

THE PROJECT QUALITY ASSURANCE/QUALITY CONTROL PLAN AND RELATED ACTIVITIES

The second phase of the quality system, the Project QA Plan, describes project-level QA/QC. QA/QC for a water-quality monitoring project begins with the planning and staffing of the project, and continues through sample design, data collection, data assessment, data interpretation, reporting, and data archiving. Each of these steps is subject to quality assurance in its planning, and quality control in its execution. Clearly, the credibility of the project's findings can be no stronger than the weakest link in the system that produces them. Omitting or slighting QA/QC in any step of this process decreases the credibility of the project's results and conclusions. It is ironic that in the past, environmental QA/QC was commonly focused primarily on laboratory analysis, even though studies have shown that environmental laboratories typically make a relatively small contribution to the overall error in environmental monitoring data (see, for example, Helsel and Koltun, 1986). A whole-system approach to QA/QC is necessary for the production of credible results.

A modern comprehensive project QA/QC plan requires that the last step of the project be a self-critique, identifying "Lessons Learned" to improve the next project or, in the words of Peter Senge (1990), to create a "Learning Organization." The project QA process is shown in figure 1 in the form of a cycle, in which self-evaluation closes the loop by providing input for improving processes for the next project.

PROJECT PLANNING

Although it is easy to skimp on efforts in the planning process, nothing is more important to developing the user's confidence in project data and conclusions than clear and full documentation of a valid planning process for use in developing the project. Elements of this planning process include a description of (1) how and by whom the project is to be managed, (2) the goals of the project and corresponding data-quality objectives, (3) detailed plans for defining and collecting the data required to meet these objectives, and (4) a plan for monitoring the quality of the data and correcting data-quality problems.

Project Management

The first element of the QA plan is to identify the persons responsible for carrying out the project, and delineating their responsibilities. An organizational chart showing the lines of responsibility and communication is desirable where more than a very few persons are involved. The credentials and, if appropriate, certifications of the persons who will perform all project tasks must be included, along with plans for training to rectify any deficiencies. The QA manager for the project must be organizationally independent of (that is, not reporting to) the project manager, to ensure objectivity. The organizational quality management plan should be incorporated in this plan, usually by reference, to provide a description of how the organization will oversee and provide resources to the project management.

A project schedule, including intermediate checkpoints and contingency plans in case the schedule is not being met, must be provided. All required and optional products and outputs must be listed. A detailed budget for the project also may be required.

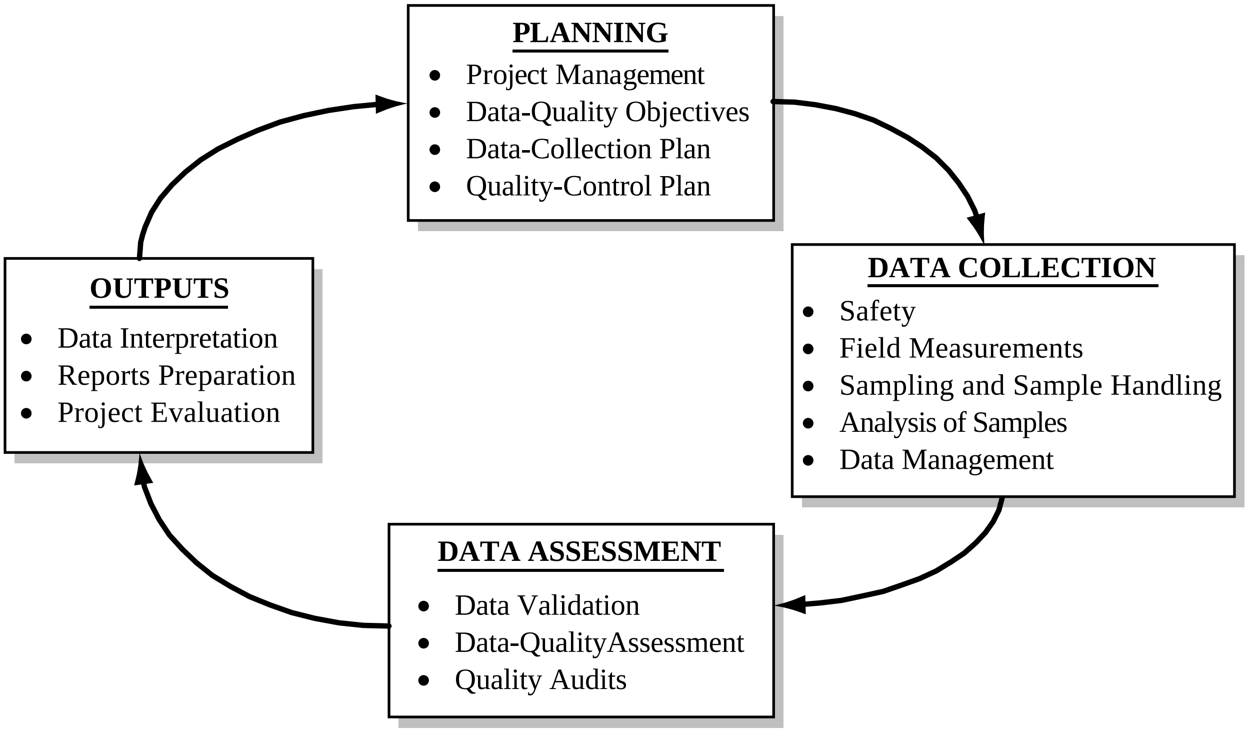

Figure 1. Project quality assurance cycle (adapted from Kulkarni and Bertoni, 1996).

Data-Quality Objectives

All too frequently, the most neglected steps in environmental projects are (A) Documenting the problem that led to the formation of the project, (B) Articulating specific, quantitative project goals, and (C) Designing a data-collection system that is tailored to meet these specific goals. Whitfield (1988) classifies the goals of environmental monitoring projects under five headings: (1) assessment of trends in some variable, (2) compliance with standards, (3) estimation of mass transport, (4) assessment of environmental impact, and (5) surveillance to determine the general level of environmental quality in an area. Highway runoff studies may fall into any or all of these categories. Data collection must be tailored to support the specific goal of the project. Data that are valid to support one goal may be inadequate for another. Worse yet, data gathered with no well-defined goal in mind may have no real usefulness at all. Each type of project and, indeed, each project within a type will require different data-quality characteristics to meet varying project goals (Shampine and others, 1992).

Once the goals of the project are clearly defined, the quality, quantity, and type of data required to fulfill them can be determined. The USEPA's DQO approach (USEPA, 1994a) is a useful way of addressing the issue of how much precision and accuracy are needed in the data. In this approach, which has been discussed by Granato and others (1998), the objective of the project is stated in the form of an hypothesis, which is tested at a defined level of uncertainty; that is, in terms of the acceptable risk of reaching an erroneous conclusion. Each risk can be translated into the required degree of certainty with which the data must be defined and, therefore, the number and types of QC and environmental samples of defined quality that are required.

A software program (DEFT) has been developed to simplify the statistical computations for computing the number of samples required to achieve the desired degree of certainty in the data. (USEPA, 1994b). A downloadable version of this software is available from the USEPA on the World Wide Web (USEPA, 1994b). The current software package addresses only comparison of the concentration of a constituent to a defined standard. Future versions are anticipated to address other types of decisions. In the ideal case, the DQOs will be used as input for a statistical calculation of numbers and types of samples that are required to meet project data requirements. Even when the quantitative statistical method is not used, however, developing qualitative DQOs is useful in planning for efficient and effective sampling design. (USEPA, 1994b, p. 7). The Intergovernmental Task Force on Monitoring Water Quality (ITFM) also has embraced the DQO concept for water-quality monitoring projects by all government agencies (ITFM, 1995).

The five attributes of data quality are often summarized by the acronym PARCC, which stands for Precision (variability), Accuracy (bias), Representativeness, Completeness, and Comparability. Descriptions of these terms, adapted from the USEPA (1998a), are as follows:

Precision: The extent of random differences among replicate measurements of the same property, such as the concentration of a specific pollutant in a water-quality sample. The precision of many environmental measurement systems is not constant over their range of utility, but is relative to the value measured. Precision is, therefore, often best represented as relative standard deviation, the standard deviation of the measurement divided by the concentration at which it is measured. The relative standard deviations of many analytical methods are more or less constant over much of their useful ranges, although this relationship tends to break down at the lowest concentration. Therefore, almost every analytical method is assigned a "limit of detection." This is the lowest concentration that can reliably be distinguished from a blank containing none of the substance being measured, usually defined to be three times the standard deviation of the blank. A "limit of quantitation" is then set at 10 times the standard deviation of the blank. Variability is an alternative term for precision.

Accuracy: The degree to which a measured value (or mean of measured values) agrees with the true value of the measured property. The measure of accuracy is bias, the degree to which the measured value differs from the true value of the measured property. Bias is the inverse of accuracy; as accuracy decreases, bias increases.

Representativeness: The extent to which a sample or set of samples possesses the same properties as the body from which it is derived. The representativeness of a sample is dependent upon scientific and statistical sample design; no single computed value measures it. If the body that is sampled (river, lake, streambed, etc.) were perfectly homogeneous, obtaining a representative sample of it would not be a problem. Every part of it would be identical to every other part, and any portion of it would have the same properties. Unfortunately, sampling is almost never that simple. Environmental materials are almost never homogeneous; many are extremely heterogeneous. Therefore, the body to be represented must be sampled in a statistically valid way to obtain a representative sample.

Completeness: The percent of the planned data that was actually obtained. Unforeseen circumstances, such as the breakdown of automatic samplers, recorders, or monitors in the field, or accidental loss of a sample in shipping or in the laboratory, often prevent collection of 100 percent of the planned data. A standard of 95- to 98-percent completeness is commonly targeted in water-quality monitoring projects.

Comparability: The degree to which different data sets represent environmental conditions in the same way and, thus, can be compared to determine changes in environmental conditions over space or time. Commonly, data obtained by widely-differing methods produce data that are not directly comparable. It also must be realized that data may be comparable for testing one hypothesis but not for another.

Each type of project has general requirements for these data-quality characteristics. When, for example, a trend is to be studied, the data must be precise enough to distinguish reliably between the expected initial and final conditions of the system. As long as the bias is the same in the before and after measurements, however, it is not a critical factor in trend analysis. If a 10 percent difference is expected between initial and final states of the system, single before-and-after measurements with 10 percent relative standard deviation are not adequately precise to confirm the existence, let alone the magnitude, of the trend. In this situation, the data collector has two choices: (1) change to a more precise measuring technique, or (2) make enough replicate measurements to reduce the uncertainty in the mean value of the measurement, so that the trend can be defined with the required degree of certainty. The worst situation of all would be failure to determine the precision of the data, resulting in random variation being interpreted as a trend. Without due attention to data-quality characteristics, this situation can easily occur.

If the goal of the project is to assess compliance with a regulatory standard, it is critical that the measurement method have a high degree of accuracy (low bias) and a limit of quantitation sufficiently below the standard to provide precise measurements in the vicinity of the standard level. The more precise the measurement, the fewer data will be required to determine with the desired level of confidence that the regulatory limit has or has not been exceeded.

The question of representativeness is addressed in project planning by the selection of a suitable sampling frame; that is, the portion of the system that will be chosen to represent the entire system. If the system to be studied is a certain river, it is obviously not possible to sample the entire river in all time and space. One must select a certain number of sites and a certain number of times each site will be measured, to provide data that adequately represent the condition of the entire river with respect to the goal of the project. For example, a project goal of describing the annual sediment load carried by a certain river cannot be answered without detailed knowledge of the variation of river stage throughout multiple years and knowledge of how the concentration of sediment varies with river stage. Valid measures cannot be obtained upstream from any tributary inlet that contributes significant amounts of sediment to the river. For the purpose of computing total load, a tributary that merely adds volume to the stream would have no effect on the outcome except to dilute the sediment concentrations, thereby making its measurement more difficult. On the other hand, a different project goal relating to sediment concentrations rather than loads would have a different sampling requirement; dilution would be a significant issue. Additional considerations might include whether data collected on one river are representative of other rivers as well, or whether several different kinds of river systems must be sampled to understand the sedimentation process in rivers in general.

In summary, data-quality objectives and plans for meeting them are very important considerations in project design and must be addressed carefully and completely in the earliest stages of the project by the project manager in consultation with field and laboratory personnel. Documentation of data-quality considerations is critical to the evaluation of the project data by potential subsequent users; therefore this documentation is a necessary part of the permanent project record.

Data-Collection Plan

Once the sampling frame is established, a sampling plan must be developed that represents the constituents of interest within that sampling frame. The sampling plan outlines all measurements to be made in the field, as well as all samples to be removed from the hydrologic system for laboratory analysis. A discussion of the hydrologic considerations that must be taken into account in developing sampling plans is beyond the scope of this report; however, the interested reader is referred to Averett and Schroder (1994) and Keith (1996), and the references therein. The project QA plan must demonstrate that the samples will represent the system accurately and will meet the DQOs. To avoid needless repetitive sampling, a literature search of the sampling area should always be a part of project planning. The quality of historical data must be assessed, and data gaps must be addressed as part of the current project. An understanding of the hydrologic system being sampled is also prerequisite to formulating the project-sampling plan. In developing the data-collection plan, the project manager should always keep in mind that project data might have uses beyond current project goals. Potential needs of other scientists and decision-makers in the future always should be considered when planning sampling and measurements for a project.

An area frequently overlooked in sample design is the collection of ambient control samples taken from sites not affected by the pollution source being studied. Another example of a control sample is the "before" sample in an environmental impact study. Not all of a contaminant found at a study site can necessarily be attributed to the source being studied; some may be natural or non-point source background. Failure to document the background concentration of contaminants can invalidate an entire study.

The development of the sampling plan requires a high level of professional judgment. This portion of the project QA plan must demonstrate that good judgment has been exercised in planning the project. Records that document the logic behind the design of the sampling plan are an integral part of project records, because later users of the data must evaluate that logic.

All sample-collection and analysis activities must be conducted according to well-defined protocols, such as those described in the FHWA Student Workbook (FHWA, 1986), or more recent publications from agencies such as the USEPA or the USGS. Written standardized protocols, when properly designed, selected, and executed, ensure the validity and repeatability of data-collection processes, and therefore of the data produced by these processes. Protocols must be written for two reasons—to make certain that all personnel who will carry out sampling or analysis know exactly how it is to be done, and to provide documentation for current and potential future users who must evaluate data usability. Also, without written documentation there is a tendency for methods to "creep" toward less and less rigorous processing. If the appropriate methods for data collection are not covered by documented and accepted protocols, extra effort is required to document and validate the procedures.

Sample preservation, packaging, shipment to the analyzing laboratory, and storage before and after shipment must be specified for every kind of sample that will be collected. Often the basic requirements for these operations are specified in either the sample-collection or analysis protocol. The plan for meeting these requirements, however, is a necessary part of project quality planning. The means by which holding time limitations between the time of sampling and the time of analysis will be met is often one of the most critical parts of this planning process. In addition, protocols for documenting continuous custody of samples throughout this handling process is required whenever there is a possibility that data will need to be admissible in court.

The analysis plan begins with selection of the laboratory to be used. This selection should be based on the laboratory's proven capability in the types of analyses required by the project, acceptance of the laboratory's QA plan and staff credentials, and adequacy (kinds and numbers) of instrumentation and facilities. Where prior experience does not provide proof of capabilities, performance testing or on-site inspection is necessary. Erdmann (1991a, 1991b) has described a set of QA requirements for analytical laboratories and a process for conducting an inspection. Alternatively, ISO 9000 or the USEPA's National Environmental Laboratory Accreditation Program certification is excellent evidence that a laboratory delivers data of acceptable quality. These selection criteria should become part of the project record, because they provide information that helps the user assess the validity of the results.

The choice of analytical protocols must be based on the DQOs of the project in terms of accuracy, precision and limit of detection, comparability with data from other studies, and consideration of any interferences to which the method may be subject. The need to select the most appropriate analytical method, rather than the least expensive one, cannot be overemphasized. Laboratory costs are usually a fairly small percentage of the actual total project cost, yet a small saving on laboratory costs may have disastrous consequences on the real value of the data. Because highway runoff water may be subject to regulation, the protocols selected should meet the requirements of the USEPA. During federal fiscal year 1999, the USEPA is moving away from requiring the use of specific analytical methods to specifying a performance based measurement system (PBMS). This new philosophy allows more flexibility in choice of protocol, but also requires that the protocols be backed up with performance data in the circumstances in which they are used. The project manager will need to be in touch with the appropriate USEPA Program Office and Regional Office to stay abreast of evolving requirements for PBMS (Federal Register, 1997).

A clear agreement must be made with the laboratory concerning the content of the analytical data package. The data package must contain enough information to identify the sample unambiguously and to allow the reviewer to determine that the project DQO's were met. A sample list of data that each report should contain is given below:

- Project name and unique project ID number,
- Field sample ID number,
- Laboratory sample ID number,
- Preparation and analysis batch numbers,
- Time and date sample was collected,
- Time and date sample was received at the laboratory,
- Time and date sample was prepared for analysis,
- Time and date sample was analyzed,
- Identifiers for all preparation and analysis protocols,
- Parameter or analyte being tested,
- Laboratory detection limit,
- Detection limit adjusted for sample-specific factors (dilution, preconcentration aliquot size, moisture content of soil, etc.) -Laboratory quantitation limit,
- Concentration reporting units,
- Dilution or concentration factor, if any,
- Percent moisture or percent solids,
- Sample aliquot size,
- Final extract volume, if appropriate,
- Sample preservation,
- Laboratory batch-specific QC information,
- Raw and interpreted analytical instrument output, as appropriate, and
- Original chain of custody documents, if any.

This list is adapted from the U.S. Army Corps of Engineers (1997) manual. Different lists may be appropriate for other organizations or purposes. Regulatory agencies, such as the USEPA, may place specific requirements on the content of data packages for some projects. All applicable regulations must be consulted before a final list of data specification can be made.

Protocols must be distributed to all members of the project staff who are required to use them. Protocol documents are usually issued to staff under a system of document control, in which copies are serially numbered, dated, and given revision numbers so that updates can be delivered to the qualified holders and outdated versions can be removed and destroyed. An archive of outdated protocols provides documentation of changes in procedures and the effective date of every change and must be maintained for use in later data evaluation. It is important to know what version of a protocol was used to collect data at any point in time. The project QA plan will provide for controlled document distribution unless it is handled by the parent organization's QMP.

Quality-Control Plan

Once the environmental data-collection plan is determined, the plan for QC samples must be developed. The QC plan is based on the principle of risk analysis. In this approach, the risks of error in each field-measurement, sample-collection, or analysis activity is estimated to be high, moderate, or low, considering both the likelihood and the seriousness of each error. Appropriate measures are developed to detect the errors that represent the higher risk factors. A lower level of QC may be directed at moderate risks, and even lower levels of QC would be directed at low-risk factors.

An example of this kind of risk analysis is in the handling of samples for analysis of volatile organic compounds (VOCs). There is a significant risk of sample contamination by absorption of airborne VOCs during shipment to the laboratory. The consequences of this contamination would be very serious, so a trip blank is usually included with each shipment of VOC samples. If the trip blank is contaminated, it is reasonable to assume that the samples also are contaminated, and the data from the shipment must be rejected. By contrast, there is relatively little risk of airborne contamination by major inorganic ions, such as calcium and chloride, so trip blanks are not necessary for these samples. There is some risk of chloride contamination from the sampling equipment, however, so an equipment blank may be sent to the laboratory to verify the cleanliness of the sampling equipment.

The most commonly used types of QC samples include: blanks, spikes, replicate samples, split samples, and reference materials. Each of these types of QC samples has many variations, but each has a single basic purpose. Blanks are used to detect and document possible contamination. Spikes are used to ensure that each constituent, if present, is being detected and accurately measured in the actual sample matrix. Replicates monitor the reproducibility of the overall sampling and analysis process. Split samples monitor just the reproducibility of the analysis process. By combining information from replicates and splits, the variability in the sampling process can be estimated. Reference materials are used to ensure that the analysis process is capable of giving accurate results. When based on a thorough understanding of the needs of the individual project, the right combination and number of QC sample types can provide the desired level of protection against the principal risks of accepting bad data.

It is not possible to specify a percentage of samples that should be devoted to QC samples in every project. The DQOs for the project must always guide this decision. When the quantitative DQO approach that was described previously is used, the number of each type of QC samples will be based on firm statistical computations. When the quantitative DQO approach is not feasible, the professional judgment of the project manager is crucial. Evaluating this judgment after the fact is difficult for subsequent users of the data. The project manager should, therefore, document fully the reasoning used in deciding which and how many QC samples to use. Common QC sample types and their uses are summarized in table 1.

Blanks are QC samples that are reliably free from detectable amounts of any of the constituents to be measured. They are used to detect contamination of the samples. The composition of the blank should mirror the matrix of the environmental samples. For example, if the samples for trace metals analysis are acidified, the corresponding blanks should be acidified also. Several types of blanks are commonly used. Field equipment blanks are passed through the sampling and (or) processing devices to document that these devices are free from contamination. Travel or trip blanks are used to ensure that samples are not contaminated during transportation from the field site to the laboratory. Preservative blanks are used to check the purity of the preservative that is added to each sample[1]. Laboratory blanks originate in the analytical facility and are used to document that none of the constituents of interest are being introduced into environmental samples during their processing in the laboratory. An overview of types of blanks is presented in table 2.

Spiked samples are used to assess the bias in an analytical method. By comparing the results of spiked and unspiked samples, one determines the percent of the spike that is recovered by the method. If it is assumed that the native concentration of the analyte is recovered to the same extent as the spike, one can infer the percent of the native concentration of analyte that is recovered by the analytical method. This assumption, although usually made, is somewhat questionable because the spiked constituent may not be bound to the matrix in the same way and to the same extent as the environmental constituent. The amount of the spike should be great enough to provide an accurate recovery figure when the concentration in the unspiked sample is subtracted from that in the spiked sample, but not so great as to swamp the very matrix effects that are being studied. A spike approximately equal to the concentration of the natural material in the sample is usually best. Ambient background samples are usually spiked at about the same concentration found in the contaminated samples. Samples may be spiked in the laboratory to evaluate the analytical process alone. Most laboratories routinely spike samples for multi-analyte organic analyses with one or more "surrogate" compounds, the recovery of which mimics that of the analytes, to monitor the effectiveness of sample preparation and analysis processes. Samples also may be spiked in the field to document that the constituent survives the process of shipping to the laboratory.

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[1] The author has personal experience with a case of contamination from paint that had been placed on the outside of vials of acid used to preserve trace metal samples. Because preservation blanks were not used, contamination was not detected in a timely manner, and a number of trace metal analyses were invalidated.

Table 1. Common types of quality-control samples used in water-quality monitoring investigations

Type	Description	Purpose	Alternative	Comments
Replicate samples	Multiple samples are collected from the environment at the same time and place, using the same method.	Evaluate the variability in sampling and analysis processes.	No other good way to estimate the reproducibility of environmental sampling.	Estimate sampling process variability, by using in conjunction with split samples
Split samples	One sample collected from the environment is divided into two or more equivalent parts. May be done in field or at lab.	Evaluate analysis variability, if sent to the same lab. Evaluate interlaboratory bias if sent to different laboratories.	Many other ways of determining laboratory variability or interlab bias are possible. This method has the advantage of being matrix-specific.	Sample-splitting process may not produce exact replicates. Also, splitting procedure may introduce contamination, or allow loss of analyte through volatilization or sorption.
Spiked samples	Measured amounts of analytes are added to known volumes of sample. Analyses are compared to those of unspiked sample, identically treated.	Evaluate recovery of the analyte(s) from the specific sample matrix by the analytical method.	Laboratories usually have recovery data for normal sample matrices. Spikes are useful for unusual matrices.	Recovery of spikes may not accurately represent recovery of native materials.
Surrogate-spiked samples	Measured amounts of surrogate compounds are added to known volume of sample.	Evaluate the recovery of analytes by monitoring recovery of a chemically similar compound.	Analyte spike provides similar data, but requires two analyses.	Typically used with multi-analyte organic methods.
Synthetic samples	A known concentration of analyte(s) is added to a matrix (commonly source water; occasionally a synthetic matrix such as seawater).	Document the bias of a laboratory's analyses.	Reference samples, spiked samples may also be used to test bias.	Unless a synthetic matrix is created, results do not take matrix effects on bias into account and therefore tend to give optimistic results.
Reference samples	An actual environmental sample in which the "true" concentration of analytes is known, through multiple analyses by multiple laboratories, using multiple methods.	Document the bias of a laboratory's analysis.	Synthetic samples, Spiked samples may also be used to test bias. Reference samples provide an absolute standard, not prepared by the user.	Matrix-specific reference materials may be difficult or impossible to obtain. Non-matrix specific reference samples may provide misleading results. Reference samples are used sparingly because they are expensive.

Table 2. Common types of quality-control blank samples used in water-quality monitoring investigations

Type	Description	Purpose	Alternative	Comments
Source water blank	A portion of the water that is used as the source of all blanks, and as the matrix for all QC samples, is analyzed.	Document that the source water is free of contamination.	Buy certified source water from the laboratory or a commercial supplier, and accept their analysis. Use water from a deionizer in the field laboratory.	Field-lab deionizers may be a significant source of contamination, and should be monitored with conductance meters, using a safe cutoff value. The value chosen will depend on the detection limit of the analyses being performed.
Field blank	Source water is taken to the sampling site and, as nearly as possible, sampled, preserved, and bottled in the same way as the environmental samples.	Document that the field sample handling process is not introducing contamination.	No reasonable alternative. Necessary for all but the roughest reconnaissance studies.	If contamination is found in the analysis of the field blank, it gives no indication of the source, only that it has occurred. Also, it is often not possible to sample the source water exactly the same way as the environmental samples.
Ambient atmosphere blank	A sample container of source water is exposed to the atmosphere at the sampling site for the same amount of time required to handle a sample.	Document that the atmosphere of the sampling site is not introducing contamination.	Test the atmosphere for analytes to be determined in the samples.	Especially important for relatively "clean" ground water samples collected in surface environments that are highly contaminated, either by volatile constituents or air borne particulates.
Equipment blank	A source water sample is passed through the sampling, splitting, or filtration equipment, then bottled and preserved like a sample and sent to the lab.	Document that the sampling equipment is not introducing contamination.	Super-clean the equipment before coming to the field, seal it in a protective container, and use it only once per trip, to ensure that no contamination is introduced.	Separate blanks for sampler, splitter, pump, filter, etc., may be used to identify individual sources of contamination. Analyze total equipment blank first. If it is blank, no further tests needed.
Preservation blank	A source water sample that has been preserved exactly as the environmental samples, is analyzed.	Document that the preservative, and the act of adding it to the sample, is not introducing contamination.	Use pretested preservative supplied by the lab, and assume that the operation of introducing preservative in the field isn’t causing contamination.	If preservation blanks show no contamination, there is no need to analyze separate source blanks.
Trip blank	A sample of source water, preserved and contained identically to the samples, is shipped with environmental samples.	Document that contaminants are not introduced during shipping.	Detect contamination during shipping, from atmospheric or container/closure sources, or from other samples.	Most necessary when volatile analytes will be determined. Cross contamination may occur between "clean" and "loaded" samples shipped together.
Laboratory blank	A source of water sample is prepared at the laboratory, and analyzed along with the environmental samples.	Document that contamination has not occured during lab storage, subsampling, and analysis.	If the blank shows no contamination thoughout the entire sampling and analysis process, the absence of contamination in both field and lab is documented, and separate lab blanks are unnecessary.	If the field blank shows contamination, the laboratory blank helps identify its source as being in the field or in the laboratory.

This is a valuable but difficult field operation, demanding precise quantitative techniques under difficult circumstances. If field spiking is called for, the protocol will address the problem of getting the spiking solution and micropipets to the field site. A protocol and training and performance evaluation programs for spiking techniques also should be developed. For comprehensive treatments of performing and calculating spike recoveries, consult Mueller and others (1997) and ASTM (1996).

Replicate samples can be used to test the reproducibility of the sampling and analysis processes. The sampling process is often the least reproducible part of the entire data-gathering system. Replication of water samples is relatively straightforward, although it becomes more difficult when the suspended sediment load is high. Bed-sediment samples are even more problematic to replicate, because a single large particle or a few moderate-sized particles can bias the result significantly. Particle-size separation is usually employed for analysis of bed sediment. Environmentally important substances usually are associated primarily with the smaller-particle fractions, which are also the fractions that are most accurately replicated (Helsel and Koltun, 1986). Replicate samples should be collected and analyzed very close together in time to get the best information, unless one is studying the long-term reproducibility of the measurement process.

Split samples are used to assess the variability of the analysis process. Their use is often confused with that of replicate samples; however, they are in fact very different. Split samples are obtained by dividing a single sample into multiple, presumably identical portions, but replicate samples are obtained by performing the sampling operation multiple times. Results of analyses on replicate samples include both sampling and analytical variability, whereas split sample analyses contain only the variability of the analysis process. Several devices are available for accurately splitting whole-water samples (that is, water-suspended sediment mixtures). As in replication, bed sediment samples offer the greatest difficulty in splitting, but if particle size separation is employed and only the smallest size fraction is used, the difficulty can be reduced. Samples may be split at various points in the analytical preparation and measurement process, to assess the variability at different stages in the process. By combining results from replicate samples with those from a series of split samples, one can assess the contribution of each step in the overall sampling and analysis process (see, for example, Helsel and Koltun, 1986).

Reference materials are indispensable in assessing the absolute accuracy of an analytical method and the laboratory that is performing it. Methods development researchers almost invariably use reference materials to validate new methods. Reference samples also are used to qualify and monitor laboratories and to define the bias in data that are used to make important environmental management decisions. It is important that the matrix of the reference material be as similar as possible to that of the environmental samples for which the method is to be used. Pronounced matrix-dependent biases exist in some analytical methods. When reference materials are used to qualify or monitor a working laboratory, they generally are submitted "blind"—that is, with the true values unknown to the analyst.

DATA COLLECTION

In this section of the project QA plan, the practicalities of carrying out the field measurement, sampling, analysis, and QC plans will be addressed. The critical parts of the project QA plan for the data-collection process are procedures to ensure the safety of field and laboratory personnel, and specifications for the exact protocols, equipment, and materials to be used in field measurements, sample collection and shipping, sample analysis, and data handling.

Safety

No portion of the water-quality monitoring investigation is as important as ensuring the safety of project personnel. Safety hazards unique to the project, such as the collection and analysis of hazardous, toxic, or radioactive samples, must be cited, and plans to protect personnel from these hazards must be developed and documented. The availability of safety equipment must be ensured, and all personnel must be informed of its location and availability and trained in its use. The project QA plan will provide information about how these responsibilities are to be organized and implemented, and how their implementation is to be documented.

Field Measurement

The project QA plan specifies what information must be collected concerning the selection and description of sampling sites, and how and by whom it is to be collected and recorded. This will include information related to site location and instrumentation as well as conditions observed at each site visit.

The exact make, model, and serial number of instruments to be used in making field measurements must be specified, and the processes and scheduled frequency for its calibration, testing, use, and maintenance must be described. The documents that contain this information are distinct from the protocols, or "standard methods," and are sometimes called standard operating procedures, or SOPs. Protocols, which are described in the planning portion of the project QA plan, document what project personnel are to do. SOPs describe how to carry out the protocols under actual field conditions. Protocols are often national standard methods; SOPs are invariably local documents, specific to the project time and place.

When possible, every instrument should be calibrated against standard reference materials traceable to the National Institute of Science and Technology (formerly National Bureau of Standards). Instruments should be tested before each use whenever feasible. Most instruments should have a plan for regular preventive maintenance. All calibration, testing, and maintenance activities for each instrument must be recorded in a signed, dated, permanent project record, which is archived so that data users and evaluators can ascertain that these procedures were carried out as specified and scheduled.

The USGS has demonstrated the advisability of regular proficiency testing of field personnel for their ability to perform accurate field measurements (Stanley and others, 1992). It is advisable to perform proficiency tests for all critical field measurement techniques and other difficult operations, such as field spiking, and include the results in project data archives. The USGS protocols for conducting proficiency testing of field personnel are described by Stanley (1995). Each project QA plan should provide for this vital function.

Sampling and Sample Handling

The type of equipment and the techniques to be used to collect samples for analysis must be specified, and processes for any required calibration, testing, and maintenance of sampling equipment must be described. Procedures for cleaning sampling equipment between uses are of critical importance and must be developed, tested, written, and distributed to field personnel. If cleaning takes place in the laboratory before going to the field site, provisions for maintaining cleanliness to the point of use must be specified. If QC blanks are to be used to ensure and document the cleanliness of sampling equipment between uses, the project QA plan will specify the nature and frequency of these blanks. The number, type, and means of preparation of other QC samples also must be specified in the sampling and shipping plan.

Availability of contaminant-free source water for the preparation of blanks and other QC samples is often problematic. Some analytical laboratories supply blank source water to their clients to ensure quality and consistency. Chemical supply houses also offer certified contaminant-free water, preservatives, and other sampling supplies in one-use quantities to maintain purity. Even when a laboratory or chemical supplier certifies the source water, its purity must be verified by testing, and the data included in project records. When field spikes are indicated in the sampling plan, provisions must be made for obtaining and verifying the spiking solutions and volumetric ware needed. Spiking procedures must be provided, and field personnel must be trained and tested in their use. The same is true for split samples, duplicates, and any other QC that the sampling plan may include.

The type of container to be used for delivering each kind of sample to the analytical laboratory must be specified, along with the logistics for obtaining the containers and procedures for cleaning them and maintaining cleanliness until they are used. Preservatives that may be required for some types of samples must be specified, along with procedures for obtaining the materials and testing them for impurities that may affect the analyses. Frequently, the analytical laboratory will supply and test the necessary containers and preservatives. If this is the case, the project QA plan must indicate this source and reference the procedures used to ensure against contamination.

Quality-control samples, including blank, spike, duplicate, reference material, and split samples, must be prepared and shipped with the environmental samples for analysis. A detailed plan for the frequency of each type of QC sample and tested procedures for preparing or obtaining these samples are a critical part of the project QA plan. QC samples should be prepared and handled exactly like the environmental samples. Where differences are necessary in the preparation and handling QC samples they must be documented. The project QA plan will include instructions to field personnel in how QC samples are to be prepared and documented. When field personnel are expected to produce the QC samples in the field, provision for training and periodic proficiency testing of field personnel is highly advisable.

The project QA plan must specify the protocol for shipping samples to the laboratory, including shipping containers, the designated shipper, labels, invoices, and paperwork identifying the samples and the analyses requested for each. If samples are time-dependent, the means of meeting the required holding times should be described. If samples are temperature-sensitive, the project QA plan should specify the means for documenting how the required temperature is to be maintained.

The project QA plan specifies the nature of logs and data files that document how all these requirements are met. In general, these records are part of the laboratory's data file, which is delivered with each batch of analytical reports.

Analysis of Samples

The project typically has little responsibility for laboratory operation, except to select a capable laboratory and to record the results of the laboratory's in-house QC as well as the results of QC samples shipped from the field for the project. The laboratory QA plan, certifications, and QC records can be included, either by reference, or by including copies in the project archive. The existence and availability of these archived records should be indicated in published reports.

The project manager must negotiate a firm agreement on the method to be used for each analysis to ensure that project DQOs will be met. Project records must document this agreement before sampling begins, and data assessments (covered later in this report) will confirm that the laboratory uses the chosen methods.

The project QA plan must provide for prompt feedback to the laboratory in case data quality proves unacceptable. This necessitates prompt review of all laboratory results, including QC reports. The project QA plan should provide for carrying out and documenting the review process. The project data review must include (1) the review of laboratory batch-specific QC data, (2) verification that the requested analyses are complete, and (3) comparison to prior data to verify that data make sense in context. The project QA plan also must specify a process for resampling, reanalysis, or other corrective actions when data are not acceptable. The project chief should require preventive action reports when field or laboratory errors are responsible for data failing the project review.

Shipping reports from the laboratory should be reviewed promptly to ensure that samples were received within the required time and in the required condition (such as temperature control, leakage and breakage). These shipping reports then become part of the project data archive to document shipping conditions.

Data Management

The project QA plan must specify the requirements for collecting, archiving, and handling project data. Provisions include requirements for preserving the original data records such as field notebooks, or laboratory instrument output. As more and more field and laboratory instruments incorporate computers that process data before reporting it, the definition of "original record" may be problematic; such problems must be addressed so that records are consistent. As a rule of thumb, the original record is the signed and dated first available written or printed output from a measuring instrument that can be converted mathematically into a finished datum. Field notes are increasingly being entered in laptop computers. In this case, the original record is a signed and dated paper copy of the first data entry, before transfer to a central database. Electronic records that are stored on magnetic media are unsatisfactory as original records because of their inherent impermanence, danger of being accidentally erased or altered, and inevitable inaccessibility when the devices that generated them become obsolete and unavailable.

Ancillary data (sometimes called 'metadata') that describe the circumstances of the data collection are an extremely important part of the record. These data may include the name of the collector, the methods and equipment used to generate the results, and the conditions at the sampling site (for example, high or low flow, ice cover or open water, rain or fair weather, industrial discharge, highway runoff, or background site, etc.). Data records generated to satisfy regulatory requirements must contain specific and usually extensive ancillary data. The project QA plan should specify what ancillary data must be recorded, and the justification for doing so.

QA of the data-management system, whether it be a filing cabinet or an electronic database, must be specified in the project QA plan. Electronic data systems are highly advisable for all but the smallest data-collection efforts. It is not trivial to ensure that the current data in a computerized system accurately and completely represent the data that were entered at the time of the study. In most instances, at least some of these rules are determined at a higher organizational level than that of the project manager and may be handled by citation of the appropriate documents.

DATA ASSESSMENT

Data assessment is conducted at three levels: (1) the review and validation of each set of measurements and observations from one field visit, or from a set of laboratory samples from one field sampling event; (2) overall data-quality assessments that occur when specified percentages or all of the project data have been collected; and (3) a site audit of field and laboratory processes. The project QA assessment plan will determine when and by whom these assessments are to be done. Validation of sets of data should always be done as soon as the data are available, in order to catch and correct errors before they affect more data. An overall data quality assessment at the end of the data-collection phase is needed to determine whether the body of data meets the project data quality objectives. Process audits may be required, and are usually very worthwhile as learning experiences.

Data Validation

The project QA plan must specify the criteria for accepting reviewed data, the process and time requirements for reviewing data, and corrective actions required if data do not meet data quality objectives. Environmental data are usually internally consistent and logical. Deviations from these conditions generally signal problems within the data. For example, a value of 300 for a constituent that has previously yielded values of around 30 at that site would be suspect unless some extreme change in conditions at the site can be identified. Likewise, the balance between milliequivalents of cations and milliequivalents of anions can be used to identify gross errors. A discussion of how to evaluate environmental data, with real-world examples, is provided by Brown and others (1991). The time interval within which it is possible for the laboratory to reanalyze the sample or the time interval within which the field site can be resampled may govern time limits for reviews. Names of persons responsible for performing the initial data review should be included in the plan. Corrective actions may involve resampling, reanalysis, or checking of original records for computational or transcription errors. In cases in which the data cannot be recovered, the project QA plan will address the possibility of compensating for missing data.

Data-Quality Assessment

The entire set of data is evaluated periodically and at the end of the data-collection phase, to ensure that data quality objectives are met. The project QA plan defines when, how, and by whom this assessment is to be made, and what corrective action will be undertaken if the DQOs are not fully achieved. Because precision and accuracy of data were evaluated during the initial data review, this assessment concentrates on completeness, comparability, and representativeness of data. All five data quality attributes, plus the defensibility of the data in court, if this is a goal of the project, must pass assessment in order to consider the project QA successful.

Beyond the assessment of PARCC data quality factors, however, the data must be evaluated for scientific sense in the context in which it is to be used. For this kind of data assessment, the USEPA's document, Guidance for Data Quality Assessment (USEPA, 1998b), provides a veritable textbook of ways to analyze data statistically for good sense in context. A very productive approach to assessing data in context is that of exploratory data analysis, pioneered by Tukey (1977). Using these techniques, it is easy to discern general patterns in the data and identify particular pieces of data that seem not to fit. Often, once attention is focused on these outliers, the record can be scrutinized, and the reasons for anomalies can be found. In fortunate cases, transcription errors can be corrected, or malfunctions in measuring devices can be detected by patterns in the data.

Quality Audits

When all of the above QA/QC requirements have been met, assessment of data quality by project personnel, the customer (second party assessment), or an independent auditor (third party assessment) is readily accomplished, and the project manager will have few unpleasant surprises from the auditors. In addition, a potential subsequent data user will find all the information needed to assess the usability of data for other purposes.

Project audits are specified in the project QA plan, unless they are provided for in the sponsoring organization's quality-management plan. Audits may include

- Whole-system audits, in which the project is reviewed for conformance with the project QA plan,
- Data-collection process audits in the field and in the laboratory, and
- Audits of the data, including QC data.

An audit of the data-management systems is also an obligation, and is usually addressed by the parent organization in the quality management plan.

System audits focus on the adequacy of quality management and project QA plans and whether they are being carried out as written. A process audit focuses on the adequacy of the protocols and SOPs to meet project and legal requirements, and whether they are being performed as written. A data audit looks at the project records, both paper and electronic, to determine whether they are complete and in good order as required by the project plans. Electronic data-management system audits will verify that the systems are being managed according to good professional practices, including QA of the data in the database.

Audits may be done by first-, second-, or third-party auditors. First-party audits should be a required part of an agency or corporate quality management plan. Many organizations routinely review the progress of each project according to a schedule, such as at 20-, 50-, and 80-percent completion. Second party, or customer, audits assure the customers that they are receiving what they paid for, or that regulations are being met. Third party audits may take the place of a customer audit and are increasingly replacing duplicative audits by multiple customers. Particularly in analytical laboratories that handle samples from many different customers, third-party audits by accrediting organizations are gaining credence. The project QA plan must describe the required audits and the corrective action plans for any deficiencies discovered by auditors.

Management Accountability

The information acquired in project record keeping and in reviews and audits is typically required by management of both the producing and receiving organizations. The project QA plan should include a description of the nature and frequency of these reports to management.

PROJECT OUTPUTS

The fourth and final section of the project QA plan describes the processes to be used for interpretation of data, the production and distribution of reports, including how they will be reviewed and approved, and a project self-evaluation for the purpose of continuous quality improvement in subsequent projects.

Data Interpretation

Statistical tools for the analysis and interpretation of water-quality data abound. The problem is less one of finding the tools than of selecting the most appropriate one for a given task. The selection of tools for data interpretation requires considerable professional judgement on the part of the project chief. The choices and the reasoning behind them should be documented in the project QA plan, so that others who must evaluate the information and the conclusions that are reached by the project personnel can access them. Helsel and Hirsch (1992) provide an overview of the tools for hydrologic data interpretation and their applications.

The conversion of raw chemical, biological, and physical data into useful environmental information, scientific conclusions, and support for management decisions increasingly involves complex computations and modeling using highly specialized computer software. The selection and quality assurance of these pieces of software is a necessary component of the project QA plan. Selection of software should be based on the appropriateness of the conceptual model that it implements. Care is taken that the process the software performs is appropriate to the task and that the process is accurately performed.

Quality assurance of software is a difficult process because commercial software providers usually do not disclose the source code for the software. Substantive errors in software for data interpretation are not unknown. Test data sets may provide the only QA evidence available. It is highly advisable to run a test data set before using any new software package and when a new version or a new operator comes online. Quality assurance of all software used in data interpretation should be given the most serious consideration in the project QA plan.

Reports Preparation

The project QA plan should specify the form in which information and conclusions are to be reported, by whom they are to be prepared, when they will be delivered, and how those reports will receive technical, editorial, and policy review by the publishing organization. Moore and others (1990) suggest that an outline of all anticipated reports in the project be made and reviewed by technical management in the first month of the project, and that an annotated outline of each report be prepared within the first several months of the project. This practice helps to ensure that planning for the report is thorough and that the necessary data are being collected and interpreted. Reports should include estimations of the uncertainty of data based on project QA/QC activities, and of the resulting uncertainty in interpreted results and conclusions made on the basis of the data.

Project Evaluation

It is advisable for all organizations to practice self-evaluation and strive for continuous improvement in all their processes. The final process in any project should be an examination of project plans and processes for opportunities for improvement. Sometimes this evaluation produces new techniques that benefit the entire field of water-quality monitoring. In such cases, the investigating organization has an obligation to publish their discoveries. More frequently, the examination results in incremental improvements in project plans, protocols, and SOP's that make subsequent projects more efficient and effective.

CONCLUSION

Planning for quality assurance and quality control (QA/QC) should be documented in a comprehensive project QA plan. QA/QC should be carried out as part of a comprehensive corporate (or agency) quality system that is centered in a quality management plan. No single QA/QC plan is likely to require all the elements described herein, but each of these elements is needed in some situation. The project manager and project QA officer must identify the elements required by the goals of the individual project or type of project and design a plan around the QA/QC elements that address those goals. Because the concepts of modern QA/QC are quite recent in origin, it should not be expected that projects conducted a decade or more ago will possess all or even many of the kinds of records and data described here. The lack of QA/QC data will, however, decrease the usefulness of much older environmental data for incorporation in future projects without extensive reverification.

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GLOSSARY

This glossary contains definitions of terms as they are used in this paper. The following references were consulted in developing these definitions: Shampine and others (1992); American National Standards Institute, International Organization for Standards, and American Society for Quality Control (1994).

Accuracy: the degree to which a measured value agrees with the true value of the measured property.

Bias: the extent to which a measured value differs from the true value of the measured property.

Blank: a synthetic sample that is free of the analyte(s) of interest.

Chain-of-custody: unbroken record of accountability that ensures the physical security of samples.

Comparability: the degree to which two pieces or sets of data represent environmental conditions in the same way, so that the difference between the data or sets of data accurately represents the change in environmental conditions over time or space.

Completeness: the percentage of the planned data that was actually obtained in a project.

Corrective action: action taken to eliminate the cause of an existing nonconformity, defect, or other undesirable situation in order to prevent recurrence.

Data-quality objectives: qualitative and quantitative statements that clarify the goals of the study, define the appropriate data to be collected, determine the most appropriate conditions from which to collect the data, and specify tolerance limits on decision errors that will be used to establish the quality and quantity of data needed to support the decision.

Limit of detection: the lowest concentration of an analyte that can reliably be distinguished from a blank by a given analytical method or measurement. Generally computed as three times the standard deviation of the blank.

Limit of quantitation: The lowest concentration that can be measured quantitatively by a given analytical method. Generally computed as 10 times the standard deviation of the blank.

Precision: the extent of random variability among replicate measurements of the same property.

Protocol: a set of instructions that describes a way to carry out an activity, such as sampling or measuring an environmental system. Standard protocols have been thoroughly investigated and have known and documented quality characteristics. Protocols are sufficiently general to be applicable in many organizations, where a variety of instrument and equipment models are used.

Quality: total characteristics of an entity that bear on its ability to satisfy stated and implied needs.

Quality audit: systematic and independent examination to determine whether quality activities and related results comply with planned arrangements and whether these arrangements are implemented effectively and are suitable to achieve objectives.

Quality Assurance: all of the planned and systematic activities implemented within the quality system, and demonstrated as needed, to provide adequate confidence that an entity will fulfill requirements for quality.

Quality control: operational techniques and activities that are used to fulfill requirements for quality.

Quality Management: all activities of the management function that determine the quality policy, objectives, and responsibilities, and implement them by such means as quality planning, quality control, quality assurance, and quality improvement within the quality system.

Quality system: organizational structure, procedures, processes, and resources needed to implement quality management.

Reference material: a substance that has been extensively analyzed to arrive at a consensus or best value of the concentration of one or more of its constituents. Used to assess measuring systems: protocols, instruments, laboratories, or analysts.

Replicate samples: two or more samples taken from the environment at the same time and place, by using the same protocols. Used to estimate the random variability of the material sampled.

Representativeness: the extent to which a sample represents the population from which it is withdrawn.

Sample: a portion of a population (environmental entity) that is measured and assumed to represent the entire population.

Spiked sample: an aliquot of an environmental sample to which a measured amount of analyte has been added. When the analysis of the spiked sample is compared to an otherwise identical unspiked sample, the percent of the spike that is recovered can be computed. This quantity is assumed to represent the percent of the analyte recovered in the analysis.

Split sample: a single sample which, after removal from the population, is divided into two or more parts believed to be identical. Used to estimate variability in sample handling or measurement processes.

Standard operating procedure: the exact description of how to carry out a protocol under project conditions. Includes organization-, equipment-, and site-specific instructions that are more detailed than a protocol.

Variability: the extent to which results from multiple results of the same measurement yield differing results. Variability may be inherent in a measuring instrument or in the sampled material.

Chapter 3. Basic Requirements for Collecting, Documenting, and Reporting Precipitation and Stormwater-Flow Measurements

By PETER E. CHURCH, GREGORY E. GRANATO, and DAVID W. OWENS

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Basic Requirements for Collecting, Documenting, and Reporting Precipitation and Stormwater-Flow Measurements

By Peter E. Church, Gregory E. Granato, *and* David W. Owens

Abstract

Accurate and representative precipitation and stormwater-flow data are crucial for use of highway- or urban-runoff study results, either individually or in a regional or national synthesis of stormwater-runoff data. Equally important is information on the level of accuracy and representativeness of this precipitation and stormwater-flow data. Accurate and representative measurements of precipitation and stormwater flow, however, are difficult to obtain because of the rapidly changing spatial and temporal distribution of precipitation and flows during a storm. Many hydrologic and hydraulic factors must be considered in performing the following: selecting sites for measuring precipitation and stormwater flow that will provide data that adequately meet the objectives and goals of the study, determining frequencies and durations of data collection to fully characterize the storm and the rapidly changing stormwater flows, and selecting methods that will yield accurate data over the full range of both rainfall intensities and stormwater flows.

To ensure that the accuracy and representativeness of precipitation and stormwater-flow data can be evaluated, decisions as to (1) where in the drainage system precipitation and stormwater flows are measured, (2) how frequently precipitation and stormwater flows are measured, (3) what methods are used to measure precipitation and stormwater flows, and (4) on what basis are these decisions made, must all be documented and communicated in an accessible format, such as a project description report, a data report or an appendix to a technical report, and (or) archived in a State or national records center.

A quality assurance/quality control program must be established to ensure that this information is documented and reported, and that decisions made in the design phase of a study are continually reviewed, internally and externally, throughout the study. Without the supporting data needed to evaluate the accuracy and representativeness of the precipitation and stormwater-flow measurements, the data collected and interpretations made may have little meaning.

INTRODUCTION

Accurate and representative precipitation and stormwater-flow data are crucial for valid, current, and technically defensible interpretations of highway- or urban-runoff study results. Additionally, results from a number of accurate and representative studies are necessary for developing a regional or national synthesis of stormwater-runoff data. Obtaining such data is not a trivial matter because the stormwater-monitoring environment is complex. Varying rainfall patterns result in runoff flows, constituent concentrations, and constituent loads that vary considerably within and between storm events (Harrison and Wilson, 1985; Hoffmann and others, 1985; Irish and others, 1996). Different antecedent conditions, different storm volumes and durations, and different patterns of precipitation intensity make each storm a unique event. These differences can cause large variations in event-mean concentrations (EMCs) and total constituent loads measured for each storm (Driscoll and other, 1990a; Irish and others, 1996). Models describing highway- and urban-runoff constituent loads will not be quantitative without detailed characterization of these complex physical and hydrochemical processes that govern constituent accumulation and release (Spangberg and Niemczynowicz, 1992).

Knowledge of variations in the intensity and duration of precipitation and the resultant effects on stormwater flows, pollutant concentrations, and pollutant loads is necessary to characterize stormwater runoff from highways, urban areas, and other areas contributing nonpoint-source pollution to receiving waters. The amount of energy available to mobilize and transport dissolved and suspended constituents is a function of rainfall intensity. A tenfold increase in intensity will increase the kinetic energy of rainfall impact by about 15 times (Smith, 1993). Average storm intensity and total flow per unit area were the most statistically significant predictors for all common highway-runoff constituents in a recent study of highway runoff that included a rainfall simulator and natural storms (Irish and others, 1996). Accurate measurement of the intensity and duration of each precipitation event and resultant total storm discharge is important to quantify the pollutant mass balance and effects upon a receiving water body (Thoman and Mueller, 1987; Irish and others, 1996). Characterization of storm intensity and duration are also important to the monitoring process because the accuracy of both time-based and flow-weighted compositing schemes depends on accurate flow measurements (USEPA, 1992). Also, because automatic samplers commonly used in stormwater studies have a fixed volume for sample collection, it is difficult to match the frequency and duration of the sampling period to variations in the intensity and duration of monitored storms for the optimization of sampling schemes. Data interpretation is also dependent upon knowledge of the intensity and duration of precipitation and resultant runoff because calculation of loads and EMCs (calculated from discrete samples, or composited manually or automatically) all depend upon the accuracy of precipitation and (or) flow measurements.

Problem

Accurate and representative measurements of precipitation and stormwater flow are difficult to obtain because of the rapidly changing spatial and temporal distribution of precipitation in the drainage system and the rapidly changing flows during a storm. The quality of precipitation and stormwater-flow measurements found in the literature is difficult to assess without the supporting data needed to evaluate their accuracy and representativeness. Accurate measurements of precipitation are confounded by difficulties in finding a representative site, the ability of instruments to record data accurately over a wide range of rainfall intensity, concerns with spatial and temporal variability, the reliability of measuring and recording instruments, and problems with freezing conditions at sites where commercial power is not available. Physical and logistical complications also affect the quality of stormwater-flow measurements.

Stormwater-flow rates can range over several order of magnitudes in a short period. Flow regimes (steady or unsteady flow, subcritical or supercritical flow) can change in response to the varying flow rates. Flow durations and intervening dry periods also vary within drainage systems. The resolution of field measurements and commercially available measuring equipment is relatively coarse for measuring flows in small streams, pipes, swales, and sheet flow over pavements and soils. The introduction of a flow-measurement device in a small channel or pipe can disturb the flow being measured. Because storm drainage systems often have little, if any, base flow, erratic measurements can result when measuring instruments are dry; instruments may not be able to accurately measure flow until stormwater flows reach a minimum water level. Also, equipment and instrumentation required for accurate flow measurements may be costly. Selecting a site where flows are consistent with the data objectives, the appropriate frequency and duration of flow measurements to fully characterize the stormwater-flow event can be obtained, and a method for measuring the full range and types of flow in a natural or controlled channel with minimal disturbance is not a trivial task, but is critical to ensure accurate and representative stormwater-flow measurements.

Documentation of the steps followed and the uncertainty involved in the selection of sites for measuring precipitation and stormwater flow, the frequency and duration of monitoring, and the methods, equipment, and instruments used to monitor precipitation and stormwater flow are needed for evaluation of the accuracy and representativeness of the data collected. This evaluation is important for assessing the validity of the data collected because errors in precipitation or flow data result in inaccurate relations between rainfall and runoff, and errors in flow and (or) pollutant concentration result in erroneous calculations of pollutant loads, event-mean concentrations, and total mean daily loads. Validation of the accuracy and representativeness of flow and constituent concentrations data in highway and urban runoff also are important because these data form the baseline on which models developed for prediction of stormwater loads and event-mean concentrations are calibrated (Guerard and Weiss, 1995; USEPA, 1997; Zarriello, 1998), and from which best management practices are developed. Without the supporting data needed to evaluate the accuracy and representativeness of the precipitation and stormwater-flow measurements, the data collected and interpretations made may have little meaning.

Additionally, it is important that precipitation and flow measurements fulfill a particular need or objective and that this objective and the acceptable uncertainty be clearly stated. Collection of data without a clear data-quality objective may result in collection of marginal or useless data (Whitfield, 1988). The accuracy and representativeness of data collected can be evaluated quantitatively only if information is available about (1) where in the drainage system the flows were measured, (2) how frequently the flows were measured, (3) what methods were used to measure flows, and (4) on what basis these decisions were made. All of this information should be documented in terms of project data-quality objectives. Furthermore, the Intergovernmental Task Force on Monitoring Water-Quality (ITFM) has recommended that flow measurement be a component of water-quality studies and that data from monitoring programs be collected, documented, and reported in a consistent manner (ITFM, 1995a,b).

Purpose and Scope

The purpose of this report is to present the basic requirements for collection of accurate and representative precipitation and stormwater-flow measurements and the supporting data that must be documented and reported to ensure that these data can be independently validated. Data requirements for determination of accurate and representative precipitation and stormwater-flow measurements are evaluated within the context of building a quantitative national data base that will be used to record and predict highway-runoff pollution (Granato and others, 1998).The methods available for measuring precipitation and stormwater flow are widely reported in the literature, so they are described only briefly here. The information that needs to be documented and reported to allow for independent evaluation of the accuracy and representativeness of precipitation and stormwater-flow measurements, however, is less well described, and therefore, is emphasized in this report. References that provide more detailed guidance for collection of accurate and representative precipitation and stormwater-flow measurements are provided.

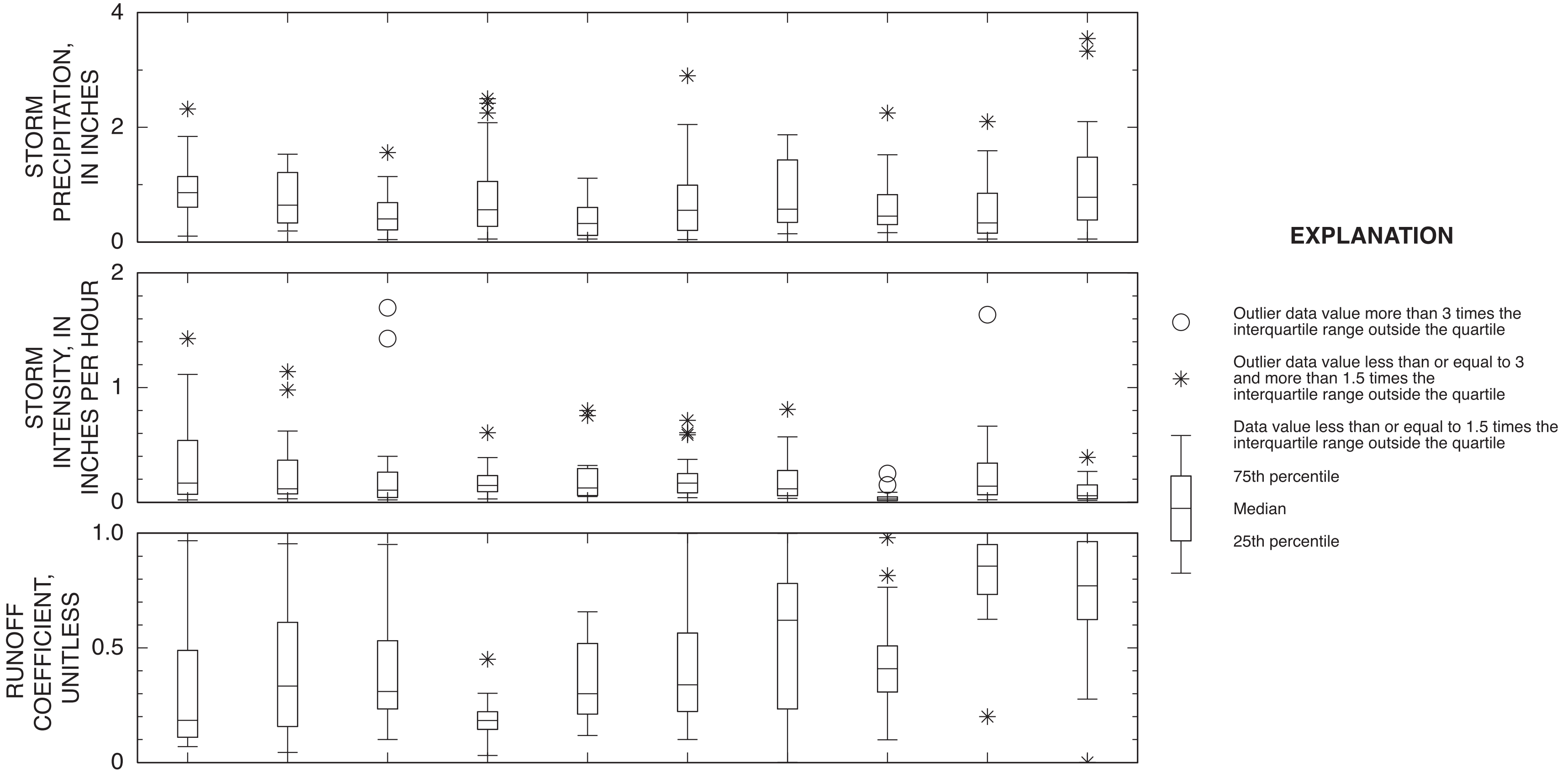
PRECIPITATION DATA

Precipitation is the driving force of the stormwater runoff process and its accurate monitoring is necessary to characterize the rainfall-runoff process. Rainfall can be highly variable in space and in time (Alley, 1977). Precipitation intensity and duration are major factors determining removal of runoff constituents during a storm. Varying rainfall patterns result in runoff flows and contaminant washoff rates that vary considerably within and between storm events (Harrison and Wilson, 1985; Hoffmann and others, 1985; Irish and others, 1996). A positive correlation between the physical and chemical characteristics of rainfall and runoff is expected and well documented (Driscoll and others, 1990a; Irish and others, 1996). Higher intensity rains wash more dissolved and suspended constituents from watershed surfaces than equivalent volumes from lower intensity events (Athayde and others, 1983; Irish and others, 1996).

Theoretically, uncertainty in precipitation measurements should be lower than uncertainty in stormwater-flow measurements because precipitation measurements are direct, whereas many stormwater flow “measurements” are calculated from a stage measurement and a discharge rating. If predictive models are implemented by using regression techniques that do not account for possible uncertainties in the independent variables, then rainfall may be considered a better regressor for water-quality variables than runoff for a given site because of these lower uncertainties in precipitation monitoring (Irish and others, 1996). It is necessary, however, to measure or derive accurate stormflow volumes for the collection and interpretation of runoff-quality data because sample compositing methods and constituent load calculations depend on the availability of runoff-flow volumes.

Examination of precipitation and runoff data from the Federal Highway Administration (FHWA) highway-stormwater-runoff data base (Driscoll and others, 1990b) indicates that precipitation data is a useful, but not a direct, surrogate for measured stormflows. Data including date, total precipitation, storm duration, and total runoff from 264 storms at 9 highway sites and at 1 grassy plot, each having the required data for at least 10 storms, were selected (Driscoll and others, 1990b). Precipitation intensities were calculated as the quotient of total precipitation and storm duration for each storm from these data. Runoff coefficients were calculated as the quotient of total runoff and total precipitation volume for each storm. Boxplots of the data for each of these ten sites are shown in order of increasing imperviousness, and increasing precipitation when percent impervious is the same (fig. 1). Although the average annual precipitation among these 10 sites varies from about 15 to about 84 inches per year, total storm precipitation, intensity, and runoff coefficients from the storms monitored are comparable. The boxplot graph of the runoff-coefficient populations is artificially truncated at 1.0 (the point where runoff equals precipitation) because, logically, the total runoff from a storm should not exceed the measured precipitation. Values above a runoff coefficient of 1 may reflect uncertainties in the data, between-storm storage within the highway catchment, base flow from ground water, and (or) contributions from additional drainage areas during some storms. Examination of figure 1 indicates that for these data, there is no single runoff coefficient that can be accurately used to predict total runoff from total precipitation at any given site. For example, the uncertainty in predictions of total stormflow based on measured precipitation would be about plus or minus 50 percent at the Route 384 site in Florida, which had the least variation in runoff coefficients among these 10 sites from the FHWA data set (Driscoll and others, 1990b).The population distributions for different sites in this figure do not indicate a simple relation between the median runoff coefficient and increasing impervious area. Common sense would suggest that catchments with a very high proportion of impervious area would have less variability in the runoff coefficient because runoff from impervious pavement would not be affected by antecedent moisture. The population distributions for runoff coefficients in figure 1, however, do not demonstrate lower variabilities at highly impervious sites.

Differences in rainfall-runoff relations from season to season caused by effects of temperature, precipitation characteristics, and the length of the antecedent dry period may obscure meaningful relations in figure 1. To explore the feasibility of establishing seasonal runoff coefficients that would be characteristic of highways nationwide, the data from the 9 paved highway sites were combined and are shown in figure 2. Each of the studies selected from the FHWA data report (Driscoll and others, 1990b) had a duration of about 1 year, but the studies were done in different years and many studies did not sample a substantial number of storms in each month. In these boxplots, total precipitation for each storm seems to be slightly more variable in the winter months than in the rest of the year (except for January, because only four storms were sampled in this month). Also, the population of intensities seems to be more variable in the summer (possibly due to the occurrence of convective storms in the warmer months). The populations featured in figure 2, however, do not indicate a characteristic runoff coefficient for highway sites even when the effects of seasonality are examined. The data reported by Driscoll and others (1990b) is a compilation of two distinct phases of the early FHWA water-quality research and similar studies conducted by transportation departments in several States. Differences in methods, equipment, and measurement installations between these monitoring programs at different sites throughout the Nation may introduce bias and contribute to the variability apparent in figure 1 and figure 2. Therefore, precipitation measurements can provide valuable information for interpretation of results, but may not be a direct surrogate for measured runoff flows, even in small catchments.



STUDY SITE INFORMATION

	Rt-45 (Grass), WI	I-81, PA	Rt-45, WI	Rt-384, FL	I-25, CO	I-40, TN	I-30, AR	Rt-270, WA	I-794, WI	Rt-12, WA
Number of Events	12	23	29	45	16	31	15	25	33	35
Percent Impervious	0	27	31	36	37	37	90	100	100	100
Area (Acres)	2.7	18.5	106	58.3	35.3	55.6	1.5	0.25	2.1	0.28
Average Annual Precipitation (In)	27.6	37.7	27.6	62	14.8	45	48.7	18	27.6	84

Figure 1. Population statistics from stormwater data recorded at 10 historical highway-runoff-monitoring sites with available total precipitation, storm duration, and stormwater-flow data from individual events (data from Driscol and others, 1990b).

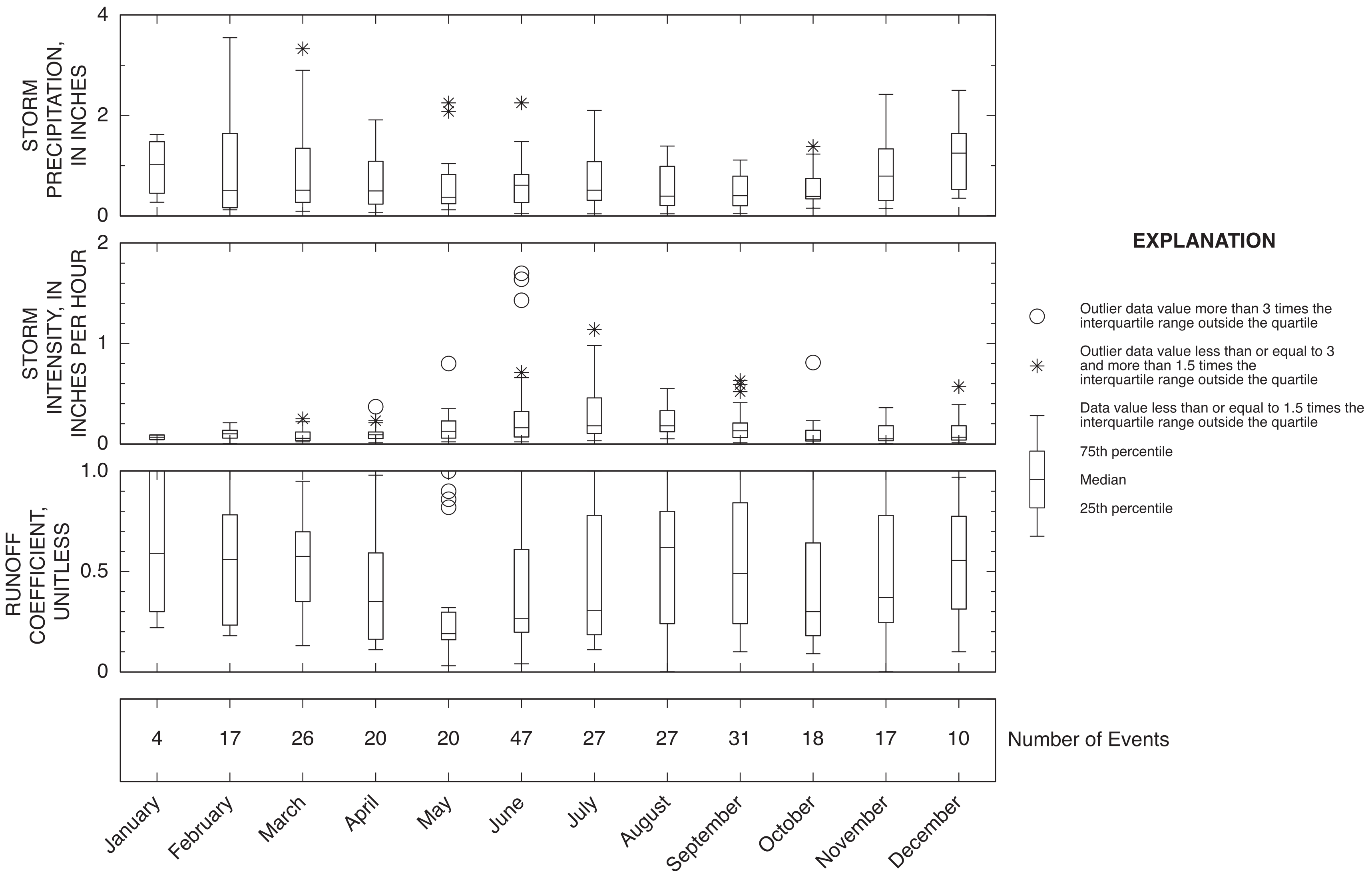


Figure 2. Seasonal population statistics of stormwater data including nine highway-runoff monitoring sites with available total precipitation, storm duration, and stormwater-flow data from individual events (data from Driscol and others, 1990b).

Many runoff models have been designed and implemented to compensate for the inaccuracies inherent in simple runoff coefficient methods used to predict runoff (Alley, 1977). Results of a recent comparative study, however, indicate that even complex rainfall-runoff models may not deliver high levels of predictive accuracy (Zarriello, 1998). When nine well documented stormwater-runoff models were used to predict stormflow volumes from precipitation data from two small watersheds (by experienced modelers using detailed precipitation and land-use data), the average root mean square model error was about 55 percent and simulated storm volumes differed from observed storm volumes by as much as 240 percent.

Despite recognized limitations in accuracy and representativeness, precipitation data are necessary to document study results in a way that is valid and technically defensible. Although the relations in the existing FHWA data set are not quantitative, it is necessary to establish relations between precipitation characteristics, measured flows, and observed contaminant loads so that results from lengthy and expensive data-collection efforts can be applied to ungaged sites. Also, the ratio of measured runoff to rainfall provides verification data that can be used to identify problems with measurement conditions, changes in stage-discharge relations, storage between storms, variations in the contributing area under different conditions, and other possible problems in the data-collection efforts. Precipitation data are necessary to define each storm and each study period in terms of long-term cycles in precipitation. For example, a 1-year study during a long-term period of drought may not accurately represent concentrations, flows, and loads for more typical wetter years.

Precipitation measurements also serve several useful functions that are not provided by runoff-flow monitoring. A recording rain gage provides detailed information about the intensity and timing of precipitation. Knowing exactly when precipitation starts and stops in relation to the beginning and end of measured flows indicates the time of concentration and the time of travel in the drainage basin. Precipitation gages will record light precipitation events, which may not cause a rise in stage sufficient to activate the stormwater-flow-measurement equipment (in which case the stage threshold for equipment activation may be reduced for subsequent events). Also, if heated gages are used, precipitation gages will record winter events that may not result in immediate runoff.

To collect accurate and representative precipitation data, a number of technical factors must be considered. These factors include the proper siting for the measuring equipment, the selection of appropriate measurement intervals, the collection of enough data to characterize conditions at a site, and the selection of methods that will meet data-collection objectives of the study design. A study may produce a detailed record of precipitation in a study area, but bias introduced by problems in the study design may limit the quality and usefulness of data collected on site.

Site Selection

Proper siting is necessary for the collection of accurate and representative precipitation data. The small drainage areas and large proportion of impervious areas characteristic of highway catchments cause large variations in measured flow within a few minutes of variations in precipitation (Harned, 1988). Therefore, the placement and density of gages in a study are critical factors for interpretation of precipitation data in highway- and urban-runoff studies. Individual placement and precipitation-gage-network density are the two main factors to consider when siting gages for a given study. Proper gage placement will help ensure that accurate and representative precipitation data may be collected at individual gage sites, and sufficient gage density within a network will help ensure the accuracy and representativeness of data for estimates of precipitation in a given area.

The magnitude of errors for each gage is a function of wind speed, siting characteristics, and the type of precipitation (Smith, 1993). High winds are recognized as the greatest source of error for rain-gage-data integrity, so some type of wind shielding is necessary (Alley, 1977; Smith, 1993; USEPA, 1992). Effects of wind created by vehicles travelling at highway speeds, therefore, is a factor to consider when siting precipitation gages for highway-runoff studies. Precipitation gages should be located near the land surface, not on buildings or other elevated structures because mean wind velocities increase with height above local land surface (Alley, 1977; Smith, 1993). Although buildings and trees provide necessary wind shielding, gages should not be placed nearer than the height of the obstacle so that they do not interfere with the path of falling precipitation (Alley, 1977; USEPA, 1992). Poorly exposed gages can underestimate measured precipitation by 5 to 80 percent (Alley, 1977). It is also important to locate gages on relatively level surfaces to prevent bias from poor exposure. In small catchments, a precipitation gage should be placed near the runoff flow gage to ensure close correlation between measurements because variations in measured runoff at the surface-water-flow gage are most sensitive to variations in precipitation near the measuring point (Alley, 1977).

Good precipitation gage locations near highways and in urban areas can be hard to find. Highway structures, slopes, buildings, and trees can interfere with precipitation. Ground-level gages are prone to vandalism and tampering. Electricity for a heated gage may not be available in the highway right-of-way, and water formed as a by-product of combustion in fuel-heated gages can bias results. Winds and spray from moving vehicles can be substantial near the roadway (Irish and others, 1996) and cause bias in measured precipitation near the roadway.

Precipitation is recognized to be highly variable in both space and time. For example, Fontaine (1990) indicated that errors in estimates of basin average precipitation from national network data were often greater than plus or minus 20 percent and that supplemental study-site gages were necessary to increase network density for urban-runoff studies. During the last major FHWA field study in the early 1980's, differences in timing, intensity, and magnitude of precipitation were visible in data records among three stations within a few miles of each other (Harned, 1988). The need for multiple rain gages in studies of areal extent is generally recognized (Alley, 1977). Precipitation-gage density is defined as the number of gages per catchment area. The placement of rain gages in a study network should represent catchment topography, and ideally should tie in with historical stations in a larger network, such as the network operated by the National Oceanographic and Atmospheric Administration (NOAA) (Alley, 1977). National networks typically have density of about 1 gage per 230 square miles. For larger watersheds (greater than 100 square miles), gage density is more important than the design of gage distribution in the network to estimate basin average precipitation (Fontaine, 1990).

Thorough documentation of precipitation-monitoring sites and network design is necessary for the validation of precipitation-monitoring data. Factors pertinent to gage siting, such as wind speed and direction of prevailing winds, site slope, proximity to obstacles, and location relative to surface-water-flow-measurement stations, must be considered. The location should be specified to the extent that the site could be reinstrumented for future studies that may later examine source or land-use changes at a given study area. Therefore, a detailed site map is warranted and it should have land features, a scale, and at least two reference points with latitude and longitude to the nearest second. The location of precipitation-monitoring stations with respect to the location of long-term monitoring networks is important to help establish the relation between precipitation-monitoring records during the study and historical records that would indicate the comparability of precipitation measured in the study period to long-term climatic characteristics.

Frequency and Duration of Precipitation Measurements

The frequency and duration of precipitation-measurement operations is dependent upon the time scales of the processes under study. Requirements for sufficient data are defined by data-analysis techniques, quality of data needed, program objectives and constraints, and the representativeness and variability of the storm events that are gaged and sampled (Alley, 1977). For stormwater-quality studies, the recording frequency must be sufficient to characterize and interpret physical (hydraulic) and chemical processes. In terms of duration, monitoring equipment needs to be able to record an entire event (at least up to a specified design storm) and to be durable enough to operate reliably between scheduled maintenance visits. The duration of the monitoring program must be designed so as to be able to put data into historical perspective. Historically, measurement frequency has been controlled by the sampling budget and the program duration has been controlled by both budget and time constraints. Although these will always be real issues, continuous improvements in automatic-monitoring instrumentation and equipment can improve upon data available from manual measurements.

High-frequency-monitoring capabilities available from state-of-the-art data logger-controlled-monitoring systems have the potential to improve the understanding of physical and chemical rainfall-runoff processes. In terms of the monitoring frequency, the apparent randomness in stormwater processes from storm to storm and from site to site may be related to lack of adequate data, especially related to the time scales of measurement (Spangberg and Niemczynowicz, 1992). The maximum recording interval for individual precipitation measurements depends upon catchment size and can range from less than 1 minute for very small paved catchments to a maximum of about 15 minutes for larger catchments (Alley, 1977; Spangberg and Niemczynowicz, 1992). In theory, the recording interval should not be longer than one-fifth to one-tenth of the time it takes for water from the furthest point in the catchment to reach the flow-gaging station during times of most rapid flows (Alley, 1977). Harned (1988) found that in one highway-runoff study, runoff in the smallest basin (with an area of 0.0032 square miles, including a highway and a rest area) responded within minutes to changes in rainfall intensity, and the maximum discharge coincided with periods of intensive rain. Stormflow recession was brief in this small catchment that had a high proportion of impervious cover and an engineered drainage system (Harned, 1988). Chemical response time for the catchment should also be considered in stormwater-quality studies. In the field studies sponsored by the FHWA that were designed to characterize highway-runoff quality, precipitation data were recorded on a time scale of about 5 minutes (Shelley and Gaboury, 1986). When Spangberg and Niemczynowicz (1992) examined relations between measured precipitation, turbidity, pH, specific conductance, and flow rate (measured on a 10-second time interval on a 0.0001-square-mile paved parking lot), cross-correlation analysis indicated that changes in water quality occurred with changes in precipitation intensity and flow rate on a time scale of less than 1 minute. Although the high costs for collection and analysis of water samples are a limiting factor for many projects, costs for installation and operation of automatic precipitation, flow, and water-quality instruments do not vary with monitoring frequency. Relatively high-monitoring frequencies provide substantially more detail and insight, but do not necessarily require substantially more labor and resources for data collection, storage, processing, and interpretation. The main drawback to high-monitoring frequencies—the possibility of the loss of data by exceeding the storage capacity of the data recording device—can be avoided by use of a regular station maintenance schedule coupled with available technology for remote data retrieval by telephone, cellular telephone, radio, or satellite link.

The required station maintenance schedule for precipitation-monitoring studies is defined by the storage capacity of the data recording device. Automated monitoring stations can be programmed to minimize measurement activity during dry periods and to maximize data collection frequencies during periods of stormwater runoff (Church and others, 1996). Additionally, many precipitation gages only record data when activated by measured precipitation. The frequency and duration of expected events in a given area are important factors in these determinations. It is important to characterize even small events because when the frequency distribution of storms of different size and duration are grouped, the proportion of annual precipitation is about equal for the different storm-size classes (Brown and others, 1995). A compromise between high-resolution monitoring and duration can be achieved using programming that measures on a high frequency but only records measurements at high frequencies during storm events when flows and water-quality measurements are changing rapidly (Church and others, 1996).

On a longer time scale, the duration of precipitation-monitoring studies is limited by the duration of the project. Studies have shown that decades of rainfall and streamflow data are necessary to generate design storm statistics in a catchment, but it is also recognized these monitoring durations are impractical for most stormwater projects (Alley, 1977). Theoretically, over long periods of time, the random variation of storm patterns in time and space in an area will be equal to reference stations and, therefore, population statistics will be similar. There are several standard methods for record extension when data from one site can be correlated to a monitoring site with a long period of record (Helsel and Hirsch, 1992). Long-term monitoring data for record extension are available from a national weather-monitoring network maintained by the NOAA (Alley, 1977). Long-term precipitation records may also be available from municipal governments, water and wastewater treatment plants, universities, airports, news organizations, and other sources. Daily precipitation values, however, are often based on a sampling day (for example, 9:00 a.m. one calendar day to 9:00 a.m. the next calendar day), so direct day-to-day correlation may be difficult if daily data is not synchronized among data sources.

Thorough documentation of the frequency and duration of data from precipitation-monitoring stations is necessary to ensure the validity and usefulness of data collected. Comparison of the characteristics of measured precipitation during the study period is necessary for immediate and future users of the data in order to put observations made during the study period into a long-term perspective that will improve the interpretive/decision-making process. Supporting data or the source of published data (such as the NOAA records from a given monitoring station) and the comparative analysis should be documented in published reports for future use.

Methods for Measuring Precipitation

Methods that allow accurate monitoring of precipitation intensity and total accumulated precipitation are necessary for planning, design, collection, and interpretation of results for stormwater-quality studies. Historically, a 0.01-inch (0.25-mm) precision level has been considered to be comparable with distortions in precipitation catch encountered in urban areas, the areal variability of precipitation, and the precision level of other stormwater-monitoring instruments (Alley, 1977). At least one recording gage is necessary to provide the detailed precipitation information needed at each study site, but data from nonrecording gages can supplement this information, and (or) be used to build correlations among established precipitation-monitoring sites.

Nonrecording precipitation gages (manual measurements) are generally sufficient for measuring total precipitation during the measurement period. These gages do not directly provide information about the actual timing, duration, or intensity of precipitation that occurs during the measurement period. Any open container with an established rating between precipitation catch and either weight or depth of precipitation collected can be used as a nonrecording gage (USEPA, 1992). Nonrecording precipitation gages can provide excellent verification (Quality Assurance and Quality Control) data because they are easily constructed and (or) inexpensive to obtain. One or more nonrecording gage(s) can be used in conjunction with a recording gage to provide substitute information in case of equipment failure. A number of these devices can be emplaced to supplement recording gages and used to examine assumptions about the areal distribution of total precipitation in and around a study area. Data from these gages can be biased by evaporation or by overflow conditions if the time between manual measurements is substantial. Results from visual gages can be biased by parallax, and water displacement, or absorption upon insertion of a measuring stick. When using nonrecording gages, records for snow events must be derived from measurements of snow depth and water content (Alley, 1977). Representative snow measurements from nonrecording gages in highway rights-of-way may be difficult because of variations caused by natural and vehicle-induced winds, as well as by snow removal/deicing operations.

Recording precipitation gages (automatic measurements) have several advantages over nonrecording gages. Recording gages can record the timing, duration, and intensity of precipitation that occurs during the measurement period, as well as indicate the total precipitation for each storm. Depending upon the design of the gage, evaporation is either not an issue or evaporation between events can be determined from data records. Also, automatic gages are generally designed to prevent or reduce errors from overflow. Most rain gages, however, have a tendency to under record when rain is greater than 3.0 inches per hour (Alley, 1977). Studies in areas with large variations in precipitation intensities may require more than one gage, each with different resolutions, at each monitoring site (Spangberg and Niemczynowicz, 1992).

Weighing, float, and tipping-bucket gages are the three main types of recording precipitation gages that are widely accepted and readily available (Alley, 1977; FHWA, 1985; USEPA, 1992). Weighing gages measure and record the weight of water in the collector at each time interval. Float gages measure accumulated rain by recording the position of a float in a collector. Float gages can be emptied by a siphon tube or by an automatic pump when full. Tipping-bucket gages measure precipitation by recording the actuation of a small seesaw each time the receptacle (the bucket) at an end of the pivot fills, tips, and empties. Tipping-bucket gages have a long record of proven ability, commercial availability, and are the most widely used (Alley, 1977).

Snow is more difficult to measure than rain. Weighing gages are generally better for snow than other gages. Float gages and tipping-bucket gages are not suitable for measuring snow unless they are heated. Requirements for heating gages raise logistical and interpretive complications due to the necessity for fuel or power for heating and accounting for the precipitation lost to condensation as a result of this heating.

Improvements in collection and interpretation of weather radar and satellite data over the last 10 years should be considered to provide information about local precipitation characteristics when planning a study or verifying data collected. Radar has high temporal (as small as 5 minutes) and spatial (as small as 0.386 square mile) resolution and range over a range of up to 130 miles (Smith, 1993). Radar measurements are subject to a number of sources of uncertainty, and so may not be sufficient as a primary precipitation-monitoring system, but they may be obtained from the National Weather Service, news organizations, and airports. Many of these organizations post these data to the internet. Precipitation estimates from satellite measurements are based upon infrared imagery of cloud-top characteristics. Although these estimates are not precise, this information may be used to estimate rainfall in areas not covered by data networks using more precise methods (Smith, 1993).

Thorough documentation of precipitation-monitoring methods and measurement equipment used is necessary for the validation of precipitation-monitoring data. Factors pertinent to manual and electronic recording device, such as calibration and maintenance records, the maintenance schedule, the measurement interval, and equipment malfunctions, should be documented and archived in project records. Details about equipment construction and operation of gages (including equipment specifications) should also be documented and archived in project records. Precipitation records in published reports should include the measurement interval and equipment specifications that are relevant to interpretation and calibration of the data. Simply recording the make and model of a device will not be sufficient if specifications change or if detailed information may not be available from the manufacturer.

STORMWATER-FLOW MEASUREMENTS

The accuracy and representativeness of stormwater-flow measurements for computation of pollutant loads and event-mean concentrations, whether from a natural stream channel, an engineered channel, a highway or urban drainpipe, sheetflow from a parking lot, or overland flow from a grassy swale, are based on many common factors that all contribute to the uncertainty of the data set. These factor include:

- The representativeness of the site selected in relation to the contributing area of concern,
- The ability to obtain accurate flow measurements at the selected site,
- The timing, frequency, and duration of flow measurements, relative to the timing, intensity, and duration of the storm, to fully characterize the flow event, and
- The ability of the flow-measurement method to accurately measure the full range of flows at a frequency required to fully characterize the flow event.

Selecting representatives sites, ensuring their suitability for accurate flow measurement, determinating appropriate measurement frequencies, and selecting the best method for measuring flows may require a significant effort, but are critical for the measurement of accurate and representative flows. For example, when receiving waters are also monitored, the stability of the stream channel bed and banks up and down gradient of the proposed site must be assessed before the site can be assumed to consistently yield accurate streamflow data. Selecting a representative section of pipe for measuring flow requires analysis of the pipe network above the site to identify all contributing areas, and analyses of the pipe network below the site to identify potential for backwater flow. The flow regime (steady- or unsteady-state flow, subcritical, supercritical, or pressure flow) and changes in the flow regime with stage need to be evaluated for selection of the appropriate method for measuring the flow. As many stormwater-flow measurements are made for the determination of pollutant loads, factors that may affect water-quality properties and constituents, and collection of water samples also must be considered in selecting a site and in determining frequency of flow measurements. Although this report is focused on stormwater flow in small streams and in highway- and urban-drainage systems, many of the principles upon which accurate and representative flow measurements are obtained in large streams are applicable to flow measurements in small streams and drainpipes, and are therefore included in this report.

Documentation and reporting of the supporting data from which decisions were made as to where along a stream channel or within a highway- or urban-drainage network flow will be measured, how frequently flow will be measured, and what method will be used to measure the flow are required for internal and external evaluation of the accuracy and representativeness of the flow data. Important questions that must be addressed in the selection of a representative site where accurate and complete flow measurements can be obtained are listed in the following sections. Although the time and effort expended to address these questions to ensure accurate and complete flow measurements at a representative site may be considerable, documentation and reporting of this effort should be a rather simple task if each step in the process is described in detailed field notes during the selection process. To ensure that the accuracy and representativeness flow measurements can be evaluated, the supporting data and information used to make the final decisions must be documented and communicated in an accessible format, such as a project description report, a data report or an appendix to a technical report, and (or) archived in a State or national records center.

Site Selection

Selecting a location for obtaining flow measurements within the drainage network requires evaluation of the representativeness of the site in yielding flow data that are consistent with the objectives of the investigation, and the hydraulic and physical suitability of the site where accurate flow measurements can be expected to be obtained. The importance of proper site selection cannot be overstated. No matter how accurate the flow data, if the site does not provide information to meet project objectives, the data have little meaning (Whitfield, 1988). Ideal sites rarely exist, however, and a compromise between many factors must be made in selecting the best site. The basic questions that need to be addressed in selection of the best, or most representative, site are:

- Will flow measured at this site represent the contribution from the area of study?
- How are the flow velocities distributed?
- How stable is the flow regime?
- Can a stage-discharge relation be developed?
- How steady would this stage-discharge relation remain over time?
- Is access to the site acceptable?
- Can equipment be installed?
- Can manual measurements of flow be made?
- Is floating debris manageable?
- Is the site safe for personnel and equipment?

Consideration of the above questions in selecting a site may require a significant amount of office and fieldwork. The time and effort expended, however, will ensure that the site selected, from among other potential sites, will yield stormwater-flow data most representative for the project objectives. The risk of having selected a poor or non representative site is significantly reduced by this initial investment. Additionally, the information obtained during the site-selection process must be clearly documented and included in a data report or in another accessible format to allow for independent evaluation of the selected site, and for potential use of the site for future investigations. Guidelines for site selection of gaging stations along streams are provided by Carter and Davidian (1968), Rantz (1982a), the FHWA (1985), and the Natural Resources Conservation Service (1996).

The initial site selection (whether along a stream channel, within a highway- or urban-drainage network, or from a paved surface or grassy swale) and alternative site selections should include review of reports and other documents concerning the hydrology of the drainage area, examination of maps or highway- and urban-drainage network plans, and personnel communication with State and town transportation agencies and residents living near the proposed site. Drainage-basin area, relief, slope, elevation, stream-network pattern, and locations of tributary streams can be determined from topographic maps or readily available geographic information system (GIS) data bases. Land use may be inferred from these maps as well. Drainpipe network, pipe slope, locations of catch basins and manholes, pervious and impervious areas, slopes of paved areas and grassy swales with drainage catchments, and other physical structures can be determined from as-built, or pre-built site plans, although in older built areas this information is sometimes difficult to find. This initial information in site selection is necessary because it provides a general understanding of the flow system, identification of location within the drainage system where the most representative data can be collected, and an initial evaluation of upgradient and downgradient factors that may unduly influence flow measurements at the selected location.

Field inspection is required to ensure that the site is hydraulically and physically suitable for accurate measurements of flow and that the site can be accessed and data collected safely. The basic hydraulic considerations are the distribution of velocities within the flow and potential changes in flow regime with stage. A uniform velocity distribution in the flowing water throughout the full range of flow, with no change in flow regime, would provide for the ideal conditions whereby the flow rate could be determined from one measurement of water depth. The velocities in most flows are not distributed uniformly, however, and the distribution of velocities and flow regimes may change over the range of flows. To account for this non-uniform velocity distribution and potential changing flow regime in streamflow measurements from moderate to large streams, flow rates are measured in many thin vertical sections along a line perpendicular to the stream channel (Buchanan and Sommers, 1969; Rantz, 1982a). In small streams and in highway- and urban-stormwater drains, however, multiple measurements are typically restricted by space and time. The small number of flow measurements attainable due to the narrow widths, and sometimes shallow depths, are insufficient for accurate flow measurements, and due to the rapidly changing flow, each individual measurement could represent part of a different flow rate and velocity distribution. In these types of flows, flow- control devices, such as weirs and flumes, are commonly used (Buchanan and Sommers, 1969; Marsalek, 1973; Alley, 1977; Kilpatrick and Schneider, 1983; Kilpatrick and others, 1985; FHWA, 1985; Natural Resources Conservation Service, 1996). Flow measurements from these devices typically require only one measurement of stage-per-unit time because they produce a consistent distribution of velocities throughout the nearly full range of flows.

Physical considerations are generally related to selecting a site where the distribution of velocities in the flowing water is minimally disturbed, and is expected to remain so over the period of investigation. Although multiple flow measurements are used in stream-discharge measurement and flow-control devices are used for flow measurements in highway- and urban-drainage systems to account for the non-uniform distribution of velocities, evaluation of the distribution of velocities remains an important part of the site selection process. Therefore, field inspection includes an upstream and downstream evaluation of flow characteristics and factors that may affect the flow in space and time, such as the stability and uniformity of the stream-channel-bed and bank sediment, the stability of the channel bank and adjacent flood-plain vegetation, the straightness of the channel, lateral location of the channel within the flood plain, flow pattern within channel, variations in channel width and depth, and the proximity of small tributaries, rivulets, seeps, and physical structures that are not shown on the map of the area, and the presence of floating or submerged debris. Visual inspection of land use and its possible effect on flow and flow measurements should be done. For highway- and urban-drainage systems, the locations and elevation of catch basins, manholes, pipe intersections, and outfalls should be checked with the plans, and corrected on the plans if needed. Although validation of location of underground pipes in highway- and urban-drainage networks may be difficult, the flow routes can usually be determined by visual inspection of the elevation and direction of pipes, and their material composition, diameter, and number, from which flow enters and exits catch basins and manholes. Field inspection should also include an estimate of the relative amount of pervious and impervious area within the catchment area. Thorough field inspection will ensure that a site of minimal-flow turbulence is selected, or can be constructed, for measurement of flow representative of the expected sources of runoff.

As the measurements of stormwater flow in highway-runoff studies are used primarily for determination of pollutant loads, factors affecting measurements of water-quality properties and constituents and sample collection should also be considered in the site-selection process. For example, sufficient flow depth for complete submergence of water-quality probes is necessary, and factors such as backwater from downstream controls that may affect the temporal representativeness of samples and water-quality measurements need to be evaluated. If project objectives allow, select a site where data may be applicable to more than one investigation, or where data collected in the future can be used to evaluate trends.

Maps, tables, and written descriptions of the hydrologic features of the stream or drainpipe network are necessary to evaluate the quality of flow data with respect to the appropriate location of the flow-measurement features. A report should clearly indicate the position of the flow-measurement station with respect to the catchment area, local and surrounding land uses, and the relative amount of pervious and impervious areas contributing. It is important to document the location and characteristics of the natural or constructed flow-control features. It is also important to document the slope of the stream/pipe/swale to help establish the flow regime. Where overland flow is measured, detailed information about the surface characteristics and flow-concentration structures are necessary.

This careful and thorough review of maps or construction plans and field inspection will help ensure that reasonably accurate and representative flow measurements can be obtained. Documentation of the initial site evaluation and the field inspection will ensure that the site located for collection of flow measurements can be validated. It would be unusual if an ideal site was found. But by documenting the information obtained during the site-selection process, archiving the documentation, and including pertinent information in a published project description or data report, or in an appendix to an interpretive report, a level of certainty of the data collected and interpretations made may be evaluated.

Frequency and Duration of Stormwater-Flow Measurements

The timing, frequency, and duration of flow measurements are critical factors in monitoring accurate flows in small streams and highway- and urban-drains because of the rapid response to stormwater runoff and the wide ranges of flow over short periods of time. As with precipitation, frequency and duration of flow measurements are dependent upon the time scales of the process under study. Additionally, flows in response to stormwater runoff typically rise more quickly than they fall, and pollutant concentrations have been shown to rise and fall more quickly than the flow in which they are transported (Vanderborght and Wollast, 1990; Spangberg and Niemczynowicz, 1992; Barrett and others, 1993). This phenomenon, referred to as the first flush or initial wash off, is especially prominent in highway- and urban-drains. Irish and others (1996) found that most of the constituents in highway runoff are attached to fine-grained sediments that tend to accumulate within 3 feet of the curb during dry periods. This proximity to the curb allows for the sediment and chemical constituents to be entrained in the pavement runoff and curb flow, and discharged into the drainpipes in the early part of a storm. The magnitude and extent of this first flush also can be affected by the nature and solubilities of the constituents being transported in the water (Hvitved-Jacobsen and Yousef, 1991). Although pollutant concentrations may be considerably less in the latter part of the runoff events than in the first part, pollutants may continue to be discharged, necessitating flow measurements throughout the entire duration of the event (Barrett and others, 1993). Stormwater flows respond differently to different types of storms and may respond differently to the same type of storm in different seasons of the year. Therefore, it is critical that measurements of flow start at the beginning of the storm, continue through the duration of the event, and are measured at a frequency corresponding to the rate of change of flow and constituent concentrations to ensure the accuracy and representativeness of the resultant flow and pollutant loads. Collection of water-quality data should be synchronized with the timing of flow measurements so that concentrations can be directly applied to measured flows.

A general understanding of the rainfall-runoff relation in the region (area) is needed to evaluate the timing, frequency, and duration of flow measurements that will ensure accurate and representative stormwater-flow data. The basic questions that need to be addressed in selecting the timing, frequency, and duration of flow measurements include:

- What is the time of concentration of flow and pollutants in relation to storm intensity?
- What is the rate of change of flow?
- What is the range of flows?
- How do rates of changes of flow and ranges of flow differ between storm types and seasons?
- Can flow measurements be synchronized with collection of pollutant samples?

Guidance in the initial selection of frequency of flow measurements, whether measuring flow in a highway drainpipe or in a stream channel, can be obtained by examining historical precipitation and hydrologic data from near the proposed site, or from other similar sites within the same type of physiographic region. For highway- and urban-drains, data should be available from the engineering firm that designed the drainage networks, or from the State or municipal agency responsible for maintaining the drainage system. Pipe diameters were likely designed for a maximum open-channel-flow depth for a specific storm intensity, duration, and recurrence interval. Field observations of flow during and after storm events can be very useful. Additionally, a numerical method for approximating the minimum frequency of flow and concentration measurements for meeting a desired accuracy is available (Nesmerak, 1986). However, a more accurate method for selecting frequencies of flow measurements to ensure the accuracy and representativeness of flow volumes and pollutant loads measured in stormwater runoff is use of continuous electronically measured and recorded-stage and water-quality measurements, such as specific conductance and (or) turbidity, in response to storm events. The times of concentration of flow and constituent concentrations can be interpreted from the electronically recorded data, and the frequencies of measurements needed at various stages and times throughout the event can be determined. Continuous measurements and recording of stage and water quality at different times of the year, during different types of storms, or under different antecedent conditions, will provide data needed to optimize recording and sampling frequency under a variety of conditions and at similar sites.

In a study in which the constituents of road salt in highway runoff were measured in the trunkline drainpipes of a six-lane highway (Church and Friesz, 1993; Church and others, 1996), stage and specific conductance measurements in the approach sections of Palmer-Bowlus flumes were electronically measured every minute, but only recorded every hour at times of minimal-to-zero flow. To account for the initial rapid flush of the road-salt constituents during runoff, flow recording and water-quality-sampling frequencies were automatically increased to a minimum of 10 minutes and a maximum of 1 minute in response to changes in stage and specific conductance (fig. 3).

Data used to establish the timing, frequency, and duration of flow measurements need to be documented and reported to help ensure that the flow data can be validated. These data include the type of drainage system (i.e., stream, highway, or urban drainage), drainage area, stream channel or pipe slope, percent impervious area, climatic and meteorological data, and, if pollutant concentrations and loads are to be measured, the source, amount, distance to monitoring station, and when pollutants are released.

Methods for Measuring Stormwater Flow

Methods have been developed for measuring flow in many types of conduits (flow in natural channels, engineered channels, pipes, sheetflow, and overland flow) under various flow regimes (steady- or unsteady-state flow, subcritical, supercritical, or pressure flow). Most of these methods have two parts: a primary device that directly interacts with or controls the flowing water, and a secondary device for measuring water depth or pressure (Marsalek, 1973; Alley, 1977).

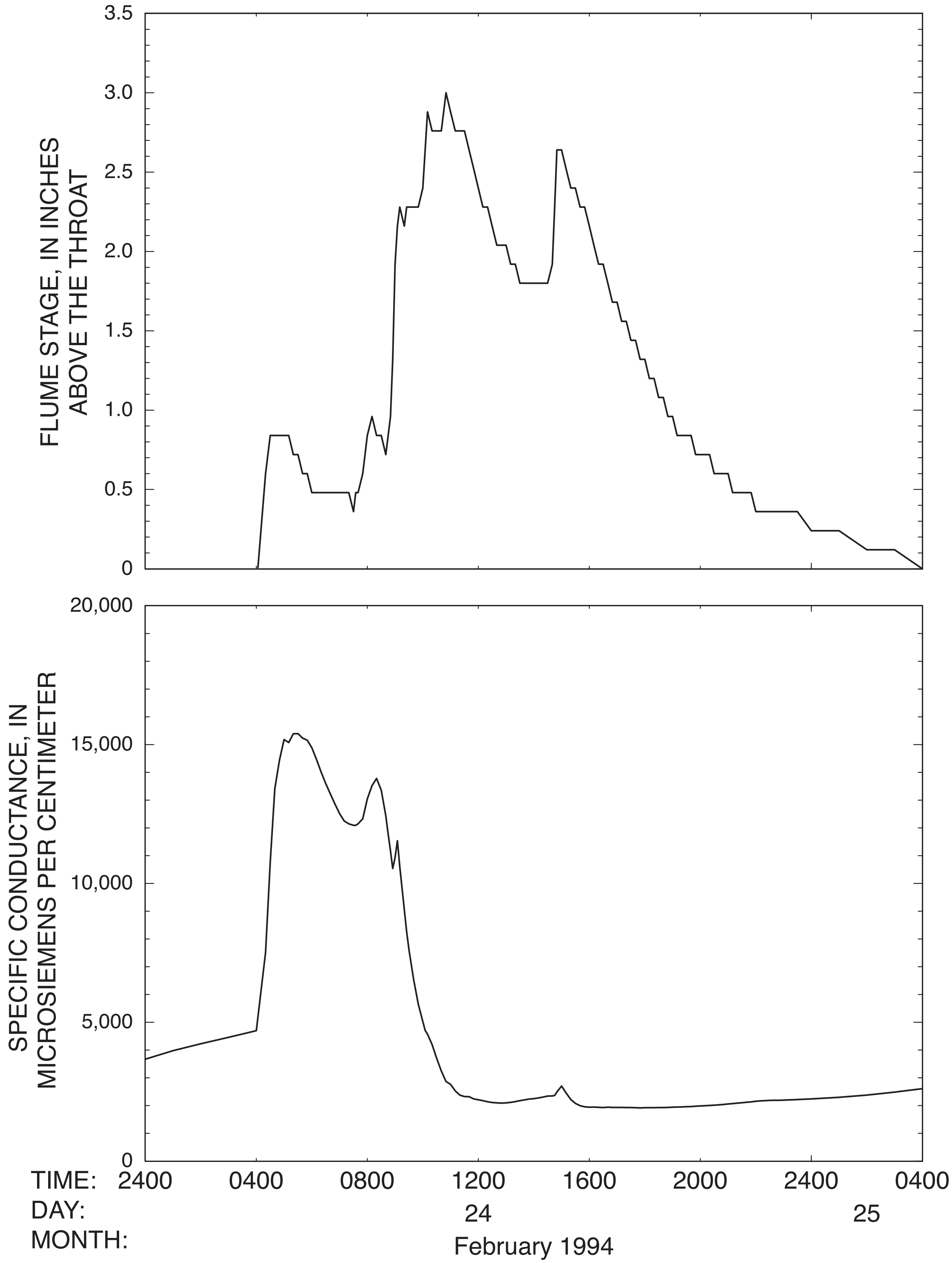


Figure 3. Stage and specific conductance monitored at various frequencies in response to changes of stage and specific conductance (Church and others, 1996).

Selection of the most appropriate method for collection of accurate flow data that are representative of the particular site requires knowledge of the flow regime(s), range of flow and flow depths, rapidity of changes in flow, channel geometry, and the capabilities and accuracies of the methods available for measuring flow. Assuming that the flow and channel characteristics were assessed in the site-selection process, the important questions that remain are:

- Is the flow measuring method applicable to the flow and channel characteristics at the site?
- Is the flow measuring method capable of measuring the full range of flows?
- Is the flow measuring method capable of measuring flow at frequencies required to fully characterize the event?
- Will the flow measurements be of sufficient accuracy to meet the objectives of the study?
- Can the accuracy of the flow measurement method be verified with another method?

Data that need to be documented and reported for validation of a selected flow measurement method, and to ensure that the flow measurement method can be independently validated, include the hydraulic characteristics of the flow and the capabilities and limitation of the method. A report should include the observed type of flow and changes in flow type during storm events, ranges of types of flows measured, and the method used to measure the flow. If a flow-control device was used, details as to the construction, installation, depth/flow relation, calibration, and maintenance should be reported. Equipment and instrumentation (primary and secondary devices), and their resolution, tolerance, and design limits, as defined by the manufacturer, should be documented as well as calibration and maintenance records. Modifications to the method and the resultant resolution, tolerance, and design limits also should be documented. With this information, the appropriateness of the selected method, the placement and use of a flow-control structure, and the accuracy and precision of the flow data measured, can be evaluated.

The most common types of flow measurement methods and their applications are described below. Further guidance in the selection of an appropriate method of flow measurement can be found in Marsalek (1973), Shelley and Kirkpatrick (1975), Alley (1977), FHWA (1985), and Natural Resources Conservation Service (1996).

Primary Devices/Methods

Channel Friction Coefficient Method

This method is best described by Manning's equation, in which flow is related to the hydraulic radius of the flow cross section, slope of the water surface, and an estimated friction of the channel, referred to as a roughness coefficient. The accuracy of flows determined by Manning's equation are dependent upon steady, uniform flow in straight channels or pipes of uniform shape, slope, and roughness. Manning's equation is useful for estimating flow in ungaged open channels and pipes. The accuracy of the flow determined, however, varies widely. Brown and others (1995) reported of errors up to 15 percent in flow measurement in short, straight channels by use of this method. Others studies have shown that the accuracy of this method, at best, is about 15 to 20 percent (Alley, 1977). Marsalek (1973) stated that under conditions of unsteady, non-uniform flow in drainpipes, typical of flows in highway- and urban-drainpipes, Manning's equation will underestimate flows in the rising stage and overestimate flows in the falling stage. As pollutant concentrations have been shown to peak before the flow in which they are transported (Barret and others, 1993; Spangberg and Niemczynowicz, 1992), errors in pollutant loads are likely to be greater than 20 percent if the flow was determined by Manning's equation.

Index Velocity Method (Current-Meter Method)

In most streams, where flows change slowly with time in comparison to flows in highway- and urban-runoff-drainage systems, point velocities are measured in multiple vertical sections along a cross section of the stream channel by use of a velocity meter or current meter (Buchanan and Somers, 1969; Rantz, 1982a; Rantz, 1982b). The velocity in each vertical section is measured at a depth that theoretically, and field verified, represents the mean velocity in that section. If depth of the flow is sufficient, velocity is measured at two or more depths, the average representing mean velocity. Mean velocities are multiplied by the cross-sectional area they represent, and are then summed to obtain the total flow, or discharge, at that stream cross section. Many velocity/area measurements are taken along the stream cross section to reduce the influences of irregularities in the stream channel and non-uniform distribution of velocities at the stream cross section on the total flow measurement. Rantz (1982a) stated that total discharge at a streamflow section is usually represented by the sum of discharges from 25–30 subsections (fig. 4). Relations between stage (the height of the water surface relative to a stable reference point) and discharge are developed and refined as more discharge measurements are made. Secondary devices, such as floats or pneumatic bubbler systems and mechanical or electronic data recorders, are used for continuous monitoring and recording of stage (Buchanan and Somers, 1968; Marsalek, 1973). Continuous records of stage are applied to the stage-discharge relations to generate continuous records of discharge.

The accuracy of a subsection discharge measurement is a function of the accuracies of the measured cross-sectional area of each vertical section, the velocity measurements, and whether the measured velocities represent mean velocities which are based on assumed velocity profiles (Alley, 1977). Errors in velocity measurements arise primarily from poorly calibrated and poorly maintained meters, and from velocity measurements obtained at inappropriate depths or under turbulent flow conditions. The accuracy of the stage measurements is dependent upon the resolution of the equipment and instrumentation, use within their designed ranges, and proper calibration and maintenance. Sauer and Meyer (1992) stated that the error of most discharge measurements using the current-meter method (with vertical axis, cup-type current meters (Buchanan and Somers, 1969)) ranges from 3 to 6 percent. Under ideal conditions, an error as low as about 2 percent can be achieved, but under poor conditions the error may be greater than 20 percent.

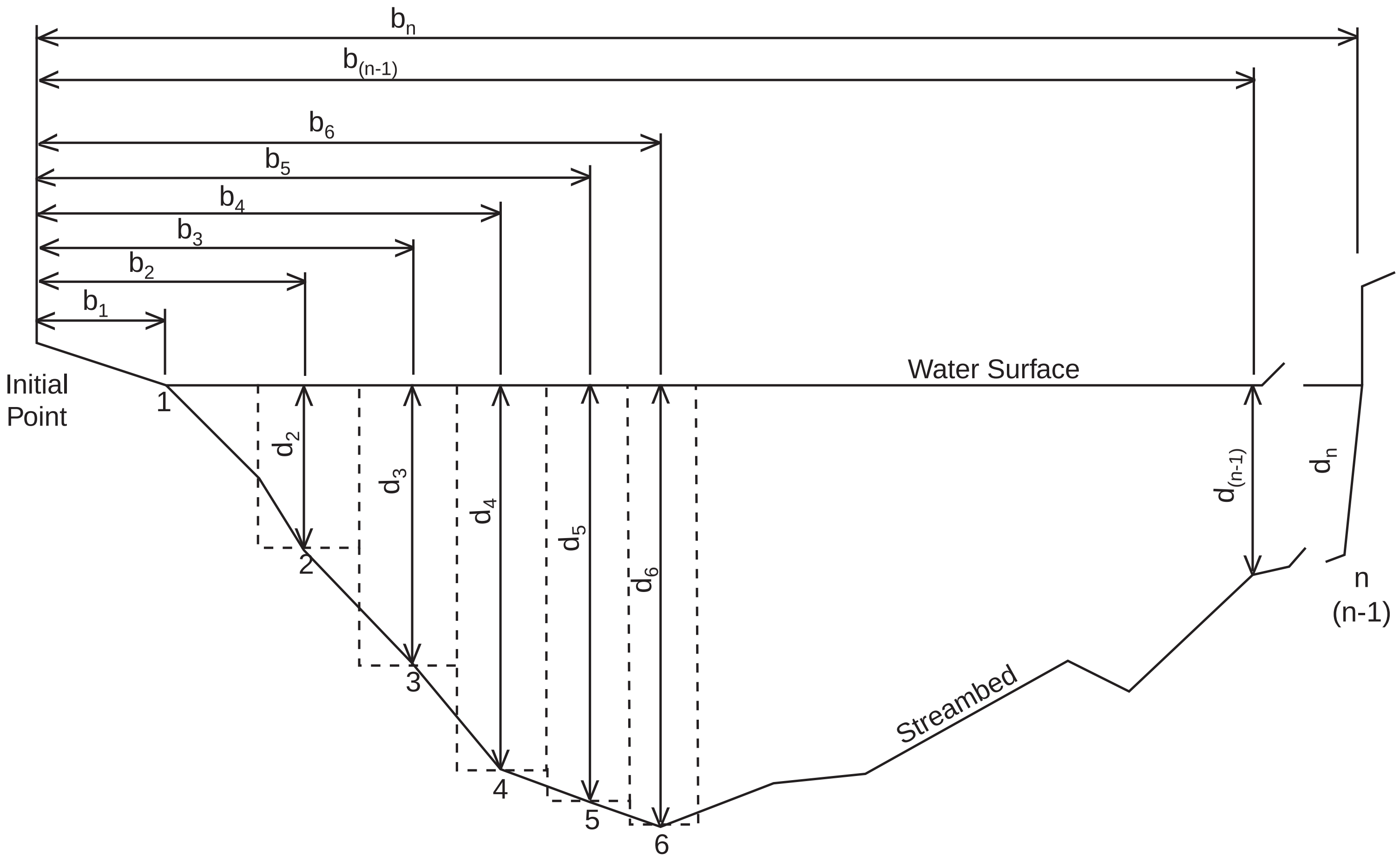
Documentation of the tolerance and resolution of the equipment and instrumentation is needed along with calibration data and service records to ensure that stage measurements can be validated. The importance of accurate and verifiable stage measurements cannot be understated because stage is used as a surrogate for flow in most reported flow measurements. The accuracy of the stage-discharge relation is dependent upon the accuracy of the individual stage and discharge measurements that define the relation, which in turn are dependent upon the accuracy of the many velocity/area measurements that constitute a single discharge measurement. The extent to which the stage-discharge relation can be confidently applied is related to the range of flows measured. Therefore, collection of flow measurements that represent the full range of discharges is desirable.

The current-meter method is used primarily for flow measurements in moderate to large streams, and in small streams with moderate to low slopes. Other methods, such as weirs, flumes, and dye dilution, yield more accurate flow measurements in small streams with high slope, and in highway- and urban-drainage pipes (Katz and Fisher, 1983).

Weirs

Weirs are overflow-control structures installed in a small stream channel or culvert that produce a relation between the depth of water behind the weir and the flow (Marsalek, 1973; Alley, 1977). Weirs are typically made of thin rectangular metal plates set vertically across the channel. Weirs referred to as “broad crested” are constructed with concrete. Flow is forced over the top edge of the metal plate or concrete weir. To measure low flows more accurately, the middle of the top edge of the metal plate is cut to form a V-shaped, trapezoidal, or rectangular notch. Stage is measured with floats or pneumatic bubbler systems and recorded with mechanical or electronic data recorders. Continuous records of stage are applied to the stage-flow relation to generate continuous records of flow. However, the stage-flow relation breaks downs under the condition of submergence or surcharge. Field calibration of the stage-flow relation is necessary.

Weirs are useful for measuring flows in small, low-velocity stream channels where the index velocity method may be inappropriate due to shallow depths and non uniform flow (Buchanan and Somers, 1969) and at outfalls and in open channels (Alley, 1977). Accuracies within 5 percent can be attained if the weir is calibrated (Marsalek, 1973). Although weirs are simple to construct and cost little compared to most other methods, they are not recommended for use within pipes because they restrict the flow and cause excessive backwater and debris accumulation, and are susceptible to submergence and surcharge (Alley, 1977).



EXPLANATION

1, 2, 3 .... n — OBSERVATION VERTICALS

b_1, b_2, b_3 .... b_n — DISTANCE, FROM THE INITIAL POINT TO OBSERVATION VERTICAL

d_1, d_2, d_3 .... d_n — DEPTH OF WATER AT OBSERVATION VERTICAL

Figure 4. Example of stream channel cross section showing current-meter method where flow velocities in subsectional areas are used to measure stream discharge (modified from Rantz, 1982a).

Flumes

Flumes are flow-constriction structures that control the flow hydraulics such that flow is directly related to head (Marsalek, 1973; Alley, 1977; Kilpatrick and Schneider, 1983). Flow in a small stream or drainpipe passing through a flume is accelerated, resulting in decreased depth, by some combination of sidewall contractions, raised floor, or increased slope. Flow exiting the flume decelerates when reentering the channel or pipe. Flumes in which subcritical flow in the approach section of the flume remains subcritical, but at a higher velocity in the contraction (throat), require head measurements at both the approach and throat sections of the flume to compute flow. A direct relation between head in the approach and flow in the throat exists in flumes where flow becomes supercritical in the throat. Due to the need for two head measurements in the subcritical flow flumes, they are seldom used today (Kilpatrick and Schneider, 1983). The most commonly used flumes are the Parshall flume and the Palmer-Bowlus flume, both of which produce supercritical flow in the throat.

The Parshall flume is used for measuring flow in small streams, at outfalls, and in open channels where the index velocity method may not be appropriate due to shallow depths, narrow widths, and non-uniform flow. Due to its rectangular shape, elongated structure, and requirement for a vertical drop through the flume, it is not very useful in measuring flow within drainpipes. The Palmer-Bowlus flume was designed for use in drainpipes, and is not very useful in any other flow conduit. A Palmer-Bowlus flume installed in the trunkline drainpipe of a six-lane highway-drainage system is shown in figure 5 (Church and others, 1996). Flumes should be installed at sites where the potential for surcharge, full-pipe pressurized flow, and backwater effects are expected to be negligible. Although the Palmer-Bowlus flume acts as a venturi meter under full-pipe pressurized flow, and flow rate can be calculated from head measurements in the approach and throat of the flume, the relation between head and flow breaks down in the transition zone from near-pipe-full to pipe-full flow (Kilpatrick and others, 1985). Advantages of flumes over weirs include less backwater and their self-cleaning abilities.

Theoretical depth/flow relations are developed for weirs and flumes based on their geometry, and in the case of flumes, slope (Buchanan and Sommers, 1969; Kilpatrick and Schneider, 1983, Kilpatrick and others, 1985). The accuracy of these flow measurements is dependent upon the accuracy of the construction and installation of the weirs and flumes in the stream channel or drainpipe (i.e., level in a direction perpendicular to stream channel or pipe, no deformation during construction or installation, no leakage at approach section), and the measured geometry, slope, and friction of flume surfaces. A well-constructed, calibrated, and maintained flume may yield flows with accuracies of 2-3 percent (Buchanan and Sommers, 1969; Marsalek, 1973); however, when factoring in the error of the secondary device used for monitoring stage, the accuracy is about 5 percent (Marsalek, 1973; Alley, 1977).

Differential Pressure Method

The differential pressure method is used to measure full-pipe pressurized flow and, as this flow condition is rare in highway- and urban-drainpipes, it has limited value in highway- and urban-runoff flow measurements (Alley, 1977). Flow-constriction devices, however, have been developed that act as critical-flow flumes under open-channel-flow conditions (the head in the approach section is directly related to flow in the throat section), and venturi meters under full-pipe pressurized conditions when the flow can be calculated from the difference in heads in the approach and throat sections of the flume. One is designed with a single-side wall constriction (Wenzel, 1975) and the other with a U-shaped throat constriction (Smoot, 1975). Flows at near-pipe-full, the transitional zone from open-channel to pipe-full flow, are difficult to measure because the flow pulsates from open-channel to pressurized flow (Kilpatrick and others, 1985). Kilpatrick and Kaehrle (1986) used a modified Palmer-Bowlus flume to measure open-channel and pipe-full flow, and an electromagnetic velocity meter to measure flow in the transitional zone from open-channel to pipe-full flow. They reported that the electromagnetic velocity meter was not successful in measuring accurate flows in this transition zone.

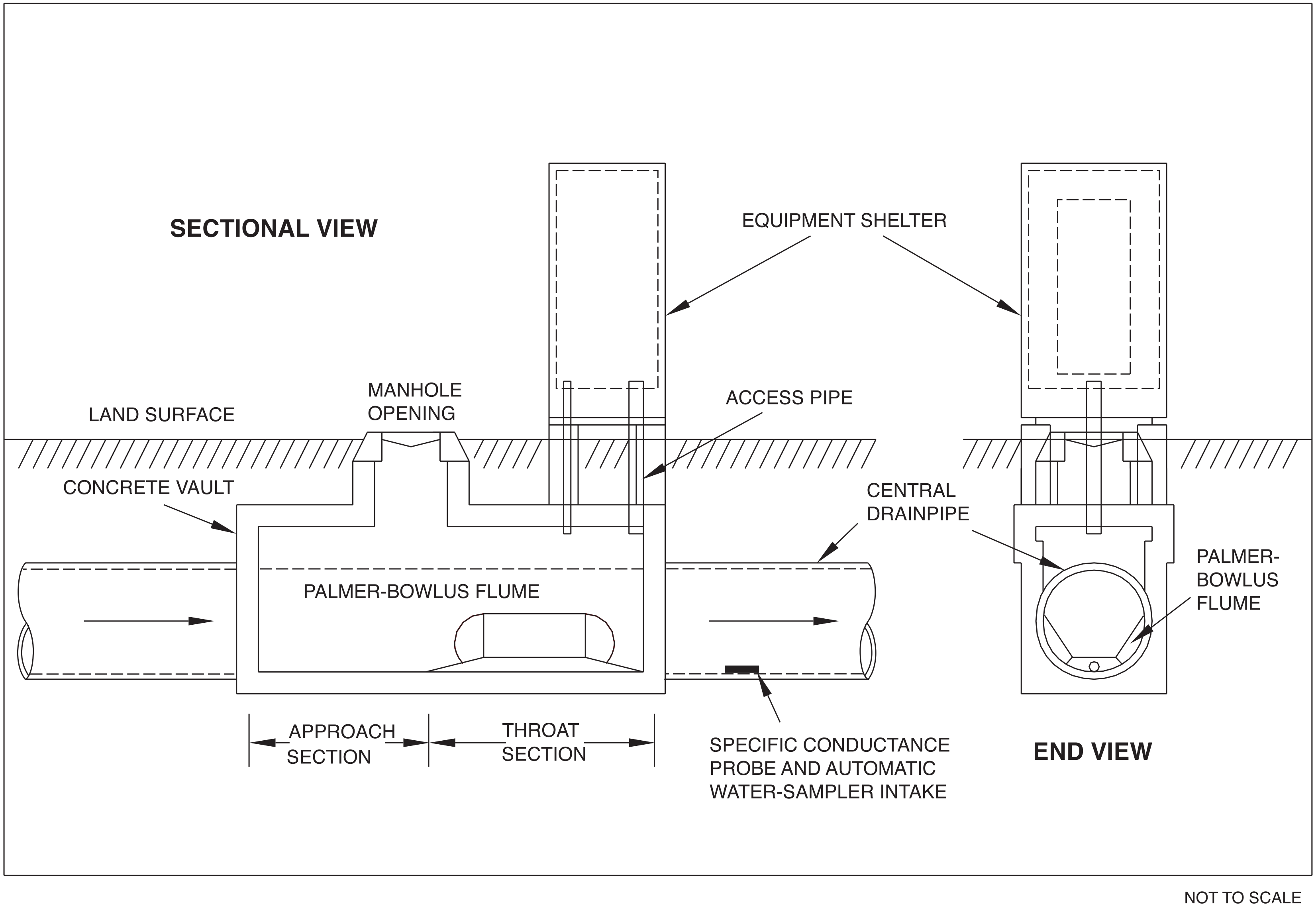


Figure 5. Highway-drainage-monitoring station with Palmer-Bowlus flume installed in trunkline drainpipe of a highway-drainage system (Church and others, 1996).

Acoustic and Electromagnetic Methods

The acoustic transit-time flowmeters (Laenen, 1985; Kilpatrick, and others, 1985; Kilpatrick and Kaehrle, 1986; Burch and Philips, 1994) and electromagnetic velocity meters (Kilpatrick, and others, 1985; Kilpatrick and Kaehrle, 1986) are designed to measure flow velocities under open-channel and full-pipe flow. Flow velocities are multiplied by cross-sectional areas of flow to determine flow rates. The acoustic flowmeter has been reported to obtain flow accuracies of 2–3 percent under open-channel flow, and 0.5–1.0 percent under pressurized flow (Burch and Philips, 1994). However, the acoustic flowmeter was not successful in measuring accurate flows in the transition zone between open-channel and full-pipe flow. As with other primary devices, the accuracy of flows measured with the acoustic and electromagnetic methods decrease when factoring in the error of the secondary stage measurement device (Marsalek, 1973; Alley, 1977).

Dilution Methods

Dilution methods involve injecting of tracer of known volume and concentration into a stream or flowing water in a pipe and measuring the concentration of the tracer in water collected at some short distance downstream (Alley, 1977; Kilpatrick and Cobb, 1985; Kilpatrick and Wilson, 1989). Dilution methods are unique because they do not require a secondary device for measuring stage. There are three types of dilution methods: instantaneous injection with steady-state flow; continuous, constant-rate injection with steady-state flow; and continuous, constant-rate injection with changing flow. The accuracy of the three methods depends upon complete mixing of the tracer by the time it reaches the point of collection and minimal dye loss during transport. The first two methods require multiple samples to provide one measurement of flow. In the third method, each sample of diluted tracer represents a specific flow.

Dye-dilution-discharge measurements have been used to verify stage-discharge relations in streams. Assuming steady-state flow and complete mixing, a streamflow measurement can be made by analyzing the concentration of dye in water samples collected at the measuring section from an upstream instantaneous injection of a known volume and concentration of dye. Flow is inversely proportional to the concentration of the tracer in the diluted sample. Due to the rapid changes in flow in highway- and urban-drains, the con tinuous, constant-rate dye-injection dilution method must be used (Duerk, 1983; Katz and Fisher, 1983; Kilpatrick, and others, 1985). This method of dye dilution has proven to be effective in calibrating theoretical stage-discharge relation from Parmer-Bowlus flumes (Katz and Fisher, 1983). Ellis and others (1984) used dye-dilution methods to calibrate a velocity-flow meter. Abrahams and others (1986) have used dye-dilution techniques to measure overland flow. In a monitoring study of road salt in highway runoff (Church and Friesz, 1993; Church and others, 1996), theoretical ratings for Parmer-Bowlus flumes were developed based on flume geometry and pipe/flume slope. Bias in the ratings caused by small irregularities in the flume sidewalls and in the floors of the throat sections were corrected by use of constant-rate dye-injection dilution measurements.

Secondary Devices/Methods

Floats

Monitoring the level of floats connected by a cable or a pivot arm in flowing water is a well-known method for monitoring water levels (Marselak, 1973; Alley, 1977). The vertical movement of the float as water levels change is typically recorded on a chart record or recorded electronically. Floats should be used in stilling wells where water-surface oscillations are dampened and the float is protected from floating debris. Under these controlled conditions, accuracy of water-level measurements of 0.01 ft can be attained (Marsalek, 1973). Highway- and urban-drainpipes, however, generally do not provide space for a stilling well.

Pneumatic Sensors

Water levels are measured with pneumatic sensors as gas (air or nitrogen) is forced through a thin tube and slowly bubbles into the water. The pressure of the gas is equal to the static pressure of the water above the orifice of the tube (Marsalek, 1973; Buchanan and Somers, 1968). Water levels are converted from pressure to depth by manometers or pressure transducers. Pneumatic sensors are well suited to measuring water levels in highway- and urban-drainpipes because they can be easily installed, do not obstruct flow, and with the exception of the thin tube, all equipment for measuring stage can be installed above ground. A small drawdown occurs as flow velocities increase; however, this can be accounted for when the stage-discharge relation is verified. Figure 6 presents an example of how pneumatic sensors were used to measure stage in Palmer-Bowlus flumes (Church and others, 1996). A pressure transducer in an equipment shelter (fig. 5) converts the pressure of the nitrogen gas at the bubble orifice in the approach section of the flume to an electrical signal recorded by the data logger. Also, a calibrated standpipe is located in the equipment shelter for field calibration of the pressure transducer.

Pressure transducers used with the pneumatic sensors are of the non-submersible type. Submersible pressure transducers can be used to directly measure water depth, but, similar to floats, a stilling well may be needed to dampen water-surface oscillations and to protect the transducer from floating debris.

Electronic Sensors

The most commonly used electronic sensors to measure water levels are capacitance probes and dipper probes. The capacitance probe is immersed in the flowing water where the water is part of the electrical circuit. The measured capacitance varies in proportion to the depth of the water. This method has been use with weirs and with flumes in drainpipes. Accuracies of better than 1-percent have been achieved during 6-month periods without failure (Marsalek, 1973). Frequent maintenance was required, however, because of the collection of floating debris. Therefore, the capacitance probe would work best in a stilling well or side-wall cavity of a flume, limiting its usefulness in sewer and storm drains. Also, the capacitance may be affected by the relative high variations of specific conductance expected in highway runoff where deicing chemicals are used.

The dipping probe, hanging from a cable controlled by a precision motor, completes an electrical circuit when in contact with the surface of the flowing water. The probe is retracted slightly by the motor after contact then is lowered again for the next measurement. The depth of flow is recorded as the amount of cable that is is paid out or retracted to meet the water surface. Marsalek (1973) reported that the dipper probe required a significant amount of maintenance and that the time resolution on the chart record was not sufficient for runoff studies.

Acoustic Sensors

Acoustic sensors measure the time of travel of sound that is emitted and reflected back from the water surface. Depth of water is determined from the known depth to the base of the pipe and the measured distance of the sensor to the water surface. The sensors have no contact and do not affect the flowing water. Marselak (1973) reported that the accuracy of an acoustic sensor tested was ± 4 mm. For these sensors to be accurate, however, the water surface must be smooth, so a stilling well may be needed. Additionally, false reflections may be encountered in pipes and narrow channels, particularly at low flows (Marselak, 1973; Alley, 1977).

Comparison of Flow Measurement Methods

An experiment done by the USGS in cooperation with the FHWA indicates that different methods for measuring stormwater flow may not be comparable, and that some methods may have considerable variability and (or) bias. Stormwater flows from about 50 storms were measured in an urban stormwater drainpipe by several different methods at a site in Madison, Wisconsin during 1995. In this experiment, flows were measured using a Palmer-Bowlus flume, the friction coefficient method, acoustic and electromagnetic velocity meters, and acoustic and electromagnetic flow meters. Stage was measured by pneumatic bubbler, acoustic, and electromagnetic methods. Flows from these storms were measured concurrently by each method in a 54-inch-diameter, 200-foot continuous section of drainpipe. A reliable and accurate stage-discharge relation for this site had been previously developed using a Palmer-Bowlus flume, stage measurements from a nitrogen gas pneumatic bubbler system in the approach section of the flume and a pressure transducer, and discharge measurements calibrated using the constant-rate dye-injection dilution method. When different flow measurement methods are compared to this reference method, potential problems associated with the bias and variability among methods is apparent (fig. 7).

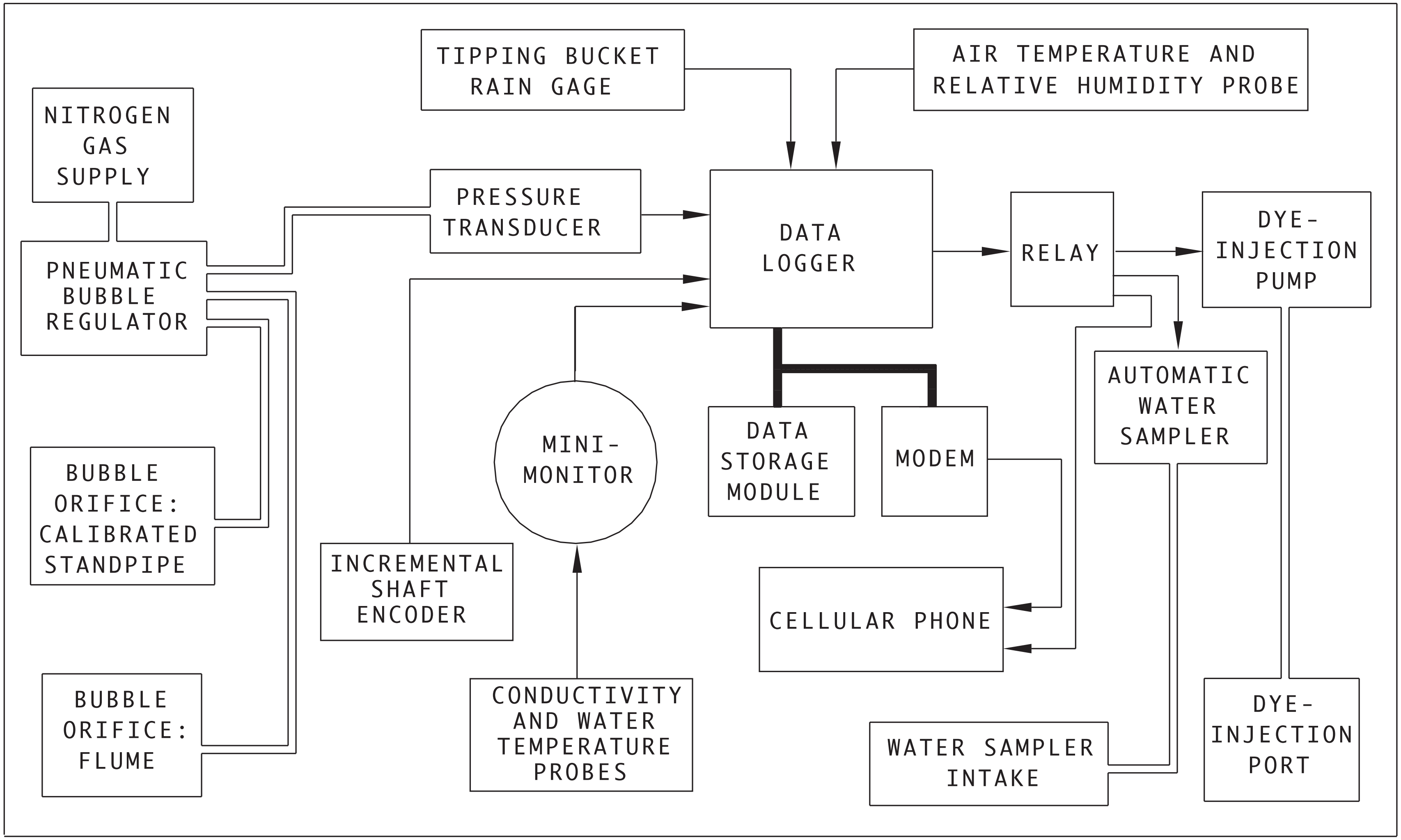


Figure 6. Instrumentation and equipment for measuring stormwater flow in a highway-drainage-monitoring station (Church and others, 1996).

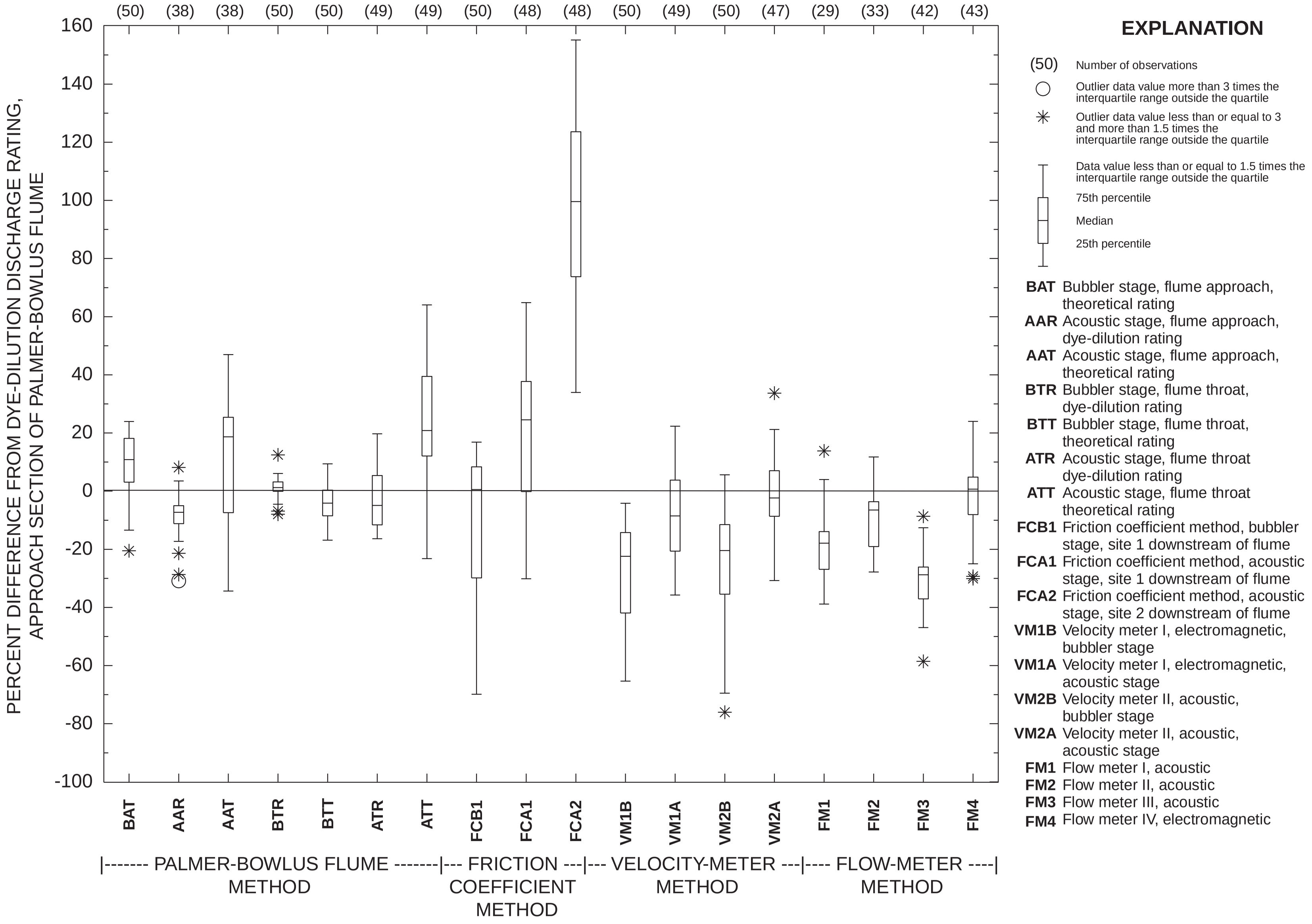


Figure 7. Comparison of results from stormwater-flow measuring methods, 1998, Madison, Wisconsin.

The comparability of stormwater-flow measurements by different methods is poor, and the variability of individual methods ranges widely (fig. 7). The data clearly indicate the need to calibrate a stage-discharge measurement method using check measurements with an independent method, such as dye dilution. Although stage-discharge relations derived from these flow measurement methods can be adjusted (using verification data) to minimize bias, the very large variation of uncertainty in flow measurements exhibited by some of these flow measurement methods is still likely to exist. These variations would add uncertainty to the representativeness of event-mean concentrations derived from flow-proportional-sampling methods, and would also add uncertainty to loads calculated from measured flows. Therefore, this comparison of flow methods emphasizes the importance of (1) selecting a flow measurement method that will yield sufficiently accurate flow data to meet project objectives and goals, (2) verifying all stage-discharge relations with proven, documented methods, and (3) documenting and reporting detailed information about the flow measurement methods and verification methods used in a given study so that the accuracy of flow data collected can be evaluated.

QUALITY ASSURANCE AND QUALITY CONTROL

Quality assurance and quality control programs (QA/QC) need to be established at the beginning of a project to ensure that precipitation and stormwater-flow measurements are accurate and representative of the flow system investigated. Clark and Whitfield (1993), Brown and others (1995), and Jones (1999) stress the importance of QA/QC programs for all phases of stormwater flow and water-quality investigations—from project planning through report preparation—and demonstrate how comprehensive QA/QC programs can be developed and implemented.

Addressing, documenting, and reporting the hydrologic and hydraulic factors for selection of (1) monitoring site, (2) frequency and duration of monitoring, and (3) methods for measuring precipitation and stormwater-flow data constitute a QA/QC program for the design of stormwater runoff studies. A QA/QC program for data-collection activities is also necessary to document that the implementation of the study design was successful. An effective QA/QC program for stormwater-flow data-collection activities would include:

- Frequent and routine site visits by trained/experienced field personnel.
- Redundant methods for measuring precipitation and stormwater flow.
- Technical training for project personnel.
- Frequent review by project personnel of precipitation and stormwater-flow data collected.
- Quality audits, in the form of periodic internal reviews.
- Quality audits, in the form of periodic external reviews.

Frequent and routine site visits by trained/experienced field personnel cannot be over emphasized. Field equipment and instrumentation must be maintained in good working order to ensure the integrity of the data collected. The site must be inspected for debris accumulation, natural corrosion of equipment, vandalism, and other potential problems, including the presence of rodents. Debris can affect measurements by interfering with the operation of measurement equipment. Debris accumulation, whether upstream or downstream from the measuring point, may affect the stage-discharge relation. Service and maintenance of equipment and instrumentation and (or) the flow-control structure is necessary for consistency in the measurements and in the stage-discharge relation. Frequent calibration of equipment and instrumentation is necessary because of the difficult monitoring environment. Standard field forms designed to record who visited the site, the date and time of each visit, site conditions, the status of equipment and instrumentation, records of instrument calibration, and other information pertinent to the operation of the station are necessary for data verification. These field forms should be archived with project records, and at the least, use of these forms should be mentioned in the QA/QC documentation in project reports.

Redundant systems for measuring precipitation and stormwater flow can be used to ensure that the data collected are correct and complete. The difficulties in measuring and recording data in a stormwater-monitoring environment create a high probability for an incomplete record, even when stations are well maintained and the instruments are properly calibrated. Redundant systems provide for comparison of primary and backup data for detection of errors and backup data collection in the event of failure of the primary system. For example, Church and others (1996) used a data-logger-controlled pressure transducer as the primary stage measurement and recording system, and a float-arm assembly with a shaft encoder as the backup stage measurement system (fig. 6). The float-arm assembly was also connected to a mechanical strip-chart recorder to serve as the backup data recording system. In this study, relations between measured stage and discharge among co-located stations were also useful as a defacto backup system for data interpretation and verification. This investigation also collected precipitation measurements near each station, which were compared to long-term data from a NOAA network station.

Training is an essential part of QA/QC programs. Consistent and correct flow data are necessary to assemble a national and (or) regional highway-runoff-quality data base. To ensure that data are valid, current, technically defensible, and comparable from project to project, a standard training program is necessary. A continued program of organized training for project chiefs and experienced field personnel is necessary to maintain state-of-the-art knowledge of advances in precipitation and stormwater-flow-monitoring technologies. A series of training sessions for less experienced field personnel is necessary to establish the knowledge base for quality in data collection and interpretation. For example, the FHWA designed a comprehensive student workbook devoted to the study of highway-runoff water quality and runoff quantity (FHWA, 1985).

Data assessment is an important component of the QA/QC process (Jones, 1999). It is necessary for project personnel to frequently review the precipitation and stormwater-flow data collected throughout the course of each project. It is necessary to do at least a cursory data review to ensure that the system is operational, and that it is collecting internally consistent information each time the data record is collected during a station visit, and (or) when the data are downloaded from a remote location. Periodically, it is necessary to do a more detailed review using the entire data record, field notes, and other available information to detect errors or anomalous data. For example, a comparison between the precipitation and runoff volumes for a given storm could indicate a bias in one or the other measurement system if the relation for this storm departed from normal values for the station in question. Analysis of field records, including calibration records, adjustments to measured values, and other information, when compared to the data record, may indicate systematic bias, long-term drift, or an abrupt change in the performance of the instrumentation.

Quality audits, in the form of periodic internal reviews, are necessary to monitor and implement the project QA/QC program (Jones, 1999). Internal audits establish that the project has a QA/QC plan and that it is being implemented and documented. Also, periodic internal reviews serve as a method to provide technical feedback from subject matter experts to examine and address problems and (or) potential problems in the data-collection program. Internal reviews should ensure that trained/experienced personnel are available for frequent and routine site visits, that appropriate and robust monitoring systems are in place and collecting data, and that project personnel are examining and interpreting data using appropriate methods on a timely basis. For example, within the USGS, each project is typically reviewed by subject matter experts within individual organizational units at the proposal stage and then again when the project is about 10-, 40-, and 70-percent complete, or at fixed intervals, such as quarterly or semiannually.

Quality audits, in the form of periodic external reviews, are also necessary to monitor and implement the project QA/QC program (Jones, 1999). External audits should examine project plans, project data, project records, and QA/QC documentation to ensure that study objectives are being met, and to ensure that study objectives will meet the goals of the monitoring project. External reviews should ensure that the project information is properly documented and that the documentation is accessible. Within the USGS, external quality audits include periodic reviews by technical specialists at different levels in the chain of command above the local organizational unit and by technical specialists from discipline offices such as the Office of Surface Water, the Office of Ground Water, the Office of Quality Water, and the Branch of Quality Systems.

CONCLUSION

Information from stormwater studies may be used to address local issues and (or) may contribute to a regional or national synthesis of highway- or urban-runoff studies. Accurate and representative precipitation and stormwater-flow data are crucial for valid, current, and technically defensible interpretations of highway- or urban-runoff study results. Equally important is knowledge of the degree of accuracy and representativeness of available precipitation and stormwater-flow data. Accurate and representative measurements of precipitation and stormwater flow, however, are difficult to obtain because of the rapidly changing spatial and temporal distribution of precipitation in the study area and the rapidly changing flows during a storm. Many hydrologic and hydraulic factors must be considered in selecting sites for measuring precipitation and stormwater flow that are representative of the objectives and goals of the study. Many hydrologic and hydraulic factors also must be considered in determining frequencies and durations of data collection to fully characterize the rapidly changing rainfall intensities and stormwater flows, and in selecting methods that will yield accurate data over the full range of rainfall intensities and the full range and changing flow regimes of stormwater flows.

Without the supporting data needed to evaluate the accuracy and representativeness of the precipitation and stormwater-flow measurements, the data collected and interpretations made may have little meaning. To ensure that the accuracy and representativeness of precipitation and stormwater-flow data can be evaluated, decisions as to (1) where in the drainage system precipitation was collected and stormwater flows were measured, (2) how frequently precipitation and stormwater flows were measured, (3) what methods were used to measure precipitation and stormwater flows, and (4) on what basis these decisions were made must be documented and communicated in an accessible format, such as a project description report, a data report, or an appendix to a technical report, and (or) archived in a State or national records center. Additionally, a quality assurance/quality control program must be established to ensure that this information is documented and reported, and that the decisions made in design phase are continually reviewed, internally and externally, throughout the duration of the study.

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Chapter 4. An Overview of the Factors Involved in Evaluating the Geochemical Effects of Highway Runoff on the Environment

By OWEN P. BRICKER

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An Overview of the Factors Involved in Evaluating the Geochemical Effects of Highway Runoff on the Environment

By Owen P. Bricker

Abstract

Materials washed by rain and snowmelt from highways into adjacent surface waters, ground waters, and ecosystems can pollute water and affect biota. To understand the chemical behavior of any one of these materials and its effects on the environment requires knowledge of the chemistry of the material and how it interacts with other components in the local geochemical system. An integrated watershed approach, therefore, would be the most effective method to assess the effects of highway runoff on local receiving waters. Analysis of one or a few specific contaminants will provide limited and incomplete information and may be misleading in terms of environmental effects. This report addresses the background geochemistry required to model highway runoff and to make realistic assessments of the potential effects of runoff on the environment.

INTRODUCTION

Highway runoff contains a variety of chemical constituents that include deicing chemicals; metals; organic compounds in gasoline, oil, grease, and hydraulic fluids; tire and brake-lining residues; components of gasoline additives; and materials from catalytic converters. Many of these constituents are harmful to the environment and are washed from roads by rain and snowmelt into adjacent surface waters, ground waters and ecosystems where they can pollute water and damage biota, including man. To understand the behavior of any one of these materials and its effects on the environment requires knowledge of the chemistry of the material and how it interacts with other components in the system. Policies and procedures for planning, designing, and maintaining the Nation’s highways as outlined by the Intermodal Surface Transportation Efficiency Act (ISTEA) are beneficial for and compatible with watershed-based environmental management (Bank, 1996). Geochemical knowledge of the watershed environment surrounding the highway is an important factor in evaluating the effects of highway runoff on local waters, the effectiveness of best management practices (BMPs), the quality of available information, and normalizing measured differences between sites in a national database.

Metal concentrations that cause toxic effects in stream biota are related to surface-water hardness (a gross measure of the geochemical environment in a watershed), which varies considerably between watersheds across the country (Driscoll and others, 1990). Wilde (1994) noted several important geochemical effects on surface and ground water near stormwater BMPs. Most notable of these is the dissolution of nonnative building materials (rock aggregate) in a BMP structure, which releases magnesium, nickel, and possibly chromium into infiltrating stormwater (Wilde, 1994). Another example is the eutrophication of a small lake in Vermont, which was caused by sulfur from the weathering of freshly exposed highway construction materials (Morgan and others, 1984). The sulfur coprecipitated natural iron in lake water that had previously scavenged available phosphate into insoluble ferric phosphate precipitates. Deicing chemicals also may be a continuing source of sulfur to feed this process, because sulfate is the largest contaminant of sodium chloride road salt by mass (Granato, 1996). Much of the inorganic sediment washed off roadways is representative of the local geology (Gupta and others, 1981); therefore, natural soils may be a substantial source of measured constituents. Shacklette and Boerngen (1984) examined 1,318 soil samples collected at 20 centimeters (cm) depth about every 80 kilometers (km) along the Nation's highway system and found that background soil concentrations of chromium, copper, iron, lead, and zinc varied by 2 to 4 orders of magnitude (1-2,000; <1-700; 100–100,000; <10–700; and 5–2,000 parts per million, respectively). The quality and comparability of data can be evaluated by using geochemical interpretations. Sansalone and Buchberger (1997) demonstrated that the partitioning of metals between suspended solids and the dissolved phase in untreated samples of pavement runoff over a 24-hour period was driven by the geochemical characteristics of the individual metals. Their data also indicate that the proportion of dissolved metals in pavement runoff may be higher than expected because the metals were not in geochemical equilibrium with available sediments.

The purpose of this report is to examine the geochemistry of highway runoff, the techniques for sample collection and analysis, and the interpretation and modeling of data pertinent to understanding the consequences of highway runoff on the environment. Gupta and others (1981) observed that “Much of the street contaminants are representative of local geology and, to a lesser extent, products abraded from the roadway surfaces, and are largely inorganic.” In this report, therefore, emphasis is placed on the inorganic aspects of highway runoff geochemistry.

BACKGROUND OF CHEMICAL PROCESSES

Assessment of the effects of highway runoff on the environment requires knowledge of the chemical behavior of the runoff components and their interactions with other components of the system into which they are introduced. The chemical behavior of substances, either natural or those introduced by human activities into the environment, depends on the intrinsic properties of these substances and the types and concentrations of other constituents in the system with which they may interact. Major processes driving geochemical interactions include:

- Dissolution
- Precipitation
- Activity and concentration
- Ion-exchange
- Adsorption and desorption
- Oxidation and reduction (redox), and
- Complexation.

In an ideal world, when two or more substances interact, the end state of the reaction is a condition of thermodynamic equilibrium. Given the appropriate thermodynamic data, the equilibrium state for any reaction can be calculated. This equilibrium state will be the one that the system will react to. In the real world, more frequently than not, the reaction will not reach the true equilibrium state in a finite time because of kinetic hindrances. Equilibrium thermodynamics is a useful tool for predicting the direction a reaction will take and the final state of the system given infinite time. Kinetics provides information on the rate at which a reaction will proceed, the rate-limiting steps, and the time necessary to achieve the equilibrium state.

Many of the chemical constituents of interest are sensitive to the acidity (pH) and (or) the oxidation-reduction (redox) conditions of the system in which they occur. Changes in these variables may control the concentration, form, and availability of the constituent and its effect on the environment. Two variables that are useful in quantitatively describing such interactions are Eh (redox potential relative to the hydrogen half-cell) and pH (activity of the hydrogen ion). These variables are so useful in describing chemical reactions that they have been referred to as “master variables” (Sillen, 1967). A third variable necessary to quantify chemical reactions in aqueous solutions is the ionic strength of the medium in which the reactions are taking place.

Dissolution of Substances

Substances may dissolve in several ways. When sodium chloride is placed in water it dissolves completely, forming sodium and chloride ions in solution:

$$NaCl = Na^+ + Cl^- \,. \tag{1}$$

This type of solution behavior is termed "congruent solution" and is exhibited by many compounds. The solid dissolves completely, leaving no residual. In contrast to congruent dissolution, some compounds dissolve by releasing a part of their constituents to solution but retaining others in the form of a new solid phase. This type of solution behavior is termed "incongruent solution", and is commonly exhibited by the silicate minerals:

$$2NaAlSi_3O_8 + 11H_2O = Al_2Si_2O_5(OH)_4$$

$$+\ 2Na^+ + 2OH^- + 4H_4SiO_4 \,. \tag{2}$$

Precipitation of Substances

Compounds precipitate from solution when the solution is saturated with respect to the solid. Ideally, precipitation occurs when the solution reaches saturation with the compound. In homogeneous systems where there are no nuclei, a high degree of supersaturation is generally required to initiate nucleation. In heterogeneous systems, other particles often serve as nuclei and precipitation occurs at saturation values very close to the thermodynamically predicted value.

The precipitation-dissolution behavior (solubility) of compounds can be described by the law of mass action. For a general reaction of the type,

$$aA + bB = cC + dD \,, \tag{3}$$

the distribution of species is given by

$$K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b} \,, \tag{4}$$

where K_{eq} is the thermodynamic equilibrium constant and A, B, C, and D are the activities of the respective species raised to their stoichiometric coefficients a, b, c, and d.

If the equilibrium constant, K_{eq}, is known for a reaction, the distribution of all of the species involved in the reaction can be calculated. Equilibrium constants for a large number of reactions have been tabulated in earlier literature (for example, Sillen and Martell, 1964, 1967; Martell and Smith, 1974–1989). Equilibrium constants may also be calculated directly, provided thermodynamic data are available for the species involved at the temperature and pressure of interest (for example, Robie and others, 1978; Wagman and others, 1982; Woods and Garrels, 1987). If zinc carbonate ($ZnCO_3$) is placed in water open to the atmosphere, for example, the resulting solution composition can be calculated

$$ZnCO_3 + H_2O + CO_2 = Zn^{2+} + 2HCO_3^- \,, \tag{5}$$

and

$$K_{eq} = \frac{[Zn^{2+}][HCO_3^-]^2}{[ZnCO_3][H_2O]P_{CO_2}} \tag{6}$$

where

K_{eq} is the equilibrium constant for the reaction,

[species] is the thermodynamic activity of the respective species, and

P_{CO_2} is the partial pressure of CO_2 (in this case, the partial pressure of CO_2 in the atmosphere).

The equilibrium constant for the reaction (K_{eq}) can be calculated from thermodynamic data using the following relation

$$\Delta G^{\circ}_{R} = -RTlnK_{eq} \ , \tag{7}$$

where

ΔG°_{R} is the standard Gibbs free energy of the reaction,
R is the gas constant,
T is the temperature in degrees K, and
lnK_{eq} is the natural log of the equilibrium constant.

For conditions of one atmosphere total pressure and 25 degrees Celsius (˚C), and converting from natural logs to logs to the base 10, the relation in units of kilocalories is

$$\Delta G^{\circ}_{R} = -1.364\log K_{eq} \ . \tag{8}$$

The ΔG°_{R} is the sum of the standard free energies of the reaction products minus the sum of the free energies of the reactants

$$\Delta G^{\circ}_{R} = \left[\Delta G^{\circ}_{Zn^{2+}} + \Delta G^{\circ}_{HCO_3^-}\right] - \left[\Delta G^{\circ}_{ZnCO_3} + \Delta G^{\circ}_{H_2O} + \Delta G^{\circ}_{CO_2}\right] \ . \tag{9}$$

Referring to a table of standard free energy values (Robie and others, 1978),

$$\Delta G^{\circ}_{R} = [(-35.19) + 2(-140.26)] - [(-174.83) + (-56.67) + (-94.26)] \ . \tag{10}$$

$$\Delta G^{\circ}_{R} = +10.05\ Kcal \ . \tag{11}$$

then

$$\log K_{eq} = -7.37 \ . \tag{12}$$

Since P_{CO_2} in the atmosphere is $10^{-3.5}$, then

$$Zn^{2+} = 10^{-3.82} \ , \text{ and} \tag{13}$$

$$HCO_3^- = 10^{-3.79} \ . \tag{14}$$

It is important to understand what these calculations are based on and how they are made, because this type of calculation forms the basis on which geochemical models are built, for example, WATEQ (Truesdell and Jones, 1974), PHREEQE (Parkhurst and others 1980), SOLMINEQ (Kharaka and others 1988), and EQ 3/6 (Wolery, 1992a).

The degree to which a compound or mineral approaches thermodynamic equilibrium is termed the saturation state. The saturation state is derived by first calculating the ion activity product (*IAP*) for the reaction and dividing by the equilibrium constant (K_{eq}). For the mineral calcite (calcium carbonate, $CaCO_3$), the *IAP* would be the activity of Ca^{2+} times the activity of CO_3^{2-} in the solution divided by the product of those activities at equilibrium

$$Q = \frac{IAP}{K_{eq}} \ . \tag{15}$$

When Q (the saturation state) is <1, the solution is undersaturated; when Q is 1, the solution is at equilibrium; and when Q is > 1, the solution is supersaturated. This ratio is referred to as the saturation index (*SI*) when it is expressed in logarithmic form

$$SI = \log\left(\frac{IAP}{K_{eq}}\right) \ . \tag{16}$$

When *SI* is < 0, the solution is undersaturated; when *SI* is 0, the solution is at equilibrium; and when *SI* is > 0, the solution is supersaturated. *SI* and Q both provide the same type of information about the state of the system relative to the solid phase of interest. If the solution is undersaturated, the solid phase should dissolve, but it cannot precipitate. If the solution is supersaturated, the solid phase may precipitate but it cannot dissolve. If the solution is saturated, the solid phase should neither precipitate nor dissolve. This information is useful in predicting the of evolution of the solution. Geochemical programs, such as WATEQ, can be used to calculate the *SI* for a large number of mineral phases for each water analysis provided.

Activity and Concentration of Ions in Solution

Calculations that use thermodynamic data, including most geochemical models, provide information on the activities of species in the system. Results of laboratory analyses provide data in terms of concentrations, generally expressed in units of weight or molar concentration. Thermodynamic activity represents the quantity of a species in the system that is available to react; concentration is the total amount of the species in the system. At infinite dilution, activity and concentration are essentially equivalent; as concentration increases, however, the divergence between concentration and activity increases. The divergence between concentration and activity is largely due to electrostatic effects, as the interactions among charged particles increases in relation to increasing numbers of particles. Lewis and Randall (1923) coined the term ionic strength to describe the electrostatic atmosphere in a solution of charged particles. Ionic strength is defined as

$$I = \frac{1}{2}\sum m_i Z_i^2 , \qquad (17)$$

where

I is the ionic strength,
m_i is the molality of the i^{th} species, and
Z_i^2 is the charge squared of the i^{th} species.

It is necessary to convert analytically determined concentrations to activities in order to make realistic chemical calculations. The activity of a dissolved species is related to its concentration by

$$A_i = \wp_i m_i , \qquad (18)$$

where

A_i is the activity of the i^{th} species,
$\wp$ is the activity coefficient of the i^{th} species, and
m_i is the concentration (molality) of the i^{th} species.

One of the most frequently used approximations for activity corrections is the Debye–Huckel approximation

$$-\log_{10} \wp_i = \frac{A z_i^2 \sqrt{I}}{1 + a i^{\circ} B \sqrt{I}} , \qquad (19)$$

where

$\wp$ is the activity coefficient of the i^{th} species,
I is the ionic strength of the entire solution,
A,B are the constants characteristic of the solvent at temperature and pressure,
ai° is the effective diameter of the i^{th} species in solution, and
z is the charge on the i^{th} species.

Examples of the deviations between activity and concentration as a function of ionic strength for some common monovalent and divalent cations are shown in figure 1. The difference between activity and concentration increases with increasing ionic strength and with increasing charge on the ion. Activity of the ion, rather than analytical concentration, must be used for all thermodynamic calculations, if valid answers are to be realized. All of the current geochemical models incorporate a routine for activity correction as an integral part of the model (for example, Plummer and others, 1976; Parkhurst and others, 1980; Parkhurst, 1995). In addition to ionic strength effects, the activities of ions in solution may be reduced by complexing

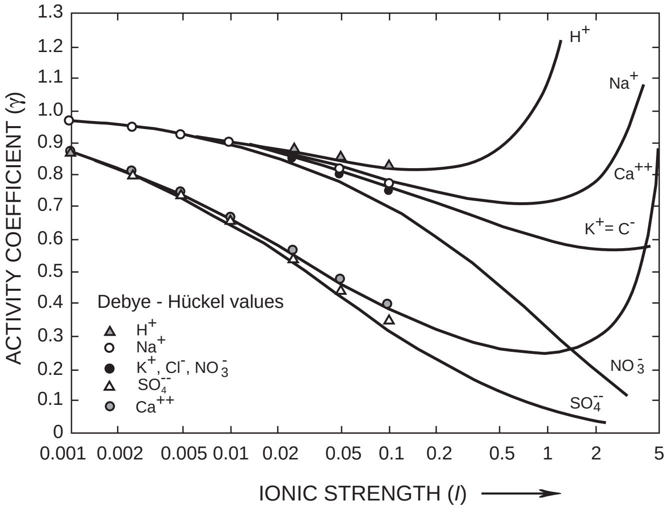

Figure 1. Single ion activity coefficient as a function of ionic strength for some common ions. Solid lines represent values calculated by the mean salt method. Debye-Huckel values were calculated using equation 19. (From Garrels and Christ, 1965).

with other ions in the solution. For example, the activities of the calcium (Ca^{2+}) ion and sulfate (SO_4^{2-}) ion may be reduced by the formation of the calcium sulfate ($CaSO_4^{\circ}$) ion pair. The formation of ion pairs is treated in a parallel manner to the solubility of a compound.

$$CaSO_4^{\circ} = Ca^{2+} + SO_4^{2-} \ , \tag{20}$$

and

$$K_f = \frac{[Ca^{2+}][SO_4^{2-}]}{[CaSO_4^{\circ}]} \tag{21}$$

where

K_f is the formation constant for $CaSO_4^{\circ}$,
$[Ca^{2+}]$ is the activity of calcium in solution,
$[SO_4^{2-}]$ is the activity of sulfate in solution, and
$[CaSO_4^{\circ}]$ is the activity of the calcium sulfate ion pair in solution.

One effect of the formation of ion pairs is not only to reduce the activities of the individual ions in solution, but to increase the total dissolved concentrations of these elements. For example, when (Ca^{2+}) and (SO_4^{2-}) form the ion pair, ($CaSO_4^{\circ}$), the activities of Ca^{2+} and (SO_4^{2-}) are reduced and ($CaSO_4^{\circ}$) is increased. This permits more of the solid phase to dissolve to bring the activities of (Ca^{2+}) and (SO_4^{2-}) to equilibrium, and the total concentration of these elements in the solution is increased. The solubility of gypsum is an example of the importance of ionic-strength corrections and ion-pair formation to the composition of electrolyte solutions. Calculation of the amount of gypsum that will dissolve in water when these corrections are ignored results in 0.86 grams per liter (g/L). If the ionic-strength correction and ion-pair formation are considered, the actual value is 3.15 g/L —more than three and a half times the amount calculated without considering the corrections (Appelo and Postma, 1993). Data from urban-and highway-runoff studies have indicated increased solubilities of metals by ion-pair formation in surface and ground waters affected by runoff pollution (Morrison and others, 1990; Warren and Zimmerman, 1994; Granato and others, 1995). A realistic assessment of the chemistry of most natural waters, which are complex electrolyte solutions, requires consideration of ionic-strength effects and ion-pair formation. Examples of other common ion pairs in natural waters are calcium carbonate ($CaCO_3^{\circ}$), calcium bicarbonate ($CaHCO_3^{+}$), aluminum fluoride (AlF_2^{+}), and aluminum hydroxide ($Al(OH)_4^{-}$).

Ion Exchange

Many solids, including zeolites, clay minerals, oxyhydroxides, colloids, and natural organic compounds exhibit ion-exchange behavior. Ion exchange is a process in which ions associated with a solid, held by forces ranging from very weak to very strong, are replaced by other ions as the composition of the electrolyte solution in which they are bathed changes. A classic example of ion exchange resulting from electrostatic forces is exhibited by clay minerals. Ionic substitution in the alumino-silicate framework of these minerals creates a charge imbalance leading to a negative charge on the framework. This negative charge is neutralized by sorption of cations on the surface of the mineral or in interlayer sites. The amount of charge and, thus, the capacity of the mineral to sorb cations is called the cation-exchange capacity (CEC). The CEC can vary depending on a particular clay mineral, the nature of the ions occupying exchange sites, and the pH of the solution. CEC values for some typical clay minerals are shown in table 1 (Drever, 1997). The exchange equilibrium can be expressed by the mass action expression

$$A - clay + B^{+} = B - clay + A^{+} \ , \tag{22}$$

$$K_{AB} = \frac{[B - clay][A^{+}]}{[A - clay][B^{+}]} \ , \tag{23}$$

or

$$\frac{a_{A-clay}}{a_{B-clay}} = K_{AB}\frac{a_{A+}}{a_{B+}} \ , \tag{24}$$

where

a_{A-clay} and a_{B-clay} are the activities of A and B on the exchange sites,
a_{A+} and a_{B+} are the activities of A^{+} and B^{+} in solution, and
K_{AB} is the exchange constant.

Table 1. Cation-exchange capacities of clay materials

[From Drever, 1997. <, actual value is less than value shown]

Clay materials	Cation-exchange capacity (millequivalents per 100 grams)
Smectites	80-150
Vermiculites	120-200
Illites	10-40
Kaolinite	1-10
Chlorite	<10

The same form of equation can be written for divalent-divalent ion exchange. For monovalent-divalent exchange, the expression is written

$$2A - clay + B^{2+} = B - clay + 2A^{+} \ , \tag{25}$$

$$K_{AB} = \frac{[B - clay][A^{+}]^{2}}{[A - clay]^{2}[B^{2+}]} \ , \tag{26}$$

or

$$\frac{a_{A-clay}^{2}}{a_{B-clay}} = K_{AB}\frac{a_{A+}^{2}}{a_{B^{2+}}} \ . \tag{27}$$

If the above equations are written with equivalent fractions instead of activities to represent the solid phases, and concentrations instead of activities to represent the aqueous ions, then

$$\frac{X_{A-clay}}{X_{B-clay}} = K_{AB}^{1}\frac{m_{A+}}{m_{B+}} \ , \tag{28}$$

and

K_{AB}^{1} is the selectivity coefficient.

Three conventions are commonly used in ion exchange investigations. For homovalent exchange, there is little difference among the conventions, but for heterovalent exchange the convention chosen can make a significant difference. For the exchange of sodium (Na^{+}) for calcium (Ca^{2+}) on clay, the reaction may be written

$$Na^{+} + \frac{1}{2}Ca - clay = Na - clay + \frac{1}{2}Ca^{2+} \ , \tag{29}$$

$$K_{\frac{Na}{Ca}} = \frac{[Na - clay][Ca^{2+}]^{0.5}}{[Ca - clay]^{0.5}[Na^{+}]} = \frac{B_{Na}[Ca^{2+}]^{0.5}}{B_{Ca}^{0.5}\ [Na^{+}]} \tag{30}$$

When B is the equivalent fraction for ion i,

$$B_{i}^{eq} = \frac{meq[i - clay]per\ 100\ g\ clay}{CEC} \ , \tag{31}$$

where CEC is the cation-exchange capacity, the above expression conforms to the Gaines and Thomas (1953) convention.

When B is the molar fraction for ion i,

$$B_{i}^{m} = \frac{mmol[i - clay]per\ 100\ g\ clay}{TEC} \ , \tag{32}$$

where TEC is the total exchange capacity, the above expression conforms to the Vanselow convention (Vanselow, 1932). If the activities of sorbed ions are assumed to be proportional to the number of exchange sites on the clay that are occupied by the ion, the reaction is written

$$Na^{+} + \frac{1}{2}Ca - clay = Na - Clay + \frac{1}{2}Ca^{2+} \ , \tag{33}$$

$$K_{\frac{Na}{Ca}}^{G} = \frac{[Na - clay][Ca^{2+}]^{0.5}}{[Ca - clay]^{0.5}[Na^{+}]} \ , \tag{34}$$

which corresponds to the Gapon convention (Gapon, 1933). All of these conventions are used in exchange studies, and the choice of a particular one is a matter of goodness of fit of the data being examined. There is little difference among the three conventions at low solute concentrations.

In general, divalent cations are favored on exchange sites of clay minerals in freshwater systems. When clays are transported to the marine environment, the divalent cations are exchanged for sodium because of the high sodium to divalent cation activity ratio in seawater. Ion exchange has been identified as an important process in affecting the composition of waters in areas where road salt is applied for deicing purposes (Shanley 1994; Granato and others, 1995). Runoff from highways to which road salt is applied is concentrated in sodium (Na^{+}), and this may promote the exchange of sodium (Na^{+}) for calcium (Ca^{2+}) and other metals if the sodium to calcium (Na^{+}/Ca^{2+}) ratio in runoff is high. In addition to its effect on water composition, the type of ion occupying exchange sites may have a significant effect on the physical properties of the clay. Clays whose exchange sites are primarily occupied by calcium (Ca^{2+})are generally permeable and granular whereas clays with sites primarily occupied by sodium (Na^{+}) tend to be cohesive and impermeable (Krauskopf, 1967).

Drever (1997) has pointed out that ion exchange is an important process in the control of water chemistry wherever water is in contact with sediments. As an example, he cites an aquifer with a *CEC* of 5 milliequivalents per 100 grams (meq/100 g) and a porosity of 20 percent. In this system, the exchange capacity of the solids is on the order of 500 milliequivalents per liter (meq/L) of water, a number larger than the concentration of cations in dilute water. Thus, the exchangeable ions can strongly influence the composition of the water.

Adsorption and Desorption

When a solid is placed in an aqueous solution, adsorption occurs at the interface. Adsorbed ions may be held by forces that range from weak to very strong depending upon the characteristics of the surface and the sorbed ion. Sorption plays an important role in controlling the behavior of trace elements in the environment and may be one of the most important chemical processes affecting the movement of contaminants in natural water systems (Drever, 1997). For example, the concentrations of heavy metals in natural waters are commonly far lower than would be predicted from mineral solubility calculations. The low concentrations are usually the result of sorption of these metals onto particulate matter, such as iron and manganese oxyhydroxides, or organic matter. Prediction of the movement of heavy metals in soils and ground water requires the quantitative description of sorption processes. The fundamental theory applicable to sorption on particles is the electrical double layer, of which two types are recognized (Berner, 1971; van Olphen, 1977). In the first type, sorption results from imperfections or ionic substitutions within the crystal lattice, which produces an electrical charge on the surface of the particle. This charge is balanced by an excess concentration of ions of opposite charge called counterions attracted to the surface from the surrounding solution. The charged surface is the fixed layer and the counterions form the mobile layer. Together they make up the electrical double layer. The clay minerals with their fixed surface charge arising from imperfections and ionic substitution in the crystal lattice and broken bonds along crystal edges are good examples of this type of sorbant particle.

Another type of double layer occurs when, due to specific chemical forces, ions are sorbed at the surface of a particle causing it to become charged. The sorbed ions are called potential determining ions and make up the fixed layer. In this type of double layer, the fixed charge on the surface is not constant but will vary as the composition of the solution changes. Thus, the sorption capacity will vary with solution composition. The counterions balancing the charge on the fixed layer constitute the mobile layer. Most particulates exhibit this type of sorption behavior.

Extensive theoretical treatments of double layer theory can be found in Overbeek (1952), Sparnaay (1972), van Olphen (1977), and Adamson (1990). Summary discussions and examples of applications of the various theories are presented in Appelo and Postma (1993), Stumm and Morgan (1996), and Drever (1997). In practice, it is usually very difficult or impossible to distinguish among various types of sorption and ion exchange in environmental systems, and empirical approaches are used to describe sorption. The most simple of these is the linear adsorption isotherm (K_d), expressed as

$$m_{i(ads)} = K_d m_{i(sol)} \ , \tag{35}$$

where

$m_{i(ads)}$ is the concentration of the sorbed species i,
$m_{i(sol)}$ is the concentrations of species i in solution, and
K_d is the distribution coefficient.

When the adsorption isotherm is used in computer codes for geochemical modeling, the i in solution is expressed in terms of its thermodynamic activity (a_i) instead of concentration (m_i) and the K_d is called an activity distribution coefficient.

Two other isotherms commonly used in adsorption studies are the Freundlich isotherm and the Langmuir isotherm. The Freundlich isotherm is similar to the linear isotherm with the addition of an exponent on the solution concentration term

$$m_{i(ads)} = K_f m_{i(sol)}^n \quad . \tag{36}$$

The n exponent is usually less than one and leads to curvature of the isotherm at higher concentrations. The Langmuir isotherm, originally developed to describe the adsorption of gas on a solid surface, can be used to describe adsorption in aqueous systems (Stumm, 1992). It is assumed that a fixed number of adsorption sites are on the surface of the adsorbent. Then the maximum concentration of sites available is $m_{i(ads,\ max)}$, the concentration of sites occupied by sorbed i is $m_{i(ads)}$, and the concentration of sites not occupied by i is $m_{(vacant\ sites)}$. The adsorption expression is

$$vacant\ site + i = occupied\ site, \tag{37}$$

and the equilibrium constant expression is

$$K_{lang} = \frac{m_{i(ads)}}{m_{i(sol)} m_{(vacant\ sites)}} \ , \tag{38}$$

or

$$m_{i(ads)} = m_{i(ads,\ max)} \frac{K_{lang} m_{i(sol)}}{1 + K_{lang} m_{i(sol)}} \ . \tag{39}$$

Adsorption, like ion exchange, is important with respect to the fate of materials released to the environment. If a potentially toxic material in aqueous form is adsorbed or exchanged onto sediment particles, it will be transported with the sediment either until conditions change and cause desorption (for example, freshwater entering brackish or saline waters) or until it is effectively removed from the system upon burial with the sediment. If conditions upon burial are favorable, the material will remain with the sediment as long as the sediment is not disturbed or resuspended and the geochemical conditions of the sediment remain the same (for example, oxic to anoxic). If conditions change upon burial, the sorbed or exchangeable material may be released and may diffuse into the water column.

Oxidation and Reduction (Redox)

Oxidation-reduction reactions involve the transfer of electrons. In an oxidation reaction, an element loses electrons; in a reduction reaction, an element gains electrons. There cannot be an oxidation without a corresponding reduction and vice versa. A number of elements can occur in more than one oxidation state. The most abundant elements displaying this behavior are oxygen (*O*), hydrogen (*H*), carbon (*C*), sulfur (*S*), and nitrogen (*N*). These elements generally drive redox reactions in natural systems. Two other elements, iron (*Fe*) and manganese (*Mn*), although less abundant, are major participants in redox reactions in some natural systems. The behavior of many of the minor elements in the environment, of concern because of their toxicity, is dependent on their redox state. The redox state of an element determines its chemical and biological behavior, including toxicity, as well as its mobility in the environment. For example, if water in a BMP designed to collect contaminated sediments, such as a retention/detention pond, catchbasin, or storm-sewer sedimentation tank, becomes anoxic between storms, metals will be mobilized in the water column or, in the case of ponds, into infiltrating ground waters, only to be flushed out with flow from the next storm.

Redox reactions can be written as half-reactions or half-cells which, when combined, form the whole reaction. The general form of the half-reaction, written as a reduction reaction is represented by

$$aA + bB + e^{-} = cC + cD \ , \tag{40}$$

where

A and B are the oxidized species,
C and D are the reduced species, and
e^{-} is the number of electrons transferred in the reaction.

A reduction half-reaction cannot proceed without being coupled to an oxidation half-reaction

$$fF + gG = hH + iI + e^{-} \ . \tag{41}$$

When the half-reaction

$$aA + bB + e^{-} = cC + cD \qquad (42)$$

and the half reaction

$$fF + gG = hH + iI + e^{-} \qquad (43)$$

are added, the whole reaction

$$aA + bB + fF + gG = cC + dD + hH + iI \qquad (44)$$

results and the electrons cancel mathematically.

Because a single half-reaction cannot take place in the absence of a corresponding opposite half-reaction, the absolute potential of a half-reaction cannot be measured. For most purposes, it is not necessary to know the absolute potential of half-reactions, but only differences in potential. By convention, the potential of the hydrogen half-reaction has been set at zero, and the potentials of other half-reactions are measured against it. This potential, usually measured in volts or millivolts, is referred to as *Eh*—the potential of the half-reaction relative to the hydrogen-half reaction. By normalizing against the hydrogen half-reaction, the differences in potential between redox half-reactions can be quantified. When the activities of all of the participating species in a reaction are unity, the potential of the reaction is the standard potential. Standard potentials for a large number of half-reactions are tabulated (Latimer (1952), Sillen and Martell (1964), Wagman and others (1982), and Bard and others (1985) and also may be calculated from thermodynamic data. If the activities of the participating species are different from unity, the redox potential of the reaction is given by the Nernst equation that relates the standard potential of the reaction to the activities of the participating species at thermodynamic equilibrium.

Consider the half-reaction

$$\text{oxidized species} + e^{-} = \text{reduced species}. \qquad (45)$$

The Gibbs free energy expression for this half reaction is

$$\Delta G_R = \Delta G^{\circ}_R + RT\ln\frac{[reduced\ species]}{[oxidized\ species]}\ . \qquad (46)$$

The Gibbs free energy of the reaction (ΔG_R) is related to the redox potential (*Eh*) by the equation

$$\Delta G_R = -nFEh\ , \qquad (47)$$

where

n is the number of electrons transferred in the reaction, and

F is the Faraday constant.

By dividing equation (46) by -*nF*, the result is

$$\frac{-\Delta G_R}{nF} = \frac{-\Delta^{\circ}_R}{nF} + \frac{RT}{nF}\ln\frac{[reduced\ species]}{[oxidized\ species]}\ . \qquad (48)$$

By substituting equation (47) in equation (48),

$$Eh = E^{\circ} - \frac{RT}{nF}\ln\frac{[reduced\ species]}{[oxidized\ species]}\ , \qquad (49)$$

where

Eh is the redox potential of the reaction,

E^{o} is the standard potential of the reaction when all species are at unit activity,

R is the gas constant,

T is the absolute temperature in K,

F is the Faraday constant,

n is the number of electrons transferred in the reaction,

[oxidized] represents the sum of all oxidized species taking part in the reaction, and

[reduced] represents the sum of all reduced species taking part in the reaction.

By converting to log to the base 10,

$$Eh = E^{\circ} + \frac{2.303RT}{nF}\log\frac{[oxidized\ species]}{[reduced\ species]}\ . \qquad (50)$$

At 25 degrees Celsius

$$Eh = E^{\circ} + \frac{0.0592}{n}\log\frac{[oxidized\ species]}{[reduced\ species]}\ . \qquad (51)$$

Equation (51) is the form of the Nernst equation most commonly used in geochemical calculations. Another way of expressing the redox state of a system is with the variable *pE*. The *pE* is defined as the negative log of the electron activity. It is related to *Eh* by the following expression

$$pE = \frac{nFEh}{2.303RT} \text{ or at } 25^{\circ}\text{C } \frac{Eh}{0.0592}\ . \qquad (52)$$

Diagrams to describe relations among redox-sensitive elements may be constructed by using either *Eh* or *pE* as the redox variable; the geometry will be the same. Because protons are commonly involved in redox reactions, such diagrams are usually constructed with a redox variable on one axis and pH on the other axis, and are referred to as *Eh*-pH or *pE*-pH diagrams. So many reactions of interest in natural systems involve both *Eh* and pH that these variables have been called “master variables” (Sillen, 1967). Theoretical *Eh*-pH diagrams provide a useful way to visualize the aqueous speciation and dominant solid phases of redox-sensitive elements.

The *Eh*-pH diagram in figure 2 (Bricker, 1965) depicts stability reactions in the system manganese, oxygen, water (Mn-O_2-H_2O) at 25˚C and one atmosphere total pressure. It can be seen at a glance that the manganous ion is the major dissolved component, with the manganese hydroxide ($Mn(OH)_3^-$) aqueous complex only dominant over a narrow range of *Eh* at elevated pH. If carbon (*C*) and sulfur (*S*) are added to the system (fig. 3; Hem 1985), the stability fields of rhodochrosite ($MnCO_3$) and alabandite (MnS) appear and begin to encroach on the pyrochroite ($Mn(OH)_2$) field, but manganous ion (Mn^{2+}) remains the dominant dissolved species, and manganese oxides the dominant solid phases over most of the *Eh*-pH conditions that are usually observed in natural waters. Similar diagrams can be drawn for any element of interest provided that appropriate thermodynamic data are available.

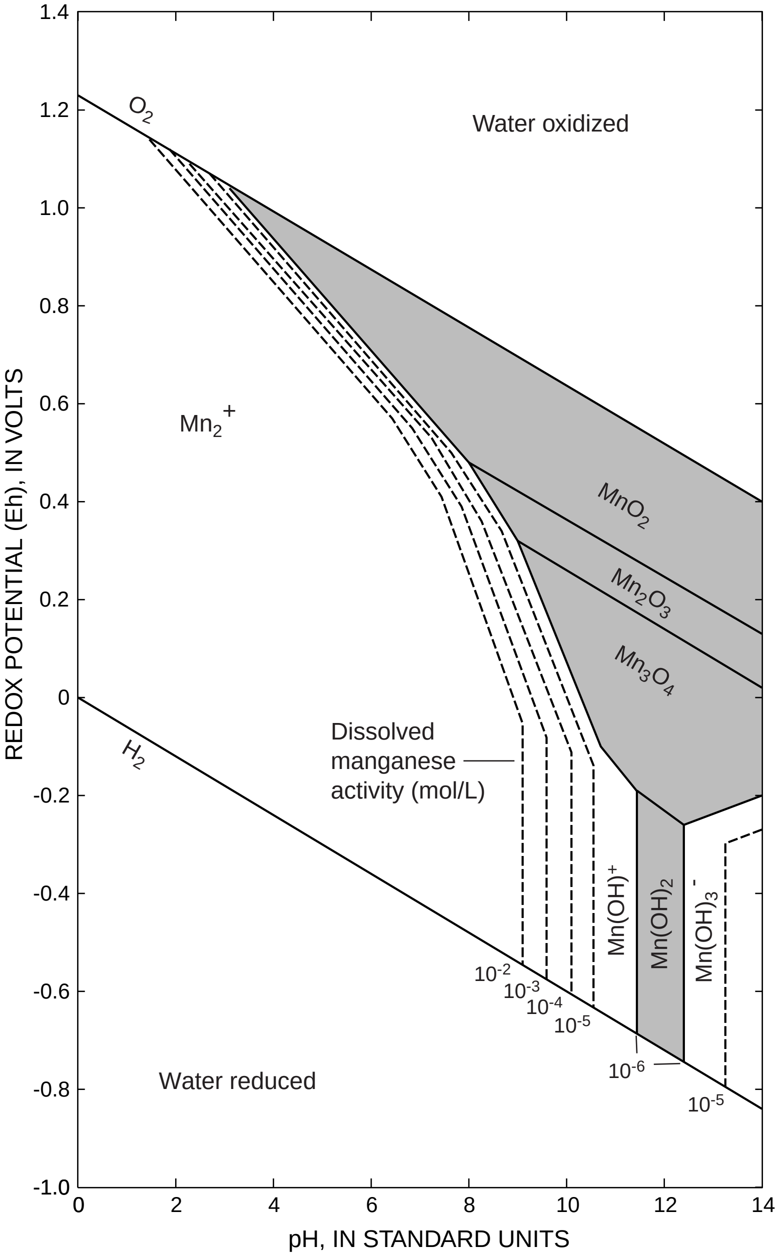

Figure 2. *Eh*-pH diagram showing stability relations among some manganese oxides and pyrochroite at 25˚C and one atmosphere total pressure. Boundaries between solids and dissolved species are drawn at activity of dissolved species = 10^{-6} contour of A_{mn}^{2+} is at 10^{-4}. (Modified from Bricker, 1965.)

There is a widespread perception that *Eh* may be easily measured in environmental systems by simply inserting an electrode into the system and reading the potential. In fact, *Eh* is difficult or impossible to measure in most natural systems by using electrodes. A number of conditions must be met if a thermodynamically meaningful *Eh* is to be measured by using an electrode (Bricker, 1982). The electrode must be inert; both the oxidized and reduced species of the half cell being measured must be electroactive at the surface of the electrode; the redox reaction must be reversible at the surface of the electrode; the concentrations of both the oxidized and reduced species must be high enough to be measured by the electrode; and the oxidizing half reaction must be coupled with the reducing half reaction and not with another half reaction that may be more electrochemically advantageous. When the oxidation half reaction of one

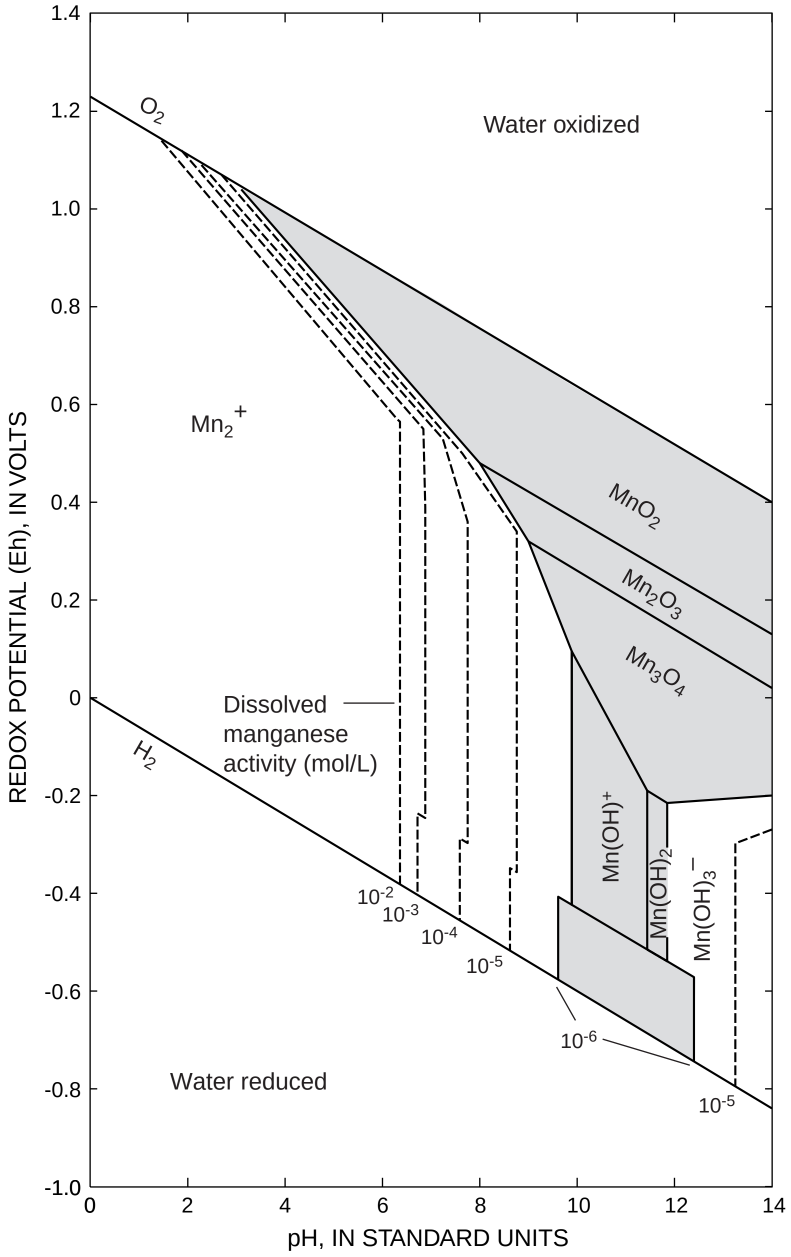

Figure 3. *Eh*-pH diagram showing stability relations among some manganese solids at 25˚C and one atmosphere total pressure. Activity of sulfur species is 96 mg/L as SO_4^{2-} and carbon dioxide species 61mg/L as HCO_3^-. (Modified from Hem, 1985.)

reaction is coupled to the reduction half reaction of another reaction or the reverse, a mixed potential results. Mixed potentials are not interpretable thermodynamically but commonly occur when *Eh* measurements are attempted in natural systems that contain more than one redox couple (Bricker, 1982; Stumm and Morgan, 1996). For that reason, it is best to measure the concentrations of the reduced and oxidized species, when possible, and calculate *Eh* by using the Nernst equation.

Another problem arises in trying to establish the *Eh* of a natural system. Many redox reactions are kinetically slow; thus, when several redox couples are present in a system, they may not be in equilibrium. Measurement of one couple may give a different value of *Eh* than measurement of another couple. The *Eh* measured by an electrode will be that of the couple most reactive at the electrode surface (or it may be a mixed potential). Regardless of the difficulties of measuring *Eh* in natural systems, the concept of *Eh* and the construction of *Eh*-pH diagrams can be extremely useful in understanding the chemistry of these systems. *Eh*-pH calculations will provide information about the state of the system at equilibrium and will indicate the direction of reactions in systems that have not reached equilibrium. The classic work on the construction and application of *Eh*-pH diagrams can be found in Garrels and Christ (1965). Additional information on the theory, application, construction and use of *Eh*-pH diagrams is detailed in Bricker (1965), Cloke (1966), Pourbaix (1966), Brookins (1988), Stumm and Morgan (1996), Drever (1997), and Langmuir (1997).

Complexation

In natural systems, the majority of trace elements and many major elements form complexes (Langmuir, 1997). Complexation increases the apparent dissolved concentrations of elements in solution and can increase their transport by reducing the potential for removal by contact with soils and sediments that are stationary or may settle (or be filtered, in the case of subsurface waters) out of solution. The formation of aqueous complexes and ion pairs is usually described by an equilibrium constant expression. For the formation of the complex CaF^+, the expression is written

$$Ca^{2+} + F^{-} = CaF^{+} \ . \tag{53}$$

The equilibrium constant expression is

$$K_{eq} = \frac{[CaF^{+}]}{[Ca^{2+}][F^{-}]} \tag{54}$$

Another convention is sometimes used for describing complexes. In this convention, the reactions are written as dissociation reactions

$$CaF^{+} = Ca^{2+} + F^{-} \tag{55}$$

The dissociation constant for this reaction is

$$K_{diss} = \frac{[Ca^{2+}][F^{-}]}{[CaF^{+}]} \tag{56}$$

This is the inverse of the equilibrium constant and has the same numerical value but the opposite sign.

Complexing affects the behavior of dissolved elements in a number of ways. Most importantly, complexing may have a profound effect on the toxicity and the bioavailability of an element. The speciation of an element in solution is often much more important with respect to its toxicity than its total concentration. Uncomplexed aluminum (*Al*) ion in waters affected by acid rain is toxic to fish, whereas the same total concentration of dissolved *Al* in the form of organic complexes or *F* complexes is much less toxic (Driscoll and others, 1984). Metals, such as copper (*Cu*), lead (*Pb*), cadmium (*Cd*), and mercury (*Hg*), which are very toxic in their uncomplexed ionic forms, are much less toxic (at the same concentration of total metal) when present as complex species (complexed dissolved components such as $CuCl_2^-$). The bioavailability of elements is also a function of speciation (Morel and Hering, 1993), as are the sorption characteristics. Simple uncomplexed ionic forms of elements usually are strongly sorbed relative to carbonate, sulfate, or chloride complexes of those elements. Hydroxyl and phosphate complexes, on the other hand, often are sorbed readily. This behavior has implications for the mobility and transport of elements. Free ions and complexed ions that have little tendency to sorb onto surfaces will be transported with the aqueous phase. Elements that sorb onto particulates will be transported with them and deposited where sediments accumulate. Elements exhibiting this behavior may be removed effectively from interaction in the system as long as they remain sorbed to particles. If chemical conditions change during transport or after deposition (for example, changes in salinity along a river or redox state after burial in the sediments), the elements may be released, perhaps in a toxic form, and become available to interact with biota or other components of the system. Complexing may significantly increase the concentration of an element in solution beyond its calculated solubility in the absence of a complexing agent. Complexing, in addition to the effect of ionic strength on activity, may lead to the solubilization and transport of much larger amounts of an element than would be predicted from solubility constant considerations alone. To understand how an element will behave with respect to solubilization, mobilization and transport, sorption, and bioavailability and toxicity to biota, its speciation in the system of interest must be known. This entails knowledge of all of the components of the system and how they interact (not just an analysis of a few regulated compounds).

This background section provides a brief sketch of some basic geochemical principles that are necessary to understand environmental systems. More detail on this material can be found in books by Garrels and Christ (1965), Appelo and Postma (1993), Stumm and Morgan (1996), Drever (1997) and Langmuir (1997).

SAMPLE COLLECTION

Investigating highway runoff and its effects on ecosystems and the environment entails the collection of appropriate samples to answer the questions posed. In addition, the techniques that are used to collect samples are critical to the success of a monitoring or research program. If proper techniques are not employed, the samples may be compromised during collection. If this occurs, subsequent analyses of the samples, no matter how good, will only provide compromised data, which at best may be misleading. Remedial or mitigative actions that are based on these data may not provide the desired results and may waste valuable resources.

A number of problems must be confronted when collecting samples. The first objective is to collect a representative sample of the system of interest. If the system is homogeneous, a sample taken from anywhere in the system will be representative of the entire system. In the real world, however, this is seldom the case. Virtually all natural systems are heterogeneous, and a sample from one part of the system will not be representative of the entire system (Hem, 1985). One approach to sampling this type of system is to aggregate (integrate) a series of subsamples taken systematically throughout the system. The larger the number of subsamples, the more representative the aggregate (integrated) sample will be of the system. Another problem arises if the system changes with time-often the defining factor in stormwater studies of urban and highway runoff. Highway runoff during snowmelt is one example, with the initial runoff commonly more concentrated in deicing compounds than subsequent runoff. For instance, changes in the concentration of dissolved sodium chloride ($NaCl$) will affect ion exchange, sorption, and complexing reactions. In this example, the runoff likely would undergo systematic changes in composition along its flow path through dilution by mixing with other waters and reaction with materials with which it comes into contact. In cases where knowledge of the temporal and spatial changes in the runoff is important, the sampling program must be designed to provide that information.

Other problems are associated with methods that are used for sampling and for control checks on the quality of the resulting data. One of the most obvious and frequently encountered problems is contamination of the sample by the sampling equipment. This can be a particularly serious problem when trace elements are the object of investigation. Trace elements typically are present in very small concentrations, so any changes in concentration due to contamination or sorption on the sampling equipment or storage container can lead to large errors (Schock and Schock, 1982; Bricker-Good and Schroder, 1984; Benoit and others, 1997). Collection equipment or sample containers constructed of inappropriate materials or the improper cleaning of these items can lead to substantial contamination (Schroder and Bricker, 1985; Horowitz and others, 1994; Shelton, 1994). For example, Windom and others (1991) and Horowitz (1997) observed that some of the earlier sampling equipment and techniques commonly used by the U.S. Geological Survey (USGS) and other water-sampling agencies resulted in biased values for some trace metals (cadmium, Cd; copper, Cu; lead, Pb; zinc, Zn) in surface waters for data reported before 1990. Subsequent studies resulted in the implementation of ultra-clean sampling techniques and quality-assurance procedures for collecting trace-element samples. Often, contamination comes from unlikely sources. In the early days of the National Acid Deposition Assessment Program, rain samples were frequently contaminated with sulfate. This contamination was finally traced to the rubber seals that were used on the lids of the collecting buckets (Gordon and others, 1998). If improper techniques are used, each step in the sample collection, handling, and analysis process can contribute a substantial proportion of the trace element concentrations measured, even in a contaminated urban stream (Benoit and others, 1997).

Sampling techniques should distinguish between dissolved and particulate material. Dissolved species are generally more available to biota and to reaction with other components of the system than are particulates. When particulate matter occurs in large-size fractions, there is little problem in separating it from the solution. As the size of the particulate decreases and approaches colloidal size, separation becomes increasingly difficult. The standard practice is to define as dissolved the material that passes through a 0.45-micron membrane filter. This is strictly an operational definition, and many colloidal particulates will pass through such a filter (Kennedy and others, 1974; Horowitz, 1997). When these filtrates containing colloids are acidified for analysis, the colloids will dissolve and be analyzed with the dissolved fraction. Colloids frequently contain coprecipitated or sorbed metals that are released when the colloid is dissolved. Colloidal materials and dissolved species each exhibit different characteristics relative to bioavailability and toxicity, and metals associated with colloids are not easily available to the biota. Thus, misidentifying colloids as dissolved components could lead to exaggeration of the potential environmental effects of a discharge. Where the presence of colloidal materials is suspected, filtration through 0.1-micron or finer membrane filters, or high-speed centrifugation techniques for separation, may be required (Rostad and others, 1998). Pressure filtration, by using a peristaltic pump or an inert gas, is preferred to vacuum filtration, which may degas the sample, causing loss of volatiles, changes in pH, and possibly precipitation of solid phases such as calcite. Filtration also may be a source of contamination if the filters contain leachable materials (Jay, 1985).

Runoff from highways may infiltrate soils and eventually reach the water table. Special techniques are required for obtaining samples of soil water and ground water. Soil solutions are frequently collected by using tension lysimeters, but some potential problems may arise in using them (Severson and Grigal, 1976; Schimmack and others, 1984; Grossman and others, 1987). The porous section of the lysimeter (the frit) is made of material that may not be inert. If this is the case, reaction of the pore waters with the frit may contaminate the solution, or such reactions may change the pH of the solution causing precipitation and loss of the element of interest. The large surface area of the frit may lead to sorption of the element of interest. The vacuum imposed on the tension lysimeters may significantly disturb the gas balance of the sample and cause changes in the pH and other chemical parameters. Other methods for collecting soil water samples include zero-tension lysimeters and expression of soil waters from soil cores by squeezing or displacement techniques. Each method has its drawbacks and limitations, and careful consideration should be given to the information needed before choosing a sampling method. Ground-water sampling presents an additional set of problems. Wells are needed to obtain ground-water samples, and contamination may be caused by disturbance during the drilling, the introduction of drilling fluids, packing materials, or well casings (Koterba and others, 1995; Lapham and others, 1995; Lapham and others, 1996). These effects can be mitigated by using appropriate methods and materials in drilling and finishing the well and by properly flushing the well before sampling.

Often, ground waters and even some soil waters are in a reducing state. When waters of this type are encountered, care must be taken so that samples are not exposed to oxygen during collection. Exposure of the water sample to the atmosphere may cause significant changes in chemistry as a result of precipitation of oxidized phases or changes in speciation of aqueous species (Ivanhnenko and others, 1996). Should this occur, subsequent analysis of the water will not reflect the *in situ* chemistry. In summary, the sampling program must be designed to provide information that addresses the problem of concern, the sampling and collection equipment must not affect the chemistry of the medium being sampled, and the sampling techniques must preserve the *in situ* composition of the sample. Appropriate experimental controls and, in particular, quality assurance/quality control (QA/QC) procedures are required to ensure the quality and utility of the data collected (especially if the data are intended to be combined and (or) compared in a national database).

SAMPLE ANALYSIS

After a representative sample has been collected, it must be analyzed for the component of interest, and for all other components of the system that may affect the behavior of that component. Historically, many studies of water chemistry have been inadequate because samples were analyzed for only one or a few components of interest (Davis, 1988). The minimum set of data necessary for geochemical studies includes the major ions (sodium, Na^+; potassium, K^+; magnesium, Mg^{2+}; calcium, Ca^{2+}; sulfate, SO_4^2; nitrate, NO_3^- ; bicarbonate, HCO_3^-; chloride, Cl^-) temperature, conductivity, and pH (Mather, 1997). Although many major ions are often neglected in contaminant studies because of the small additional cost and because they are not regulated compounds (Davis, 1988), analysis of samples for the major ions is important because the composition of the major ions in solution will commonly control the partitioning of trace constituents between the dissolved and available solid phases (Appelo and Postma, 1993).

Specific conductance can be used as a gross measure of ionic strength and as a quality-control check on water-quality analysis (Rossum, 1949; Lind, 1970; Hem, 1982). The specific conductance and, therefore, ionic strength of highway stormwater runoff has been demonstrated to vary by several orders of magnitude within and between storm events (Church and others, 1996). Thus, specific conductance measurements in samples facilitate the analysis and interpretation of discrete and composite samples of highway and urban runoff, and a continuous record of measured specific conductance in stormwater flows will put sample analysis into a context with storm runoff processes. Concentrations of major ions and values of pH and specific conductance are required to calculate the ionic strength and other solution characteristics that influence the behavior of all of the dissolved constituents in the system. Concentrations of nutrients and sources of oxygen demand in highway and urban runoff can be substantial (Smith and Lord, 1990; Makepeace and others, 1995). Measurement of dissolved oxygen (DO), nutrients, and measures of oxygen demand are important to assess the geochemical status and potential effects of runoff. The analytical methods that are used must provide the precision and accuracy needed for interpretation and modeling of the species of interest in the system. In the last decade, rapid developments in analytical methods have decreased detection limits for many elements to unprecedented low levels (Horowitz, 1997). This has significantly increased the capability to model the behavior of trace constituents in environmental systems.

The objective of analysis is to represent, as closely as possible, the *in situ* chemical composition of the system of interest. Some parameters are quite sensitive to change if a sample is removed from the system. These parameters, including pH, redox potential, DO, specific conductance and, in some cases, alkalinity, are best measured in the field. For example, if carbon dioxide (CO_2) degasses from the sample after collection, the pH will increase. This, in turn will cause changes in the speciation of hydrogen ion (H^+) sensitive constituents. If the sample is close to calcite saturation, a change in pH may induce precipitation of that phase, which will cause concomitant changes in the calcium (Ca^{2+}), the alkalinity, the specific conductance, and the total dissolved inorganic carbon. The chemistry of a water sample can change from exposure to the atmosphere after collection and ingress of oxygen, which changes the redox potential and causes oxidation of species such as ferrous iron (Fe^{2+}), hydrogen sulfide (H_2S), and other reduced constituents. For example, the following reaction will take place in water samples containing ferrous iron (Fe^{2+}) and carbonate alkalinity when exposed to the atmosphere:

$$2Fe^{2+} + 4HCO_3^- + 1/2O_2 + 5H_2O$$

$$= 2Fe(OH)_3 + 4H_2CO_3 \qquad (57)$$

If the water initially contains 20 parts per million ferrous ion (20 ppm Fe^{2+}), equivalent to 0.36 millimoles per liter (0.36 mmol/L), virtually all of the Fe will be removed in the solid phase, twice that amount of bicarbonate (HCO_3^-), equal to 0.72 mmol/L will be removed, and carbonic acid will be produced, which will significantly change the chemistry of the sample (Appelo and Postma, 1993). Any trace metals in the sample will likely be scavenged from solution by the freshly precipitated ferric hydroxide.

It should be pointed out that measurements using electrochemical techniques, such as pH, ion-specific electrode determinations, or *Eh* should be done on separate aliquots of the sample, which are then discarded. These electrochemical techniques depend upon controlled leakage of electrolyte from the reference electrode to establish electrical continuity with the solution; thus, the sample aliquot will be enriched in the components of the reference electrolyte. As discussed above, *Eh* measurements using electrode techniques in natural systems are qualitative at best. Except under unusual conditions, they will not provide data that are thermodynamically meaningful, but might reflect the general redox state of the system relative to whether it is oxidizing or reducing (Bricker, 1982; Appelo and Postma, 1993; Stumm and Morgan, 1996).

The parameter pH is of major importance in the quantitative calculation of mineral stability and in other aspects of geochemical modeling. It is, therefore, important to have accurate pH data. With care, pH can be measured to within plus or minus 0.02 unit, the error margin associated with certified buffer solutions. Measurement of pH requires careful consideration of the nature of the sample. A number of problems may cause difficulty in accurately determining pH. If the sample is supersaturated with carbon dioxide (CO_2) relative to equilibrium with the atmosphere (commonly the case with stream, lake, soil, and ground waters), degassing is likely to occur after the sample is taken, especially if samples are collected with automatic samplers that require suction to withdraw the samples. This will cause pH to increase as carbon dioxide (CO_2) evolves. The pH will rise during measurement until equilibrium with atmospheric carbon dioxide (CO_2) is achieved, then stabilize at a value not representative of the *in situ* value. If the water is near saturation with calcium carbonate ($CaCO_3$) initially, precipitation may be induced, changing the calcium and inorganic carbon concentration of the sample (Suarez, 1987). Similar problems can arise if the water contains reduced species, such as ferrous iron. In this case, if the water is exposed to the atmosphere during measurement, the iron will oxidize, causing the pH to decrease. In addition to change in pH, the precipitated ferric hydroxide may scavenge trace metals and other constituents from the sample. Effects of this type can usually be avoided if the measurements are made *in situ* (directly in the water body of interest) or in a closed vessel with no air space.

Another common problem in measuring pH arises from the liquid junction between the reference electrode and the sample. Electrical continuity must be established between the electrode system and the sample. This is usually accomplished by the use of a fiber wick or a porous frit in the reference electrode, which allows the reference electrolyte to contact the solution being measured. A liquid junction potential will be established across the wick or frit, and the magnitude of the potential will vary with the composition of the solution being measured. In dilute waters, the liquid junction potential can lead to significant errors in pH measurement even though the electrodes respond correctly in buffer solutions. Techniques for calibration and use of pH electrodes in dilute waters are discussed by Neal and Thomas (1985), Davison (1987), and Busenberg and Plummer (1987).

The chemical analysis for most other constituents in water is usually done in the laboratory. Numerous analytical methods are available, and the method of choice depends on the constituent being analyzed, its range of concentration in the system, and whether the total concentration or concentration of each of the species of the constituent in the sample is desired. Currently, the most commonly used methods for cations are flame or flameless atomic adsorption spectrometry (AA), inductively coupled plasma atomic emission spectrometry (ICP–AES), and inductively coupled plasma mass spectrometry (ICP–MS). A comparison of detection limits for selected elements is shown in table 2. For anions, one of the most commonly used chemical analysis methods currently is ion chromatography. This method also has been used in the analysis of cations, but not as commonly as for anions. Detection limits for selected anionic species are shown in table 3. The number of techniques available for specialized analyses is too large to cover in detail. A few of the newer types of analytical capabilities that may be useful in characterizing the chemistry of specific materials in highway runoff include: (1) sedimentation, field flow fractionation-inductively coupled plasma mass spectrometry for the separation of submicrometer size particles and determination of their composition, including surface adsorbed trace elements (Taylor and Shiller, 1997); (2) static secondary ion mass spectrometry (SIMS) for the detection of sorbed contaminants on the surface of soil and sediment particles (Ingram and others, 1997); (3) hydride generation in combination with atomic fluorescence spectrometry for determination of a number of trace elements (for example, *As, Bi, Ge, Sb, Se, Te*) (Ping, Zhou and Guo, 1997); (4) scanning electron microscope with electron dispersive x-ray spectroscopy (Goldstein and others, 1992); (5) electron probe (Reed, 1996); and (6) x-ray fluorescence techniques (Glanzman and Closs, 1997). The analytical methods selected must be based on the questions to be answered and must provide data that have the necessary accuracy and precision to address those questions.

Table 2. Atomic spectroscopy detection limits for a representative series of elements in natural waters

[From Perkin Elmer Corporation, 1995. AA, atomic absorption; GFAA, graphite furnice atomic absorption; Hg, mercury; ICP, inductively coupled plasma; ICP-MS, inductively coupled plasma–mass spectrography. All values in microgram per liter; <, actual value is less than value shown]

Element	Flame AA	Hg/ Hydride	GFAA	ICP emission	ICP-MS	Element	Flame AA	Hg/ Hydride	GFAA	ICP emission	ICP-MS
Ag	1.5		0.02	0.9	0.003	Mo	45		0.08	3	0.003
Al	45		0.1	3	0.006	Na	0.3		0.0	3	0.003a
As	150	0.03	0.2	50	0.006	Nb	1,500			10	0.0009
Au	9		0.15	8	0.001	Nd	1,500			2	0.002
B	1,000		20	0.8	0.0	Ni	6		0.3	5	0.005
Ba	15		0.35	0.09	0.002	Os	120			6	
Be	1.5		0.008	0.08	0.01	P	75,000		130	30	0.3
Bi	30	0.03	0.25	30	0.0005	Pb	15		0.06	10	0.001
Br					0.2	Pd	30		0.8	3	0.003
C				75	150	Pr	7,500			2	<0.0005
Ca	1.5		0.01	0.02	0.05a	Pt	60		2.0	10	0.002
Cd	0.8		0.008	1	0.003	Rb	3		0.03	30	0.003
Ce				5	0.0004	Re	750			5	0.0006
Cl					10	Rh	6			5	0.0008
Co	9		0.15	1	0.0009	Ru	100		1.0	6	0.002
Cr	3		0.03	2	0.02	S				3	70
Cs	15				0.0005	Sb	45	0.15	0.15	10	0.001
Cu	1.5		0.1	0.4	0.003	Sc	30			0.2	0.02
Dy	50			2	0.001	Se	100	0.03	0.3	50	0.06
Er	60			1	0.0008	Si	90		1.0	3	0.7
Eu	30			0.2	0.0007	Sm	3,000			2	0.001
F					10,000	Sn	150		2.0	60	0.002
Fe	5		0.1	2	0.005a	Sr	3		0.025	0.03	0.0008
Ga	75			4	0.001	Ta	1,500			10	0.0006
Gd	1,800			0.9	0.002	Tb	900			2	<0.0005
Ge	300			20	0.003	Te	30	0.03	0.4	10	0.01
Hf	300			4	0.0006	Th					<0.0005
Hg	300	0.009	0.6	1	0.004	Ti	75		0.35	0.4	0.006
Ho	60			0.4	<0.0005	Tl	15		0.15	30	0.0005
I					0.008	Tm	15			0.6	<0.0005
In	30			9	<0.0005	U	15,000			15	<0.0005
Ir	900		3.0	5	0.0006	V	60		0.1	0.5	0.002
K	3		0.008	20	0.015a	W	1,500			8	0.001
La	3,000			1	0.0005	Y	75			0.3	0.0009
Li	0.8		0.06	0.3	0.0001a	Yb	8			0.3	0.001
Lu	1,000			0.2	<0.0005	Zn	1.5		0.1	1	0.003
Mg	0.15		0.004	0.07	0.007	Zr	450			0.7	0.004
Mn	1.5		0.035	0.04	0.002						

Table 3. Minimum detection limits for the determination of anions by ion chromatography—EPA Method 300.0

[From Pfaff et al, 1991. mg/L, milligram per liter]

Analyte	Minimum detection limit (mg/L)
Fluoride	0.01
Chloride	0.02
Nitrite–N	0.004
Nitrate–N	0.002
Bromide	0.01
Ortho-Phosphate–P	0.003
Sulfate	0.02
Chlorite	0.01
Chlorate	0.003
Bromate	0.02

GEOCHEMICAL MODELING

The major objective of investigating highway runoff is to determine the effects on the environment of materials that are contained in runoff waters that are derived from highway operations, local soils, and natural and anthropogenic inputs from local atmospheric deposition. Predictions of the effects of these runoff materials on surface and ground water and biota can be made when knowledge and understanding of how the system functions is more complete. Understanding system function and making quantitative statements about processes require the application of theoretical analysis and can effectively be done through the development of models. Geochemical models can be used to assess the bioavailability and mobility of contaminants in a particular geochemical environment by predicting the behavior of the contaminants based on the chemical and physical properties of local soils, sediments, and solutions (precipitation and surface and ground waters). This type of geochemical information also is critical for the evaluation of appropriate BMPs for a given site. For example, much of the work demonstrating the effectiveness of swales and infiltration structures to remove metals has been done in areas with soils containing high cation exchange capacities, but these same BMPs may contribute to the contamination of ground water in sand and gravel aquifers because of the lower capacity of these materials to retain the contaminants (Granato, 1996).

Depending on the system and the questions to be addressed, models can range from quite simple paper and pencil calculations to those requiring advanced computer capabilities. In most cases, highway runoff consists of relatively complex aqueous solutions and is most easily interpreted through the use of geochemical computer models. A number of these models have been developed for different applications, but they are all based on the processes outlined in the background section of this report. The quality and completeness of the water analyses that are used to develop the models are critical to the model output. If the analyses are inaccurate or incomplete, the model results have a high probability of being meaningless or misleading. Even with good quality analyses, the model results should not be accepted blindly but should be carefully examined to determine if they are consistent with what is known about the system being modeled and the assumptions inherent in the models. Following are examples of some of the better known and more widely used types of geochemical models.

Speciation Models

Speciation models are used to calculate the partitioning of an element among different aqueous species and complexes. They also calculate, to the extent of the thermodynamic information in the program, the saturation state of the solution with respect to solid phases and gases. The thermodynamic database must be internally consistent and must contain data for all of the species present in the system being modeled if reliable results are to be obtained. Because the thermodynamic databases as well as the aqueous species and mineral phases considered commonly differ among models, care must be exercised in choosing the model that best suits the system of interest. Most existing models will simulate solutions comparable to seawater (salinity of 35 parts per thousand) in ionic strength. For more concentrated waters, such as brines, other models must be used. Widely accepted ranges for the salinities of freshwater, brackish water, and brines are 0–1, 1–35, and greater than 35 parts per thousand, respectively (Bates and Jackson, 1987). Speciation models provide data that aid in the interpretation of the relative importance of aqueous complexes and the toxicity of contaminated waters. Current models provide good approximations for speciation of the major elements but are not as good for speciation of trace metals. Thermodynamic data for many trace metal species are not easily available and often are not of the same quality as data for major ion species. Nordstrom (1996) discusses trace metal speciation and compares computational versus analytical techniques for assessing trace metal speciation in natural waters. Examples of speciation models are WATEQF (Plummer and others, 1976) and WATEQ4F (Ball and Nordstrom, 1991).

Mass-Transfer Models

Mass-transfer models are used to simulate changes in solution chemistry caused by mass-transfer processes. They are useful in modeling the mixing of two waters, evaporation, boiling temperature and pressure changes, dissolution and precipitation, ion exchange and adsorption and, ingassing and outgassing processes, and are commonly used in reaction-path modeling. Such models can be used to predict the overall geochemical behavior of contaminants and whether reactions in a system will go to equilibrium. As in the speciation models, these models have routines for speciating aqueous solutions. Some drawbacks of these models are that they do not consider solid-solution mass transfer, and they are restricted in the area of mass transfer due to ion exchange and adsorption. The models EQ3/6 (Wolery, 1992a, 1992b) and the Geochemist's Workbench (Bethke, 1994, 1996) include routines for specifying rate laws and mass-transfer kinetics, and keep track of water mass. Other models, such as PHREEQE (Parkhurst and others, 1980), PHRQPITZ (Plummer and others, 1988), and MINTEQA2 (Allison and others, 1991), do not contain these options; however, they are extremely useful for many modeling applications. Other models of this type are SOLMNEQ.88 (Kharaka and others, 1988), MINEQL+ (Schecher and McAvoy, 1991), MINTEQ(4.00) (Eary and Jenne, 1992), and PHREEQC (Parkhurst, 1995).

Mass-Balance Models

Mass-balance models are used to simulate the net changes in the masses of reactants and products in waters along a flow path. Given the initial and final water compositions and the mineral phases present in the system, these models calculate how much of each phase must dissolve or precipitate to account for the observed difference in the water compositions. The models are independent of any assumptions about thermodynamic equilibrium or reaction kinetics and are based solely on mass-transfer considerations. Most of these models, such as NETPATH (Plummer and others, 1991, 1994) contain a routine that speciates the water and calculates saturation indices (SI) for each of the minerals in the data bank. It is incumbent upon the user to determine which of the phases that have SIs less than 0 are likely to dissolve and which that have SIs greater than 0 are likely to precipitate in the system. Usually, a number of plausible conceptual solutions are found for the system of interest, and the user must choose, based on his or her knowledge of the mineralogy, geochemistry, and hydrology, the conceptual solution that is most realistic. These types of models also can incorporate isotopic data for both the waters and minerals, if available, and the use of these data may help to eliminate unrealistic solutions. A major strength of these models is that they aid in identifying and quantifying the most important geochemical processes controlling the evolution of the chemistry of the waters.

Geochemical Mass-Transport Models

Geochemical mass-transport models can be used to simulate hydrodynamic advection and dispersion of dissolved species in porous media, as well as speciating the aqueous solution and determining geochemical mass transfer. Currently, a major drawback of the models is that they generally assume steady-state, one-dimensional flow fields in homogeneous media with simple boundary conditions. These constraints are seldom, if ever, found in real natural systems. Nevertheless, such models can be valuable in providing insights into the processes that are responsible for the chemical evolution of natural waters and for designing BMP's and strategies for cleanup of contaminated sites. Some examples of this type of model are CHMTRNS (Noorishad and others, 1987), PHREEQM-2d (Nienhuis and others, 1994) and PHREEQC (Parkhurst, 1995). For some examples of the application of geochemical transport models, see Appelo and Postma (1993, chap. 10).

The modeling field is developing rapidly, and geochemical models are becoming more powerful and realistic in terms of the detail with which they can simulate real systems. It must always be kept in mind, however, that these are models and are only as good as (1) their ability to represent real processes and (2) the accuracy and completeness of the data that are entered into them. Even the best models today are not reliable for predicting future changes. Their greatest value is in providing insights into the way systems function, identifying gaps in our knowledge of the systems of interest, and indicating the kinds of data that are needed to fill these gaps. Many of the latest versions of the USGS software and documentation for geochemical and hydrological models are posted on the Internet and can be downloaded at no charge (USGS, 1998). Additional information on the location of models can be obtained on the appropriate Agency homepages (for example, USGS, USEPA) and in Langmuir (1997).

DISCUSSION

This report is an attempt to provide a brief overview of the factors that must be considered in evaluating the geochemical effects of highway runoff on the environment. It should be apparent that focusing on a single component and examining total concentrations of that component will usually provide incomplete and potentially misleading information about its role in the system. Both the toxicity and the bioavailability of metals in waters depend on the aqueous speciation or complexation of the metals. For example, if an element such as aluminum is present as the trivalent aluminum (Al^{3+}) ion in water, its toxicity to fish will be much greater than if it is present as an organo-aluminum complex (Driscoll and others, 1984). Therefore, an analysis of the total aluminum concentration of the water may provide misleading information about the toxicity of the water. To obtain an accurate picture of the role of aluminum (Al) in the system, the complete chemistry of the waters, including all of the other components that might interact with Al, must be considered. This is true for the evaluation of any constituent of interest in the system (Davis, 1988). In general, the toxicities of metals such as cadmium (Cd^{2+}), copper (Cu^{2+}), mercury (Hg^{2+}), nickel (Ni^{2+}), lead (Pb^{2+}), zinc (Zn^{2+}), and others, are a function of the aqueous activities of the metal ions and their complexes and not of total metal concentrations (Makepeace and others, 1995; Morel and Hering, 1993; Manahan, 1994).

Failure to consider the effects of aqueous speciation on toxicity may result not only in incomplete understanding of the system but also in unnecessarily restrictive and expensive regulations for controlling metal discharges (Lee and Jones, 1990; Lee and Jones-Lee, 1996). For instance, until recently, the USEPA did not take into account the relation between metal speciation and toxicity in its water-quality assessments (Hall and Raider, 1993). Just as the speciation of metals affects their toxicity, it also affects their bioavailability. The ability of plants to use essential metals, for instance, is related to the speciation of the metals in solution (Morel and Hering, 1993). Another type of process, often referred to as speciation, is the partitioning of metals between the aqueous and solid phases. This partitioning is a result of sorption or ion exchange processes and plays a major role in determining the bioavailability of trace metals in the environment.

A number of investigations have addressed the partitioning of trace pollutants between the aqueous and solid phase. Gjessing and others (1984) found that significant amounts of the toxic inorganic and organic pollutants in highway runoff in Norway are strongly adsorbed to the particulate matter. Harrison and Wilson (1985a, b) investigated metal concentrations in runoff from a highway in England and found that the metals were strongly associated with the particulate matter. They observed that metal concentrations on particulates increased with decreasing particle size (increasing surface area), and that the suspended particulates in highway runoff contained higher overall metal concentrations than road surface dusts. This was attributed to the preferential mobilization and transport of the finer particulates from the road surface during storm washoff. The strong association of metals with particulate street dust also was observed by Gibson and Farmer (1984) in urban Glasgow and by Hamilton and others (1987) in a suburb of London. The metals are adsorbed on both inorganic and organic particulate matter and may be released to aqueous solution if they encounter different chemical conditions in the receiving waters or soils or if the organic matter is decomposed. Morrison and others (1984) investigated the physicochemical speciation of zinc, lead, cadmium, and copper in stormwater from urban catchments in England and Sweden and found that zinc and cadmium preferentially partition into the aqueous phase, lead onto the particulate phase, and copper is about equally divided between the aqueous and particulate phases. They also observed that the high metal concentration associated with the particulate phase may be easily released on contact with receiving waters and is a major source of bioavailable metals.

Another source of trace constituents to the environment is the application of deicing salts to highways (Granato, 1996). Although deicing salts are relatively pure, because of the large amounts applied to roads, the small amounts of impurities translate into significant amounts of trace constituents being introduced into a watershed. The major constituents of deicing chemicals, in addition to adversely affecting water quality by increasing total dissolved solids, play a role in the mobilization of metals by promoting processes such as ion exchange, desorption, complexing, acidification and mineral dissolution (Amrhein and Strong, 1990; Shanley, 1994; Granato and others, 1995). These investigations, including those by Davis and others (1993), which addresses geochemical and hydrologic parameters affecting metal transport in ground water systems, and by Breault and others (1996), which examines the speciation and binding of copper by organic matter in contaminated streamwater, all point to the necessity of considering all of the components in a system in order to understand the behavior of any individual component.

Recently, the use of catalytic converters for vehicle emission control has introduced platinum, palladium, and osmium into the environment. Concentrations of these metals in road dusts along highways have increased concern relative to their environmental and human health implications (Farago and others, 1997; Pearce and others, 1997; Schaefer and Puchelt, 1997). The road dusts are transported by storm runoff and winds to adjacent soils and surface waters, where they may become solubilized and enter the food chain. Platinum is a good example of the importance of speciation to toxicity; although platinum in metallic form is inert, some platinum compounds are known to be cyclotoxic and have mutigenic and carcinogenic effects. They also affect micro-organisms at very low concentrations. Charged platinum complexes that contain reactive ligand groups, particularly chloride, appear to be the most toxic (Farago and others, 1997).

One of the most productive approaches to examining the effects of contaminants on the environment is through the study of small watershed systems (Bricker and Kennedy, 1997; Peters and others, 1997). This approach was extensively used in the National Acid Precipitation Assessment Program (NAPAP) to investigate and document the effects of acid deposition on the environment and was used recently to examine the transport and fate of atmospherically deposited trace elements in a forested watershed in central Maryland (Church and others, 1997). In the NAPAP program, small watersheds in settings with minimal influences from human activities, except those from atmospheric deposition, were chosen for long-term monitoring and research (Bricker and others, 1983; Bricker, 1986). The watershed approach addresses the entire watershed system and allows evaluation of the relative importance of the inputs of constituents, both natural and anthropogenic, on system function (Velbel, 1985; Swank and Waide, 1988; Bricker and Rice, 1989; Moldan and Cerny, 1994). Also, watershed-level studies are key to support watershed-based environmental management, which has potential benefits within national surface transportation planning policies and procedures (Bank, 1996).

The effects of road salt on the chemistry of some small watersheds in central Maryland (Katz and others, 1985) and in Vermont (Shanley, 1994) have been discussed in the context of watershed systems. A synopsis of recent developments in solute modeling in watershed systems is provided by Trudgill (1995).

The watershed approach would potentially have direct application to the investigation of the environmental effects of highway runoff. In the ideal situation, where a road traverses across a watershed, investigation of the upstream and downstream portions of the system would permit evaluation of the effects of the road. Alternatively, the use of paired watersheds, one containing a road and a hydrological similar, but roadless watershed, would provide valuable information on the effects of highways. In a region where a new highway is planned, study of the watershed prior to, during, and after road construction would provide invaluable information on the effects of the construction process and the subsequent use of the highway. For example, the use of upstream and downstream water-quality monitoring around several streams and ponds, as well as monitoring in an unimpacted subwatershed during a watershed study before, during, and after highway construction along I-84 in Danbury, Conn., showed that protective highway-construction BMPs were successful and the main sources of contaminants were from other construction activities in the watershed (Maguire, 1985). Investigations at the watershed level give an integrated picture of system behavior that cannot be obtained from fragmented studies of specific parts of the system.

CONCLUSION

The first step in assessing the impact of highway runoff on the environment is the collection of representative samples. If the samples do not accurately represent the chemical compositions of the system at the time of study, or are compromised by improper sampling techniques, subsequent chemical analyses will provide data that are misleading or worthless. The second step is the chemical analyses of the samples using methods that have the appropriate sensitivity and detection limits for each component of the sample. The analyses should provide as complete a chemical characterization of the sample as possible, including all of the major constituents as well as the specific contaminant species of interest. This is essential to provide the information necessary to calculate the ionic strength of the water and the activities and speciation of the dissolved constituents, both major and minor. If the analyses are incomplete for the major dissolved constituents (even though these may not be of interest from the toxics standpoint), it will not be possible to evaluate the behavior of the contaminant species in terms of solubilities, speciation, complexing, sorption, ion exchange, ion pairing, mobilization, and transport- all of the processes that determine toxicity and bioavailability. Analyses of samples only for the total concentrations of selected elements of interest provide, at best, limited information and almost certainly will give a misleading picture about the effects of those elements on the ecosystem. Geochemical modeling, whether it is a simple pencil and paper effort or a sophisticated and complex computer project, requires chemical analyses as complete as possible, beginning with the data on major dissolved constituents that determine the electrolyte characteristics of the water.

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Chapter 5. A Synopsis of Technical Issues for Monitoring Sediment in Highway and Urban Runoff

By GARDNER C. BENT, JOHN R. GRAY, KIRK P. SMITH, and
G. DOUGLAS GLYSSON

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A Synopsis of Technical Issues for Monitoring Sediment in Highway and Urban Runoff

By Gardner C. Bent, John R. Gray, Kirk P. Smith, *and* G. Douglas Glysson

Abstract

Accurate and representative sediment data are critical for assessing the potential effects of highway and urban runoff on receiving waters. The U.S. Environmental Protection Agency identified sediment as the most widespread pollutant in the Nation's rivers and streams, affecting aquatic habitat, drinking water treatment processes, and recreational uses of rivers, lakes, and estuaries. Representative sediment data are also necessary for quantifying and interpreting concentrations, loads, and effects of trace elements and organic constituents associated with highway and urban runoff. Many technical issues associated with the collecting, processing, and analyzing of samples must be addressed to produce valid (useful for intended purposes), current, complete, and technically defensible data for local, regional, and national information needs. All aspects of sediment data-collection programs need to be evaluated, and adequate quality-control data must be collected and documented so that the comparability and representativeness of data obtained for highway- and urban-runoff studies may be assessed.

Collection of representative samples for the measurement of sediment in highway and urban runoff involves a number of interrelated issues. Temporal and spatial variability in runoff result from a combination of factors, including volume and intensity of precipitation, rate of snowmelt, and features of the drainage basin such as area, slope, infiltration capacity, channel roughness, and storage characteristics. In small drainage basins such as those found in many highway and urban settings, automatic samplers are often the most suitable method for collecting samples of runoff for a variety of reasons. Indirect sediment-measurement methods are also useful as supplementary and (or) surrogate means for monitoring sediment in runoff. All of these methods have limitations in addition to benefits, which must be identified and quantified to produce representative data. Methods for processing raw sediment samples (including homogenization and subsampling) for subsequent analysis for total suspended solids or suspended-sediment concentration often increase variance and may introduce bias. Processing artifacts can be substantial if the methods used are not appropriate for the concentrations and particle-size distributions present in the samples collected.

Analytical methods for determining sediment concentrations include the suspended-sediment concentration and the total suspended solids methods. Although the terms suspended-sediment concentration and total suspended solids are often used interchangeably to describe the total concentration of suspended solid-phase material, the analytical methods differ and can produce substantially different results. The total suspended solids method, which commonly is used to produce highway- and urban-runoff sediment data, may not be valid for studies of runoff water quality. Studies of fluvial and highway-runoff sediment data indicate that analyses of samples by the total suspended solids method tends to underrepresent the true sediment concentration, and that relations between total suspended solids and suspended-sediment concentration are not transferable from

site to site even when grain-size distribution information is available. Total suspended solids data used to calculate suspended-sediment loads in highways and urban runoff may be fundamentally unreliable. Consequently, use of total suspended solids data may have adverse consequences for the assessment, design, and maintenance of sediment-removal best management practices. Therefore, it may be necessary to analyze water samples using the suspended-sediment concentration method.

Data quality, comparability, and utility are important considerations in collection, processing, and analysis of sediment samples and interpretation of sediment data for highway- and urban-runoff studies. Results from sediment studies must be comparable and readily transferable to be useful to resource managers and regulators. To meet these objectives, supporting ancillary information must be available to document the methods and procedures that are used and to describe quality-assurance and quality-control procedures that are used in the studies. Valid, current, and technically defensible protocols for collecting, processing, and analyzing sediment data for the determination of water quality in highway and urban runoff therefore need to be documented with study results.

INTRODUCTION

Recognition of the importance of sediment as a water-quality constituent has increased dramatically in recent years. The U.S. Environmental Protection Agency (USEPA) (2000) identified sediment as the most widespread pollutant in the Nation's rivers and streams, in that sediment affects aquatic habitat, drinking-water treatment processes, and recreational uses of rivers, lakes, and estuaries. To address the combined, cumulative impacts of both point and nonpoint sources of sediment, the USEPA has adopted a watershed approach, of which total maximum daily loads (TMDLs) are a part (USEPA, 1998 and 1999).

In addition to sediment itself being a major pollutant, many trace elements, such as copper, zinc, cadmium, chromium, lead, and nickel—constituents often detected in highway runoff—are associated with sediments (Gupta and others, 1981; Horowitz, 1995). Some organic constituents associated with highway runoff are also associated with sediments (Lopes and Dionne, 1998). Sediment in highway runoff is a potential problem as a physical contaminant and as a source of potentially toxic substances to the local ecosystem (Schueler, 1997; Buckler and Granato, 1999). Hence, sediment in highway runoff can be a dominant factor in water quality, particularly when selected trace elements or organic constituents are associated with the sediment.

Highways affect sediment transport in runoff through several processes. Reduced infiltration from impervious surfaces, rapid concentration of flow with minimal flow resistance, and relatively high slopes of roadside drainage structures combine to increase velocities, volumes, and peaks of storm runoff, thus increasing the potential for erosion and increased entrainment of sediment. Materials entrained in highway runoff from road-surface and vehicle degradation can be discharged to receiving streams, as can materials such as sand or cinders that may be applied for traction on snow or ice. Particles from atmospheric deposition that include combustion and other by-products from vehicles also can be entrained in highway runoff.

This report addresses technical issues pertinent to the methods for the collection, processing, and analysis of sediment samples to determine the concentration and physical characteristics of sediment in highway and urban runoff, best management practice (BMP) structures, and receiving waters. Data-quality issues and appropriate quality-assurance techniques for sediment data collection and laboratory-analysis methods are also discussed. Although this report focuses on sediment-transport issues related to highway use, information presented in this report also is applicable to many issues related to sediment in urban runoff. Sediment-transport issues related to highway construction are presented within the Nonpoint Pollution Discharge Elimination System (NPDES) (USEPA, 1992; 1995) and are not included herein. Many of the techniques discussed herein may be used to monitor receiving waters, although those discussed by Edwards and Glysson (1999) may be more appropriate in fluvial systems. Hence, this paper focuses on valid, current, and technically defensible protocols for collecting, processing, and analyzing sediment data for the determination of water quality in highway and urban runoff.

SEDIMENT CONCEPTS RELATED TO HIGHWAY RUNOFF

Sediment comprises particles derived from rocks, biological materials, or chemical precipitates that are transported by, suspended in, or deposited in flowing water (ASTM, 1997b). Highway sediments can be a mix of materials including pavement dust and particles; atmospheric dust, natural soils, traction sand and cinders; vehicle rust particles; tire dust and particles; trash; and plant and leaf material. The mode of transport can be described by the origin of the material as bed-material load and wash load; or operationally (as measured by sediment samplers) as suspended load and bedload (International Standards Organization, written commun., 2000). Wash load is material atypical of the bottom-material size distribution that tends to flow through a reach without significant interaction with the bed. Suspended-sediment load is material carried in suspension by turbulence. Suspended particles less than about 0.04 mm are typically well mixed within the water column profile (Butler and others, 1996a). As particle-size distribution (PSD) increases to include sand-size material (larger than 0.062 mm median diameter), a vertical gradient may form, with largest particles concentrating near the bed. For example, the theoretical vertical distribution of sediments in the water column calculated using the Rouse equation (Graf, 1996) for highway sediments of different grain sizes are presented in figure 1. The concentration distribution (relative to a normalized sampling point that is at 0.1 of the water level above the bed) is uniform for finer particles (diameters less than 0.062 mm). As grain size increases from very fine sand to coarse sand (0.062 to 1.0 mm), however, the relative concentration increases with depth as a function of increasing grain size under standard conditions (fig. 1). These theoretical concentration distributions compare favorably with patterns in data that have been collected in fluvial systems (Guy, 1970) and in the results of an experiment designed to assess the vertical distribution of sediments in a small highway drainage pipe (Smith, 2000).

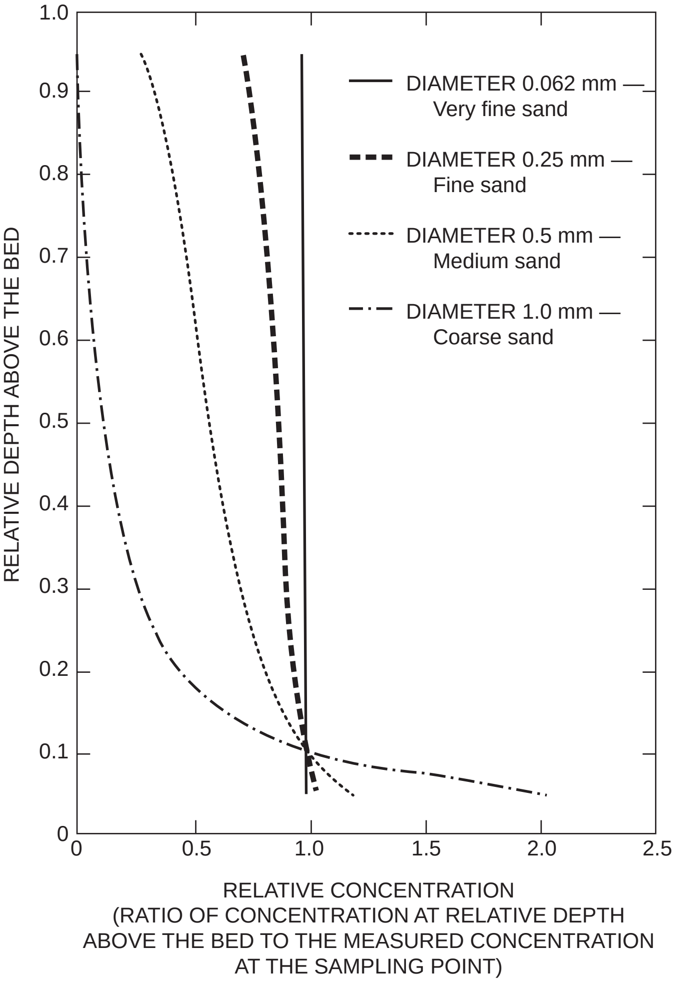


Figure 1. Theoretical vertical distribution of sediments (specific gravity 2.65) in a runoff drainage pipe with a 5-percent slope in open channel flow under standard conditions based on the Rouse equation (Graf, 1996).

Bedload is material that moves by rolling, sliding, or saltating along the channel bottom. Butler and others (1996a) indicate that bedload particle sizes are typically larger than about 0.3 mm in storm sewers. This distinction, however, is not quantitative because it depends on several hydraulic variables including channel slope, specific gravity of solids, particle shape, and flow energy. Material composing the bed at a low flow may move as bedload at a higher flow, and as suspended load at still higher flows. In comparison, bedload in fluvial systems rarely includes sediment that is finer than 0.1–0.2 mm in diameter, because once disturbed, the finer particle sizes go directly into suspension (Gomez and others, 1991). Because storm flows can vary from zero to peak flow in minutes, the dominant phase of transport can change rapidly. For example, 0.25 mm material might be transported predominately as bedload at flows of 1 ft^3/s, but at flows of 10 ft^3/s the dominant phase of transport might be suspended sediment.

Sediment transport in highway and urban runoff is controlled by precipitation runoff and the availability of erodible and (or) transportable sediments. The amount and timing of runoff is largely dependent on rainfall intensity and depth. Rainfall intensity has a two-fold effect on entrainment and transport of sediment through (1) raindrop splash erosion and (2) through sheet flow. The kinetic energy imparted by rain, which causes splash erosion when incident on sediment, increases exponentially with rainfall intensity (Hudson, 1981). The volume and velocity of sheet flow tends to increase with rainfall volume and intensity, entraining sediment from paved surfaces. Large flows resulting from high-intensity rains can lead to suspension and transport of sediment on paved areas and in drainage structures. Therefore, a lone sample collected during the first 30 minutes of the runoff period, such as is required by the USEPA (Bailey, 1993; Stillwell and Bailey, 1993), is a somewhat arbitrary requirement and may not adequately describe sediment concentrations associated with the "first flush" of runoff sediment. Also, because of the effects of varying rainfall intensities on the timing and the magnitude of runoff, a maximum sampling duration of 3 hours, as recommended by the USEPA (Bailey, 1993; Stillwell and Bailey, 1993), may result in substantial underestimation of sediment discharges for extended runoff periods.

The erosive capacity of runoff from highways and urban areas can be substantial because runoff from paved areas, ditches, and storm drains can be hydraulically supercritical and turbulent. The area contributing to surface runoff is usually small, water-surface slope is commonly relatively steep, and surface roughness is usually low. Under these conditions, runoff quickly becomes concentrated. Although some coarser sediment can move as bedload, most highway drainage systems are designed to maintain sediments suspended in runoff so that the volumetric capacities of the highway conveyance structures are not diminished (Butler and others, 1996a).

Most highway runoff sediment-monitoring programs are implemented in areas ranging from a fraction of an acre to several square miles. These are small areas compared to the median drainage area of 296 mi^2 for the 1,593 U.S. Geological Survey (USGS) gaging stations listed in the USGS historical daily-value suspended-sediment and ancillary data base (USGS, 1999b). Monitoring sediment and flow in small drainage systems in which runoff responds rapidly to rainfall usually requires a combination of manual and automatic methods for data collection (Robertson and Roerish, 1999). Water-discharge and sediment-concentration data are required to calculate suspended-sediment transport (Porterfield, 1972; Koltun and others, 1994). Samples for sediment-concentration analyses should be collected during the rising limb, peak, and falling limb of the runoff hydrograph to describe adequately variations in sediment concentrations for the runoff period. This data-collection scheme is important because the relation between the concentration of suspended material and runoff is generally not the same on the rising limb of the hydrograph as the falling limb of the hydrograph (fig. 2) (Porterfield, 1972; Mustard and others, 1987). In the case of highway runoff, consecutive samples may need to be collected only minutes apart, particularly on the rising limb of the hydrograph, due to large temporal variations in sediment concentrations, and a “first-flush” effect that may occur at highway and urban monitoring sites where sediments have accumulated between runoff periods. The “first-flush” effect with sediment in highway runoff results when a period of the rising limb of the runoff hydrograph is disproportionally enriched in sediment compared to the remaining period of the hydrograph (fig. 2), and has been quantified in highway-runoff studies by Patrick (1975), Ellis (1976), Ellis and others (1981), and Mustard and others (1987). The “first-flush” effect is likely due to an accumulation of fine sediments that are entrained in the initial runoff. These finer sediments available for transport could have been previously deposited in the drainage conveyance structures or could have accumulated on the road surface, usually near the curb or road edge, which is generally the flow path of runoff going to the

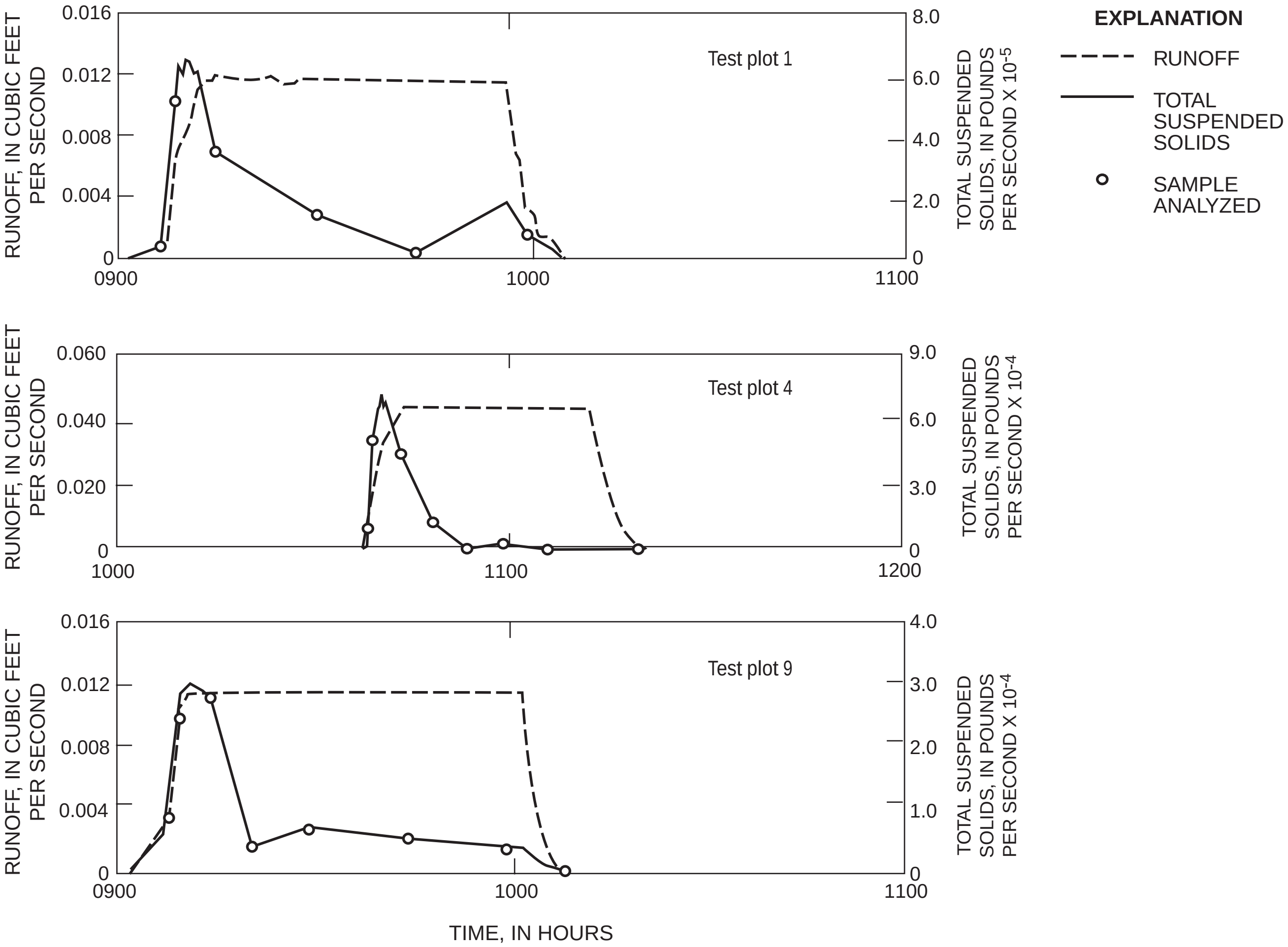


Figure 2. Runoff and washoff load of total suspended solids from test plots in Lakewood, Colorado, June 3, 1980. (Modified from Mustard and others, 1987.)

drainage conveyance structures from, or since, the last runoff period. For example, Gupta and others (1981) reported that 85 to 90 percent of street debris (solids) was within 12 in. of the curb. However, sediment transport at many highway and urban sites may vary with precipitation intensity and therefore the “first flush” may not represent the maximum sediment concentration or load that occurs during a runoff period.

Characteristics important to the monitoring, analysis, interpretation, and ultimately the treatment of water quality in highway and urban runoff include sediment concentrations and PSDs. Review of studies from the United States, Australia, Canada, France, Sweden, and the United Kingdom related to sediment runoff from highways, streets, and urban areas over the last 25 years (table 1) have shown concentrations of total suspended solids (TSS) ranging from 4 to 129,000 mg/L (table 2). In comparison, mean TSS concentrations in table 2 range from 29 to about 18,000 mg/L. The median particle size (d_{50}) of sediments collected in these studies range from 0.013 to 1.00 mm (table 3). These particle sizes range from about medium silt to very coarse sand (Guy, 1969; Folk, 1980), with sand-size particles being those larger than 0.062 mm (table 4).

Table 1. List of selected studies of sediment in highway and urban runoff

[**Report type:** D/I, data and interpretation; S, summary. **Location:** I, Interstate; SR, State Route. >, greater than; %, percent]

Reference	Report type	Location	Site type	Study year
United States				
Asplund and others, 1982	D/I	Seattle, Wash. (I-5)	urban highway	1979–80
	D/I	Seattle, Wash. (I-5 with grit)	urban highway	1979–80
	D/I	Montlake, Wash. (SR-520)	suburban highway	1979–80
	D/I	Vancouver, Wash.	highway	1979–80
	D/I	Snoqualmie Pass, Wash.	agricultural highway	1979–80
	D/I	Montesano, Wash.	agricultural highway	1979–80
	D/I	Pasco, Wash.	urban highway	1979–80
	D/I	Spokane, Wash.	agricultural highway	1979–80
	D/I	Pullman, Wash. (site 9)	agricultural highway	1979–80
Mustard and others, 1987	D/I	Lakewood, Colo. (4-lane street)	city street	1980
Smith and Lord, 1990	S	Selected Highways	highway	1976–77
Driscoll and others, 1991	S	Selected Urban Highways	urban highway	1980–90
	S	Selected Rural Highways	rural highway	1980–90
	S	Selected Urban Highways	urban highway	1980–90
	S	Selected Rural Highways	rural highway	1980–90
Moser, 1996	D/I	Silverthorne, Colo. (I-70)	highway	1994
	D/I	Silverthorne, Colo. (I-70)	highway	1994
	D/I	Silverthorne, Colo. (I-70)	highway	1994
Sansalone and Buchberger, 1996	D/I	Cincinnati, Ohio (I-75)	urban highway	1995
Sansalone and others, 1996	D/I	Cincinnati, Ohio (I-75)	urban highway	1995
Corsi and others, 1997	D/I	Southeastern Wisconsin	>90% urban land use	1975–96
Dudley and others, 1997	D/I	New Sharon, Maine (SR-2)	rural highway	1992–93
	D/I	New Sharon, Maine (SR-27)	rural highway	1992–93
Sansalone and others, 1998	D/I	Cincinnati, Ohio (I-75)	urban highway	1995–97
Waschbusch and others, 1999	D/I	Madison, Wisc.	residential streets	1994–95
Austrialia				
Ball and Abustan, 1995	D/I	Sydney	residential area	1994
Canada				
Vermette and others, 1987	D/I	Hamilton, Ontario	street	Not Reported
France				
Roger and others, 1998	D/I	Herault Region	highway	1993–94
Andral and others, 1999	D/I	France	highway	1993–94
Legret and Pagotto, 1999	D/I	Loire-Atlantique	rural highway	1995–96
Sweden				
Viklander, 1998	D/I	Lulea	street	1996
United Kingdom				
Ellis and others, 1981	D/I	London, England	residential and others	Not Reported
Pratt and Adams, 1981	D/I	Nottingham, England	residential streets	1979–80
Ellis and Harrop, 1984	D/I	London, England	highway	Not Reported
Ellis and others, 1987	D/I	London, England	highway	Not Reported
Butler and others, 1992	D/I	Lambeth, London, England	urban highway	Not Reported
Boxall and Maltby, 1995	D/I	United Kingdom	urban highway	Not Reported

Table 1. List of selected studies of sediment in highway and urban runoff—*Continued*

Reference	Report type	Location	Site type	Study year
United Kingdom—*Continued*				
Butler and others, 1996a	S	United Kingdom	Not Reported	Not Reported
	S	United Kingdom	Not Reported	Not Reported
No Specified Location				
Bertrand-Krajewski and others, 1993	S	Not Reported	Not Reported	Not Reported

Table 2. Sediment concentrations measured in highway and urban runoff

[**n:** number of sediment concentration analyses (data points); g/m^3, grams per cubic meter; mg/L, milligrams per liter; --, no data]

Reference	Sediment concentrations reported (mg/L)			Comments
	n	Range	Mean	
Asplund and others, 1982	54	32–848	--	Urban highway
	9	50–1,370	--	Urban highway
	43	76–894	--	Suburban highway
	61	13–168	--	Highway
	12	23–586	--	Agricultural highway
	27	51–1,260	--	Agricultural highway
	17	19–587	--	Urban highway
	6	67–2,490	--	Agricultural highway
	6	14–522	--	Agricultural highway
Mustard and others, 1987	9	27–150	83	City street
Smith and Lord, 1990	159	4–1,156	261	Highway
Driscoll and others, 1991	16	51–406	--	Rainfall, urban highway
	8	9–126	--	Rainfall, rural highway
	9	61–752	--	Snowmelt, urban highway
	6	11–465	--	Snowmelt, rural highway
Moser, 1996	30	12–854	213	Rainfall, highway
	9	1,948–69,141	18,036	Snowmelt, highway
Sansalone and Buchberger, 1996	2	84–127	--	Rainfall, urban highway
Sansalone and others, 1996	8	510–3,200	1,419	Snowmelt, urban highway
Corsi and others, 1997	--	17–297	139	>90% urban land use
Dudley and others, 1997	35	18–129,000	--	Rural highway
	27	92–114,000	--	Rural highway
Sansalone and others, 1998	13	29–259	131	Rainfall, urban highway
Waschbusch and others, 1999	--	--	67–99	Residential streets
Andral and others, 1999	8	15–58	29	Highway
Legret and Pagotto, 1999	49	16–267	71	Rural highway
Ellis and others, 1987	34	--	156 g/m^3 and 194 g/m^3	Highway
Butler and others, 1996a	--	50–1,000	--	Stormwater solids
		10–200	--	Grit
Bertrand-Krajewski and others, 1993	--	21–2,582	--	Roads, curbs, runoff, and sewers

Table 3. Particle-size distribution measured in highway and urban runoff

[**n:** number of particle-size analyses (data points). **Median (d_{50}):** d_{50} median diameter of particles. **Comments:** Modal is the value of the most commonly occurring particle size. phi, log2 of the particle diameter; µm, micrometers; %, percent; >, actual value is greater than value shown; <, actual value is less than value shown; --, no data]

Reference	Particle-size distribution				Comments
	n	Median (d_{50})	Mean	Range	
Sansalone and others, 1998	13	555 µm	570 µm	370–875 µm	d_{50}
	13	--	--	1–10%	>62 µm
Waschbusch and others, 1999	--	--	--	75%	>250 µm
		--	--	85%	>62 µm
		--	--	5%	<63 µm
Ball and Abustan, 1995	--	40-60 µm	--	--	--
Vermette and others, 1987	8	--	--	354–707 µm	modal size class
	8	--	2.1 phi	1.7–2.9 phi	--
Roger and others, 1998	--	--	--	86%	<50 µm
		--	--	53%	500–1,000 µm
Andral and others, 1999	8	86%	86%	82–91%	<50 µm
	8	13 µm	--	10–16 µm	d_{50}
Viklander, 1998	--	--	--	1,000–3,000 µm	d_{50}
Ellis and others, 1981	--	--	--	2 and 20 µm	bimodal
Pratt and Adams, 1981	1	500 µm	--	--	--
Ellis and Harrop, 1984	2	--	--	650–1,400 µm	--
Butler and others, 1996a	--	60 µm	--	20–100 µm	d_{50}
		750 µm	--	300–1,000 µm	d_{50}
Bertrand-Krajewski and others, 1993	--	30–1,000 µm	--	--	--

Table 4. Recommended particle-size classes for sediment analysis

[Modified from Guy, 1969. **Phi value:** Maximum size of the given class. --, not expressed in terms of micrometers; NA, not applicable]

Class name	Metric units		Phi value
	Millimeters	Micrometers	
Boulders	>256	--	NA
Large cobbles	256–128	--	-8
Small cobbles	128–64	--	-7
Very coarse gravel	64–32	--	-6
Coarse gravel	32–16	--	-5
Medium gravel	16–8.0	--	-4
Fine gravel	8.0–4.0	--	-3
Very fine gravel	4.0–2.0	--	-2
Very coarse sand	2.0–1.0	2,000–1,000	-1
Coarse sand	1.0–0.50	1,000–500	0
Medium sand	0.50–0.25	500–250	+1
Fine sand	0.25–0.125	250–125	+2
Very fine sand	0.125–0.062	125–62	+3
Coarse silt	0.062–0.031	62–31	+4
Medium silt	0.031–0.016	31–16	+5
Fine silt	0.016–0.008	16–8	+6
Very fine silt	0.008–0.004	8–4	+7
Coarse clay	0.004–0.0020	4–2	+8
Medium clay	0.0020–0.0010	2–1	+9
Fine clay	0.0010–0.0005	1–0.5	+10
Very fine clay	0.0005–0.00024	0.5–0.24	+11

SAMPLE-COLLECTION METHODS

The collection of representative samples for measurement of sediment in highway and urban runoff involves a number of interrelated issues. The temporal and spatial variability in runoff can be large because of a combination of factors including volume and intensity of precipitation, rate of snowmelt, and features of the drainage basin such as drainage area, slope, infiltration capacity, channel roughness, and storage characteristics. As the runoff rate increases, the stage (water level) and (or) mean velocity increases also. Rapid changes in flow may be associated with rapid changes in the sediment concentration, PSD, and density distribution. For example, Butler and others (1996a, 1996b) indicate that sediments accumulated in pipes may be mobilized (as bedload or suspended load) or remain immobile depending on concentration and size distribution of the sediment, and the energy of flow. Therefore, measurement of precipitation and flow are necessary for measurement and interpretation of sediment transport in highway and urban runoff systems (Church and others, 1999). Information necessary for measurement and interpretation of precipitation and runoff flows in highway and urban systems is discussed by Church and others (1999) and so is not included herein. The complexity of the precipitation-runoff-transport process necessitates sampling plans and methods that characterize the temporal and spatial variability in sediment transport in these systems.

Sampling plans for the study of nonpoint-source contamination may include discrete and (or) composite sampling by manual and (or) automatic sampling methods (USEPA, 1992). Discrete samples (also referred to as grab or dip samples) may represent sediment concentrations for only a short period of time. Composite samples are mixed or combined samples that should be flow-weighted to represent concentrations and loads during the monitoring period (USEPA, 1992; Gray and Fisk, 1992). Discrete samples collected during a runoff period may be physically composited and analyzed as one sample or mathematically composited from an analysis of multiple discrete samples (Driscoll and others, 1991). Discrete and (or) composite samples may be spatially representative—such as those collected by the Equal Discharge Increment (EDI) or Equal Width Increment (EWI) methods (Edwards and Glysson, 1999)—or may be representative of only the point in the stream from which the sample was collected. Automatic sampling methods include pumping samplers as well as passive devices that are designed to collect a discrete sample. The USEPA (1992) describes some of the relative advantages and disadvantages of manual and automatic sampling techniques (table 5). The remoteness or inaccessibility of some study sites makes it difficult to monitor runoff periods manually, and it can be difficult to get personnel to the sites before the onset of runoff. Costs associated with deployment of trained and properly equipped personnel, in addition to uncertainties related to the location and timing of runoff, can be prohibitive for manual sampling of storm-runoff periods. For example, Thiem and others (1998) employed a meteorologist to predict storm events and still had difficulty in implementing manual sampling efforts because storm runoff was predicted with an accuracy of about 50 percent. The difficulty in collecting a relatively large number of samples during storm runoff and the dangers to field personnel operating in adverse conditions (including traffic, weather, reduced visibility, and rapid changes in discharge) reduces the practicality of manual sampling efforts. In contrast, automatic samplers can be deployed before, and samples can be retrieved after cessation of storm runoff, thereby reducing logistics and increasing the safety for field personnel (Federal Interagency Sedimentation Project, 1981; USEPA, 1992). Also, the large temporal and spatial uncertainty in precipitation and runoff, and the coordination possible between automatic precipitation, flow, and water-quality-measurement instruments and automatic samplers (Church and others, 1996) favor the use of these devices in the monitoring of runoff quality in highway and urban systems. For example, Lewis (1996) describes a means for activating an automatic sediment sampler based on real-time turbidity measurements. Edwards and Glysson (1999) describe manual methods for sediment sample collection, which are typically more suitable for monitoring receiving waters than highway- and urban-drainage systems. The automatic samplers commonly used to sample highway- and urban-drainage systems are discussed as follows.

Table 5. Comparison of manual and automatic sampling techniques

[Modified from USEPA, 1992.]

Sample method	Advantages	Disadvantages
Manual grabs	Appropriate for all pollutants Minimum equipment required	Labor-intensive Environment possibly dangerous to field personnel May be difficult to get personnel and equipment to the storm water outfall within the 30-minute requirement Possible human error
Manual flow-weighted composites (multiple grabs)	Appropriate for all pollutants Minimum equipment required	Labor-intensive Environment possibly dangerous to field personnel Human error may have significant impact on sample representativeness Requires flow measurements taken during sampling
Automatic grabs	Minimizes labor requirements Low risk of human error Reduced personnel exposure to unsafe conditions Sampling may be triggered remotely or initiated according to present conditions	Samples collected for oil and grease may not be representative Automatic samplers can not properly collect samples for volatile organic compounds analysis Costly if numerous sampling sites require the purchase of equipment Requires equipment installation and maintenance Requires operator training May not be appropriate for pH and temperature May not be appropriate for parameters with short holding times (for example, fecal streptococcus, fecal coliform, chlorine) Cross-contamination of aliquot if tubing/bottles not washed
Automatic flow-weighted composites	Minimizes labor requirements Low risk of human error Reduced personnel exposure to unsafe conditions May eliminate the need for manual compositing of aliquots Sampling may be triggered remotely or initiated according to on-site conditions	Not acceptable for volatile organic compounds sampling Costly if numerous sampling sites require the purchase of equipment Requires equipment installation and maintenance, may malfunction Requires initial operator training Requires accurate flow-measurement equipment tied to sampler Cross-contamination of aliquot if tubing/bottles not washed

Automatic Samplers

Automatic samplers include active (pumping samplers) and passive sampling devices. Automatic pumping samplers typically collect water from the water column by suction and control the sampling rate using the pump speed (Dick, 1996). Passive sampling devices typically are installed in the flow path and control the sampling rate by placement, orientation, and design of the water intake. Each type of sampler has benefits and design limitations, which must be recognized and quantified to produce representative data.

Pumping Samplers

Automatic pumping-type samplers (fig. 3) generally consist of (1) a pump to draw suspended-sediment samples from the water column and, in some cases, to provide a back flush to clear the sampler intake before

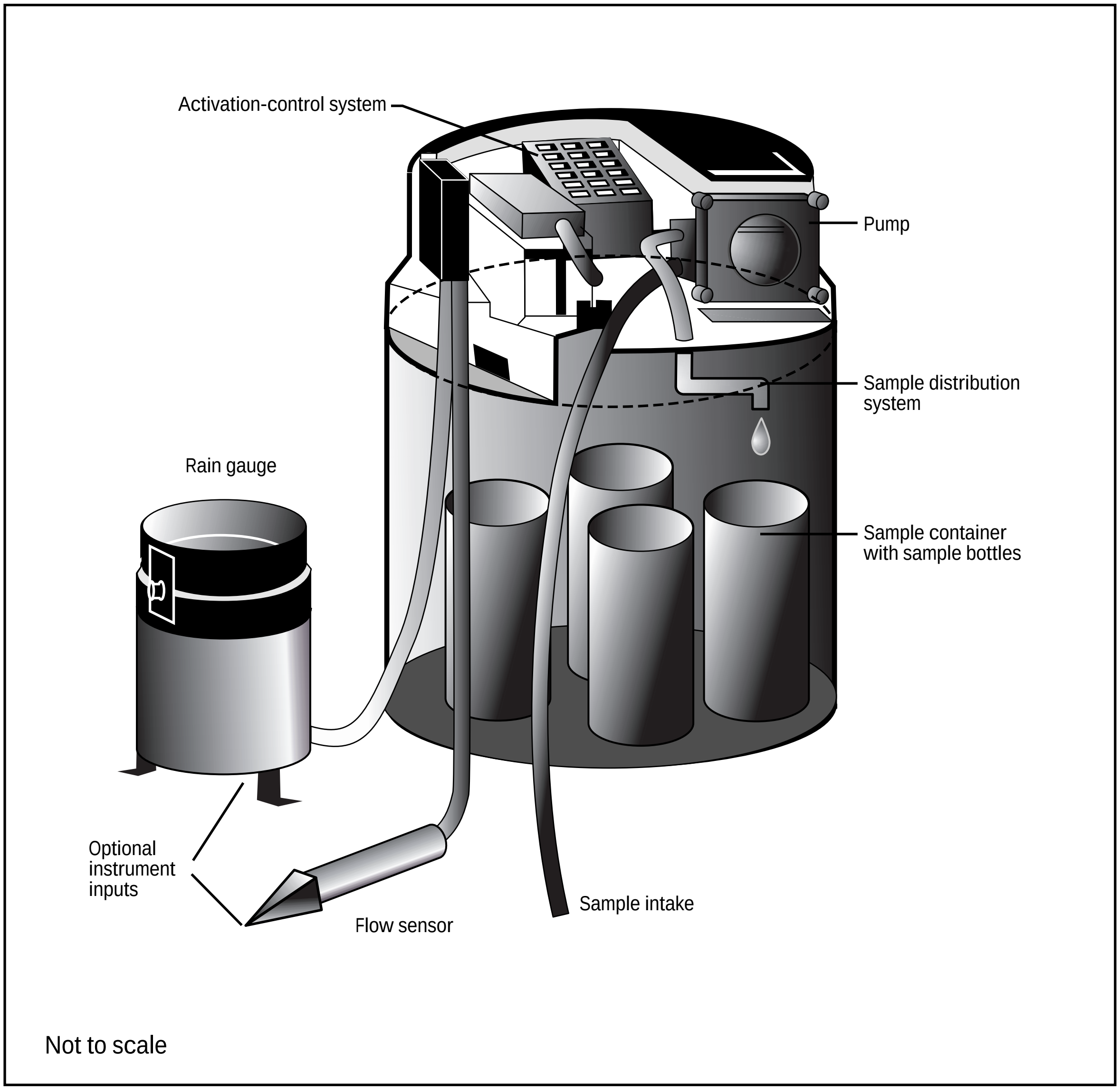


Figure 3. Automatic pumping sampler (modified from USEPA, 1992).

or after each sampling cycle; (2) a sample-container unit to hold sample bottles in position for filling; (3) a sample distribution system to divert a pumped sample to one or more sample collection bottle(s); (4) an activation-control system that activates the sampling cycle on a time interval, stage, rate-of-stage-change, or from an external signal (such as in response to a telephone call or a signal generated by a data logger); and (5) an intake system through which samples are drawn from a point in the water column's cross-section. Ideally, this combination of components should be designed to meet the following criteria based on site-specific conditions:

- A suspended-sediment sample should be delivered from the water column to the sample container without a change in sediment concentration or PSD.
- Cross contamination of a sample caused by residual sediments in the system between sample-collection periods should be minimized.

- The sampler should be capable of sample collection over the full range of sediment concentrations and particle sizes up to about 4 mm (very fine gravel). For example, about 90 percent of the sediment retained in a highway catch basin was less than 4 mm and about 80 percent was less than 2 mm in a highway-runoff study in eastern Massachusetts (Smith, 2000).
- Sample-container volumes should meet minimum sample analysis volume requirements.
- The intake's inside diameter should be maximized to facilitate representative concentrations and PSD of samples [typically 9.5- or 19.0-millimeter- (3/8- or 3/4-inch-) diameter intakes depending on the minimum pumping rate of the sampler used].
- The sampler should be capable of vertical lifts large enough to maintain sample PSD integrity.
- The sampler should be capable of collecting a reasonable number of samples, depending on the purpose of sample collection and the flow conditions.
- Some provision should be made to protect against freezing, evaporation, and dust contamination.
- The sample-container unit should be constructed to facilitate removal and transport as a unit.
- The sampling cycle should be initiated in response to a timing device, flow change, or external signal.
- The capability of recording the sample-collection date and time should exist.
- The provision for operation using alternating current power or direct current (battery) power should exist.

Recent field tests conducted by the USGS in cooperation with the Federal Highway Administration (FHWA) indicate that newer types of automatic pumping samplers meet these criteria, but older vintage (before about 1993) samplers typically do not meet all these criteria (David Owens, USGS, written commun., 2000). For example, several vacuum and peristaltic samplers of post-1993 design used for the field test collected samples with representative PSDs from 20 to 128 µm, but samplers operating on older technologies and construction were not able to collect representative samples when the sampler elevation exceeded the sampler intake elevation by 12 ft or more. In highway systems, it is important to be able to sample larger grain sizes that may be in transport. For example, sediment particle sizes as large as fine gravel (table 4) were collected by an automatic sampler in a highway-runoff study in eastern Massachusetts (Smith, 2000).

Automatic samplers also have technical limitations that must be identified and addressed for representative data-collection and interpretation. Tai and others (1991) and Horowitz and others (1992) provide information and evaluations of automatic-pumping samplers to collect dissolved and solid-phase water-quality constituents, including sediment. Technical limitations may be substantial depending on site and runoff-quality characteristics. Proper site selection and sampling design may compensate for limitations if they are recognized. These limitations include the following:

- Automatic samplers generally are not capable of collecting an isokinetic sample (which is defined as the velocity in the sampler's nozzle being about equal to that of the stream velocity incident on the nozzle because intake velocity is fixed).
- Sample line velocity is reduced with increased elevation between the automatic pumping sampler and the water surface (head), which can compromise measured suspended-sediment concentration (SSC) and PSD values. This effect is caused by the reduced ability of the sampler to lift larger particles (assuming similar particle densities and shapes) over greater heads.
- No currently available samplers are capable of collecting samples at sites where the elevation of the sampler is more than about 28 ft above the sampler intake while maintaining a line speed greater than the minimum of 2.0 ft/s specified by the USEPA (1982) without the addition of an auxiliary pump (David Owens, written communication, 2000).
- Line lengths greater than about 100 ft may impair the sampler's ability to collect water samples due to line friction.
- Increased intake diameters may be necessary to capture larger grain sizes, but an increase in the inside diameter leads to reduced intake velocities at the same pumping rate.
- Cross contamination of the sample line is a concern and is a function of the line-length (for example, a 1 ft section of a 3/8-inch-diameter tube has an inside surface area of about 0.1 ft^2), and the

quality of runoff (for example, runoff water that contains other viscous liquids, such as oil and grease) may increase sediment retention.

- Composite samples may be affected by sample volume repeatability, which should be tested for each sampler at each site (David Owens, written commun., 2000).

Samples collected non-isokinetically by automatic samplers may not provide data representative of the mean cross-sectional concentrations and PSDs, particularly when sand-size material is in transport (Edwards and Glysson, 1999). In one study, however, the constituent concentrations of samples collected with an automatic pumping sampler were shown to be similar to those of manually collected, cross-sectionally integrated water-quality samples (Krug and Goddard, 1986). Research is needed to develop relations between data collected by automatic and isokinetic sampling methods in highway and urban drainage systems. In fluvial systems, a depth-integrated sample is required because of potential variations in the cross-sectional distribution of sediment (Guy, 1970). Use of depth-integrating samplers typically requires depths exceeding a foot, and minimum mean flow velocities of about 2 ft/s. In highway and urban drainage structures, however, depth- and width-integrated sampling techniques may not be possible for a number of reasons, such as brief duration of runoff, limited access to the drainage structure, size of the conduit, depths and velocities of water in the conduit, and rapidly varying flows. Also, because of the turbulent flows and rapid mixing characteristic of highway and urban drainage systems, these methods may not be necessary depending on site-specific conditions. If use of the EDI or EWI method to collect samples is possible, samples can be collected over a range of flows on the rising and falling limbs of the hydrograph during different runoff periods to document the difference between the collection of a representative sample and the collection of a sample at a single point by an automatic pump sampler. EDI and EWI samples can be used to develop a cross-section coefficient with concentration values from samples collected with an automatic sampler (Porterfield, 1972) as part of the quality-assurance and quality-control (QA/QC) activities.

To obtain the most reliable and representative data, the automatic sampler intake should be placed at the point at which the concentration approximates the mean sediment concentration for the cross section over a full range of flows. This idealistic concept has great merit, but the mean cross-section concentration almost never exists at the same point or vertical under varying flow conditions. It is even less likely that specific guidelines for locating an intake under given flow conditions at one stage would produce the same intake location relative to the flow conditions at a different stage. For example, there are five possible intake orientations (fig. 4), including (A) horizontal and against flow, (B) horizontal and perpendicular to flow, (C) upward and perpendicular to flow, (D) downward and perpendicular to flow, and (E) horizontal and with flow (Edwards and Glysson, 1999). In laboratory tests of several nozzle orientations, including orientations (C), (D), and (E), Winterstein and Stefan (1986) found orientation (E) to provide the most representative sample in spite of the fact that this is counter-intuitive when considering isokinetic manual sampling techniques (Edwards and Glysson, 1999, p. 14). Winterstein and Stefan (1986) hypothesized that this downstream (with flow) intake minimizes debris accumulation and a small eddy is formed at the intake, which envelops the sand particles and thus allows the sampler to collect a more representative sample of the coarse load than intakes located in other directions with respect to the flow. There are, however, many site-specific issues that must be considered. Therefore, objectives for placing a sampler intake in the flow at any given cross section are as follows:

- Select the intake location so that, if possible, it is submerged for the complete range of flows.
- Identify or install a means to fix the intake at the desired location in flow. The attachment feature and intake should have a high probability of remaining in place at high flows, and should not be prone to collecting debris.
- Make sure the sampler intake is not located where bed material can be drawn into or can bury the intake.
- Locate and configure the sample intake to reduce any potential for debris collection, such as in the downstream direction.
- Sample intake location should be in areas of high velocities and turbulence that offer the greatest potential for mixing, that provide for rapid removal of any particles disturbed during a purge cycle of sample line, (such as downstream of

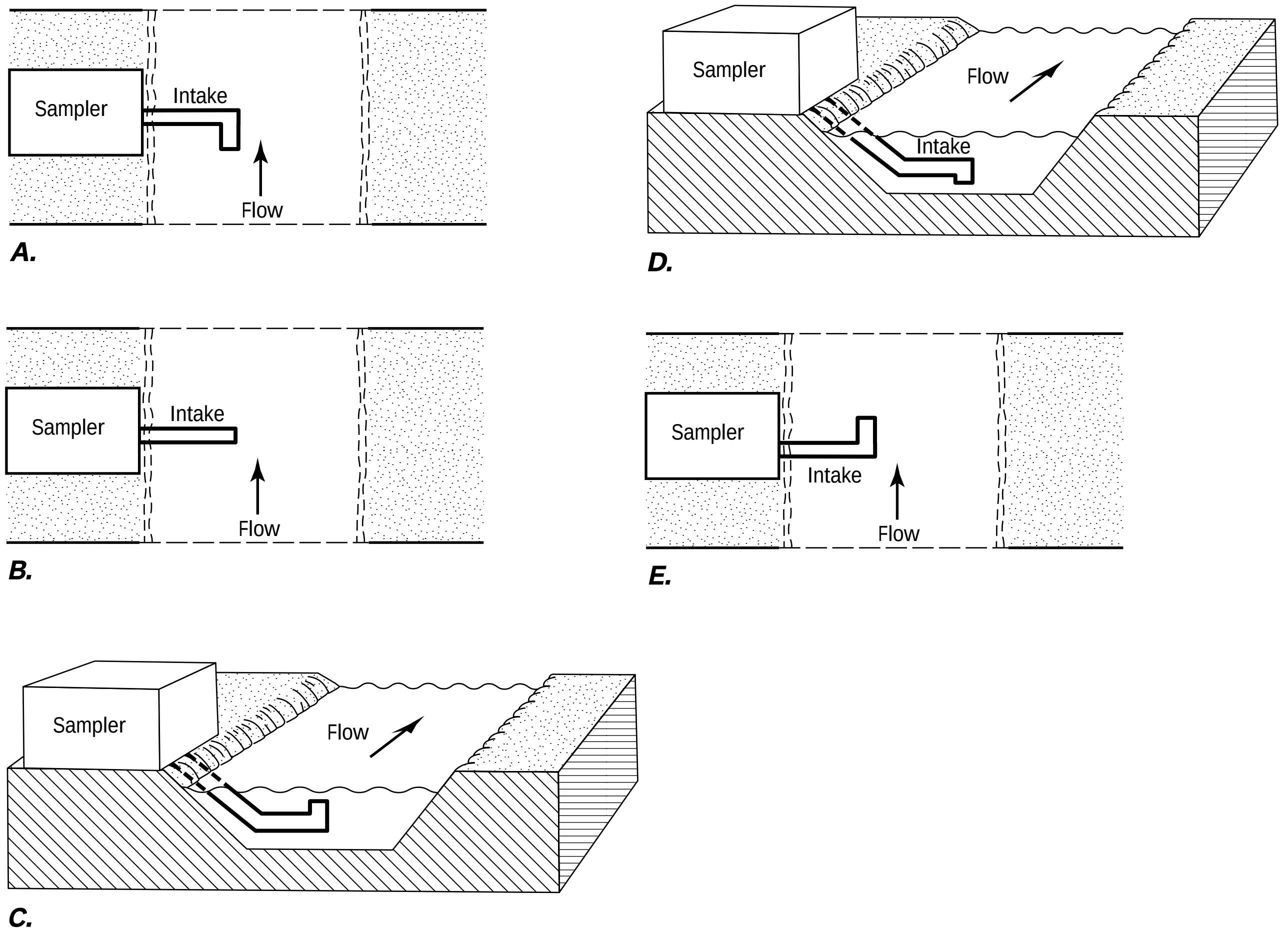


Figure 4. Pumping sampler intake orientations: (*A*) horizontal and against flow; (*B*) horizontal and perpendicular to flow; (*C*) upward and perpendicular to flow; (*D*) downward and perpendicular to flow; and (*E*) horizontal and with flow (modified from Edwards and Glysson, 1999).

storm drainage distribution boxes), or that incorporate static mixing devices just upstream of the sampler intake.

- Mount the tubing with a slope from the intake to the sampler intake to minimize low points in tubing that may retain water and sediment after pumping has ceased. This will reduce the potential for cross contamination between subsequent samples.
- Position one or more intakes as a manifold to collect the most representative (mean) SSC and PSD samples.

Site conditions commonly preclude sampling arrays that meet these guidelines. The investigator should endeavor to install a sampling system that minimizes deviations from these guidelines. It is therefore incumbent upon the investigator to clearly document site-specific conditions and to implement QA/QC measures to quantify the performance of sampling efforts.

Automated pumping samplers can be controlled by a data logger with sampling criteria based on time, stage, rate-of-stage change, or water-quality measurements. An operator can optimize sampling rates in response to changes in expected precipitation volumes during a storm from a remote location, using a communication device such as a cell phone. Gray and Fisk (1992) describe a method for controlling an automatic water sampler based on time, stage, and rate-of-stage-change criteria. Their technique is designed to provide an adequate definition of the flood hydrograph to enable reliable computations of daily sediment and associated chemical constituent discharges. Gray and deVries (1984) describe a system for measuring surface runoff and collecting sediment samples from small areas (on the order of hundreds of square feet). Their automatic pumping mechanism splits the sample into 10 equal parts and retains one or more parts as a representative composite sample for the entire runoff period. A technique for controlling an automatic water sampler based on a time-stratified sampling technique is described by Thomas (1985, 1991), and Thomas and Lewis (1993). This capability increases the amount and quality of data derived at a sampling site, and provides a resource to enable the project manager to make informed decisions on allocations of human resources during runoff at one or more sampling sites.

Automatic pumping samplers, however, are not well suited for all sampling sites. The cost, complexity, and logistics (power, communication requirements, and installation) associated with automatic samplers can discourage their use. Also, the sampler intakes need to be positioned in a location with a sufficient cross-sectional area and flow rate to be submerged enough to obtain representative samples. When automatic pumping samplers are impractical, passive automatic samplers may be a viable alternative.

Commercially available automatic samplers are not designed for collection of bedload. Bedload may represent a part of the sediment carried in highway and urban runoff (Bertrand-Krajewski and others, 1993; Waschbusch, 1999). Although newer samplers have collected sediment with particle sizes as large as fine gravel (Smith, 2000), these samplers do not meet specifications for bedload samplers. For example, manual bedload samplers developed by the Federal Interagency Sedimentation Project (2000a; 2000b), such as the BL-84 or the BLH-84 samplers, are designed to collect particles from about 0.25 to 35 mm in diameter using a pressure-difference principle and a nylon mesh screen to retain the sample (Helley and Smith, 1971; Hubbell and others, 1981; Edwards and Glysson, 1999). The necessary tube diameters, pumping rates, and sample volumes required to collect representative samples by automatic samplers may be prohibitive. Research may be needed to develop and test adaptations of automatic pumping samplers to collect representative samples of bedload material for highway runoff studies.

Passive Samplers

Passive automatic samplers are designed to collect a proportion of flow during the time when runoff submerges the sampler intake port(s). Passive samplers generally include a sample intake, an inflow control assembly, a sampling container, and a housing designed to emplace the sampling container and facilitate sample retrieval. A number of automatic types of passive samplers are available. The following are described in greater detail in the noted references.

- A flow splitter described by Clark and others (1981) uses baffles on a steep inclined plane—to cause supercritical flows—(fig. 5) to obtain a representative and flow-proportional sample of an entire storm. Clark and others (1981) indicate that the composite sample reflects the event mean concentrations calculated from a series of discrete samples taken during a monitored storm. To use this sampler, however, the site must be on a fill section of highway so that this sampler may be employed on the highway shoulder at a steep enough slope to function hydraulically. Racin (1995) also describes use of a similar sampler for NPDES monitoring of highway runoff quality in California.
- A catch-basin sampler described by Pratt and Adams (1981) utilizes a series of five conical mesh screens with decreasing slot sizes to capture sediment greater than 1.25, 0.60, 0.40, 0.15, and 0.09 mm, respectively, while allowing runoff water to pass through (fig. 6). Sediments are retained on the screen and concentrations may be estimated by calculating the total flow passing through the screens during the monitoring period.
- A catch-basin sampler described by Ellis and Harrop (1984) uses a number of sieve trays with decreasing mesh sizes from 2.00 to 0.63 mm to capture sediment while allowing runoff water to pass through (fig. 7). This device is similar to the device described by Pratt and Adams (1981) in that sediment loads are retained on the screen and

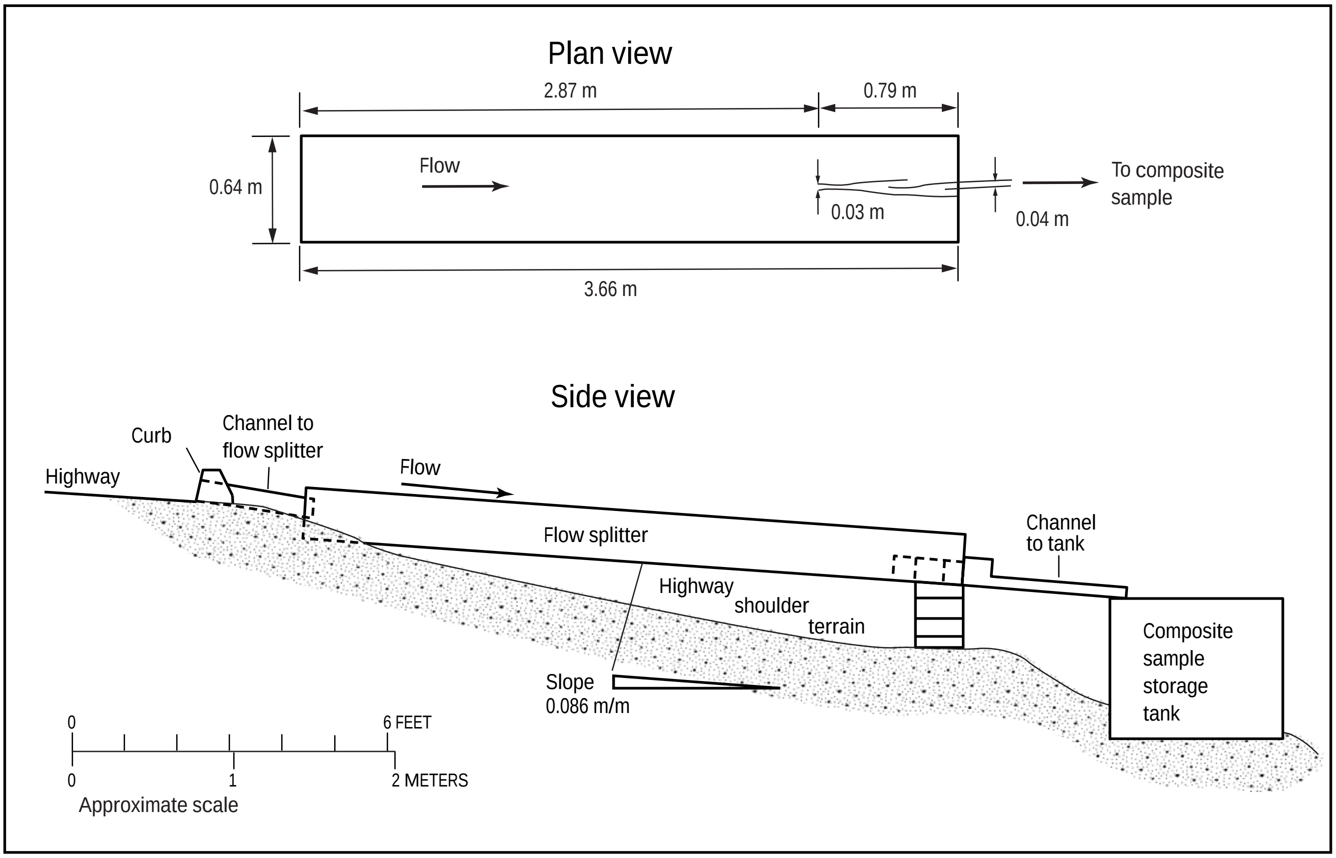


Figure 5. Typical flow splitter (modified from Clark and others, 1981).

concentrations may be estimated by calculating the total flow passing through the screens during the monitoring period.

- A modified single-stage sampler described by Gray and Fisk (1992) is used for passively collecting water samples when the water surface reaches each inlet port in a vertical array of sampling ports (fig. 8).
- A "gully pot" (catch basin) insert described by Spangberg and Niemczynowicz (1992) includes a funnel inlet, water-quality measurement chamber, and a v-notch weir for flow measurement (fig. 9). This device uses a turbidity meter and sampling port to measure turbidity and sediment, respectively.
- A flush mounted sampler (fig. 10*A*) and an "in the pipe" sampler (fig. 10*B*) are described by Dudley (1995). These samplers are designed to collect a water sample by employing a double ball valve so that the sampler is only open during periods of flow immersion and so that the sampler will close once the sample bottle is full.
- A sheet-flow sampler described by Stein and others (1998) is designed to be mounted flush with the pavement (fig. 11). This sampler is normally open to the atmosphere and has a buoyant flap designed to close each inlet port once the receptacle is full.
- A sheet-flow collection system described by Sansalone and others (1998) utilizes a gutter at the pavement edge to concentrates flow through a Parshall flume (to measure flow volume) into a 2,000-liter runoff collection tank (fig. 12). This

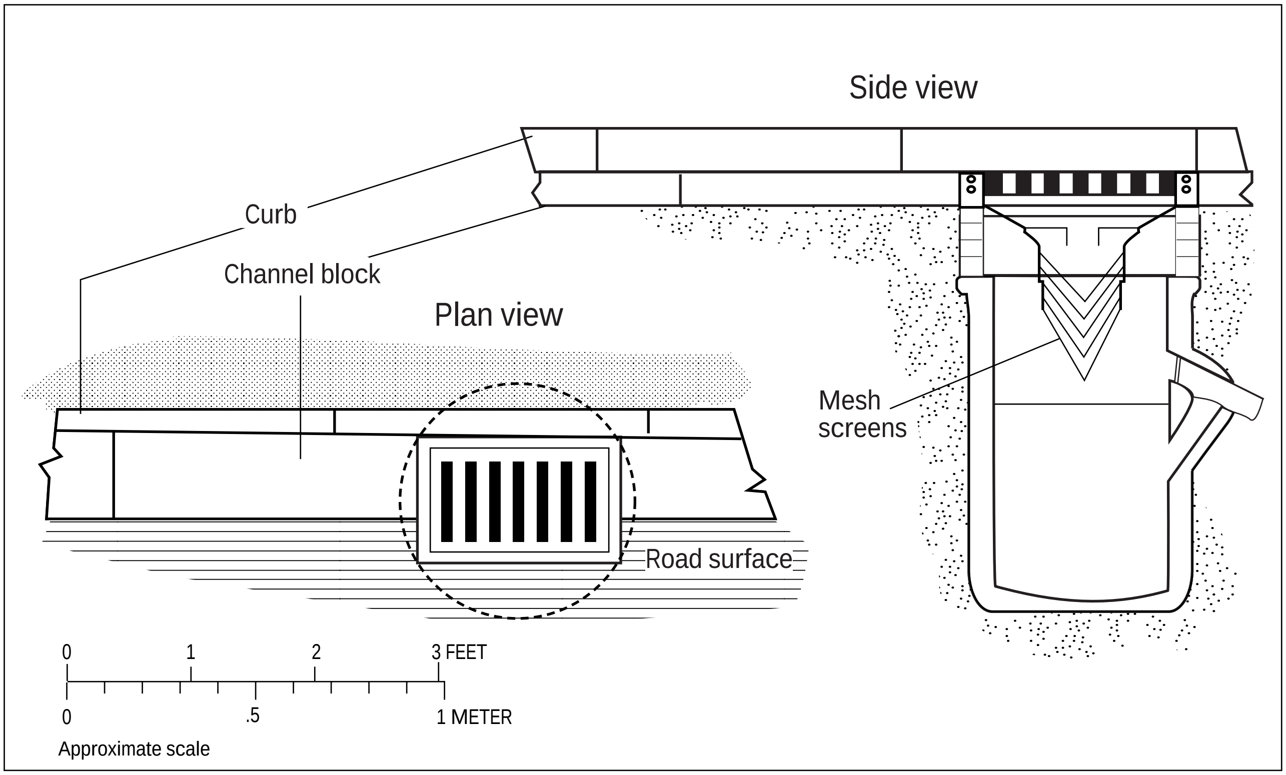


Figure 6. Road washoff material collector for a catch basin (modified from Pratt and Adams, 1981).

passive sampling design also enables use of an automatic pumping sampler by collecting runoff in the flume where flows are concentrated.

- A street-runoff sampler described by Waschbusch and others (1999) is designed to be mounted flush with the pavement for collection of a water sample (fig. 13). This device is normally open and has a setscrew designed to control the inflow volume. Waschbusch and others (1999) also described driveway, lawn, roof, parking lot, and storm-sewer outfall samplers of similar design.

Passive samplers also have technical limitations that must be understood and addressed for representative data collection and interpretation. The quality-control data needed to establish that these samplers perform as expected under the normally harsh highway- and urban-monitoring conditions is not extensive enough to establish comparability and repeatability with other methods. Technical limitations may or may not be substantial depending on site characteristics. Proper site selection and sampling design can compensate for limitations if they are recognized. These limitations include the following:

- Most passive samplers do not have provisions for recording the period of flow sampled.
- Debris buildup on sampler intake(s) can alter the flow of water and sediments completely, precluding sample collection, or partially, thereby affecting the representativeness of samples collected. This may not be apparent, as debris could accumulate and wash off during a single runoff period. However, pumping samplers of relatively recent vintage usually have a purge cycle that may minimize debris buildup.

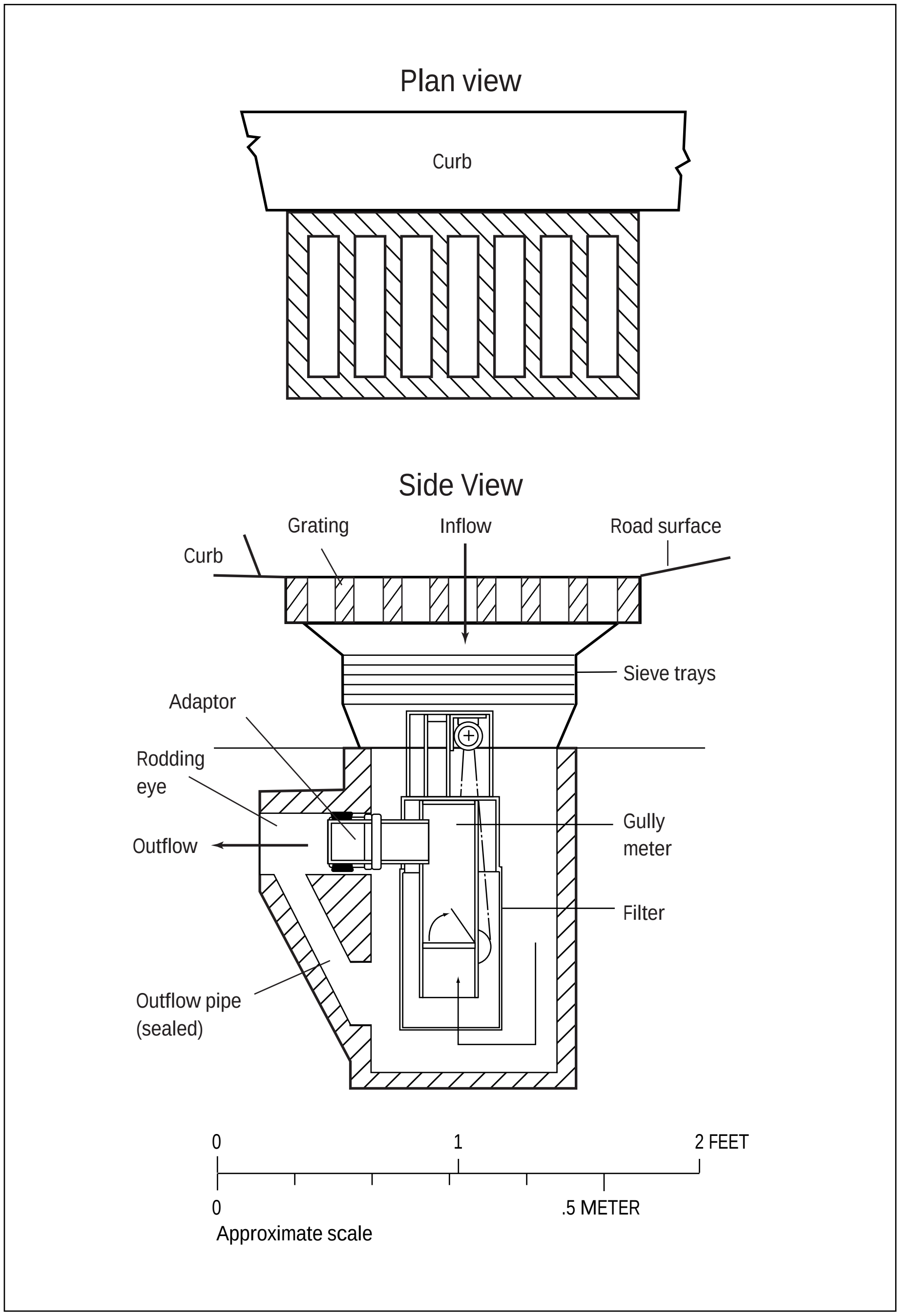


Figure 7. Road washoff material collector for a catch basin (modified from Ellis and Harrop, 1984).

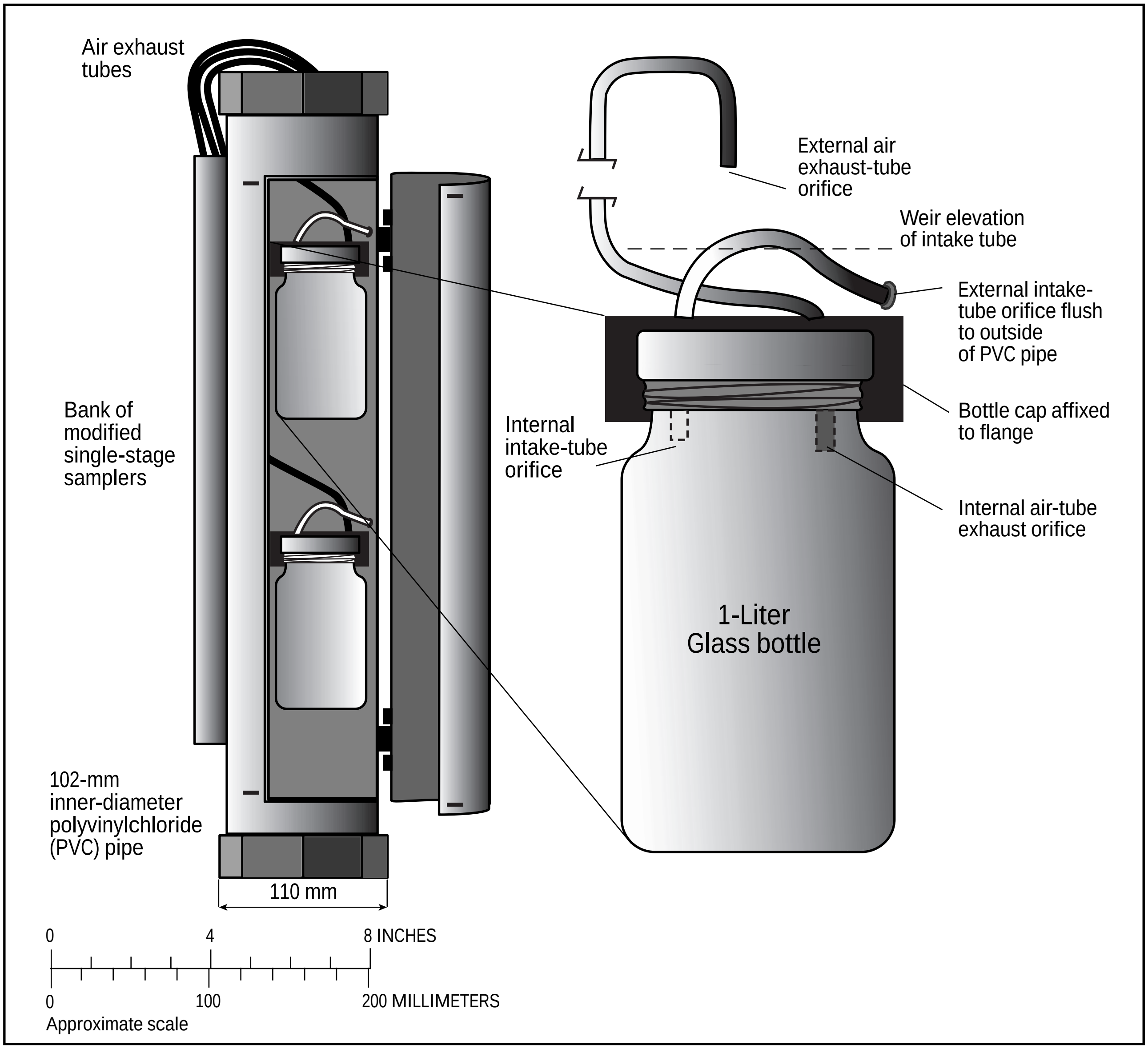


Figure 8. Single-stage sampler (modified from Gray and Fisk, 1992).

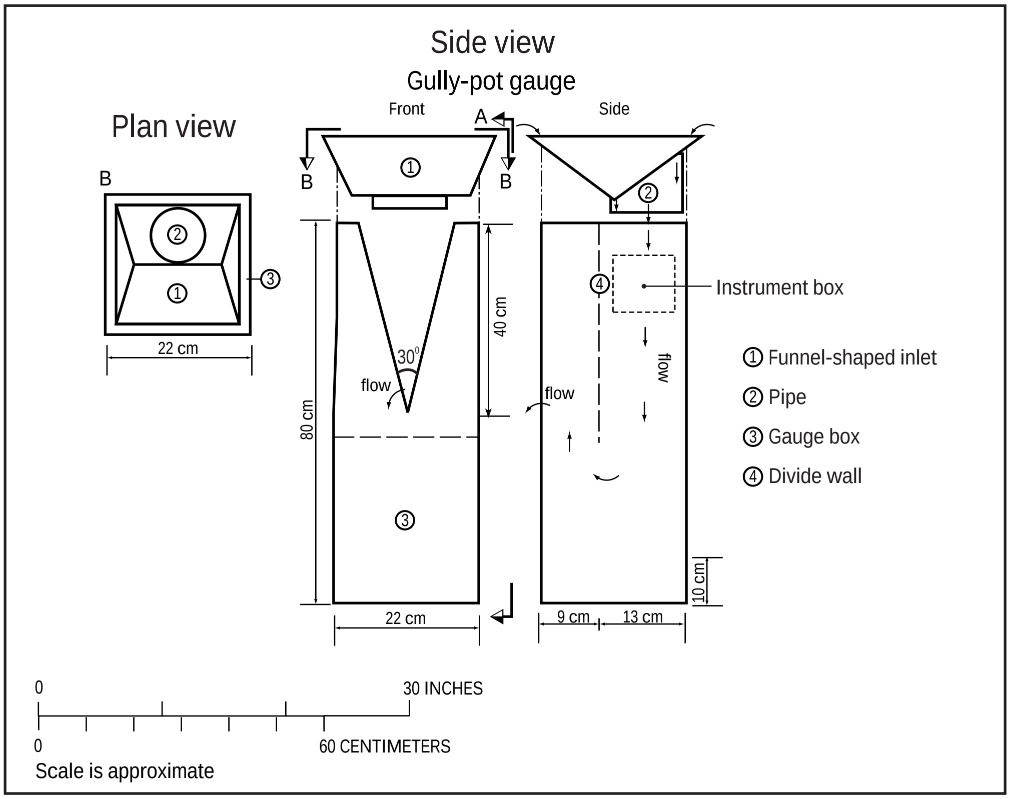


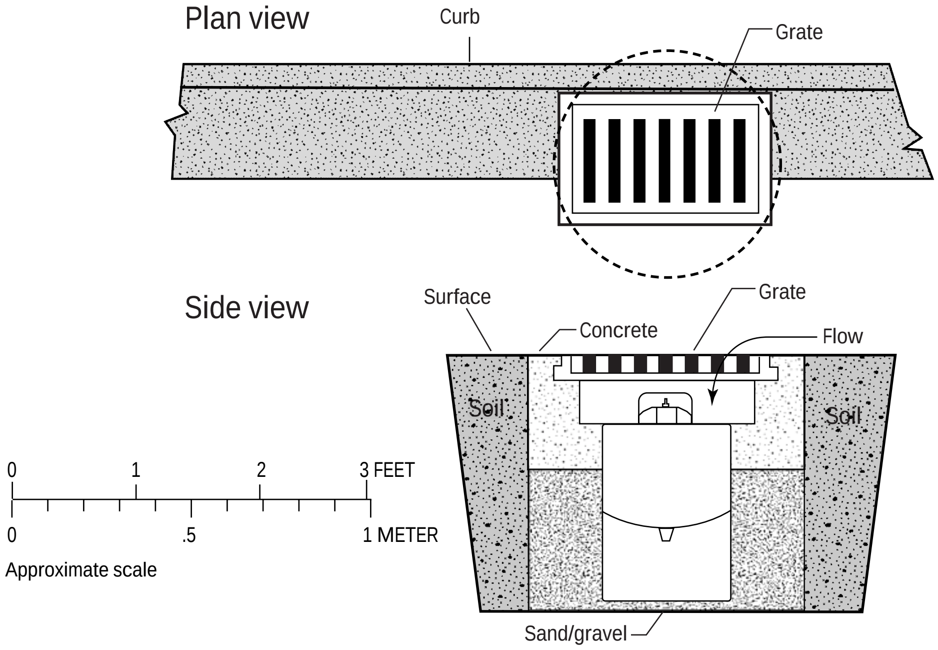
Figure 9. Road washoff material collector for a catch basin (modified from Spangberg and Niemczynowicz, 1992).

- Relatively small contributing areas magnify problems of determining the effective drainage area, and the effects of traffic, bypass flow, and surcharging.
- Relatively small flow-contributing areas also may affect the representativeness of the area sampled and variability in measured concentrations. For example, one piece of rust or tire from a vehicle in a small sampling area could substantially affect a storm load calculated for that area of the highway.
- Samples collected by passive samplers installed on the pavement may be dangerous to retrieve under heavy traffic conditions.
- Passive samplers that are open to the atmosphere may collect debris, sediments, and atmospheric dust blown toward the pavement edge by vehicle action between storms.

To obtain the most reliable and representative data, the passive sampler intake should be placed carefully at a point where sediment concentrations are characteristic of the larger system under study. Therefore, objectives for placing a sampler intake in the flow at any given cross section are as follows:

- Select locations representative of larger study areas.
- Select the intake location so that if possible it is submerged over the complete range of flows or, for single stage sampler(s), the intake is submerged during the intended sampling stage(s).
- Identify or install the device in a position that would not be prone to collecting debris.
- Position one or more intakes to collect the most representative (mean) SSC and PSD samples.

***A.* Flush mounted sampler, sump and grate set in ground**



***B.* Pipe sampler**

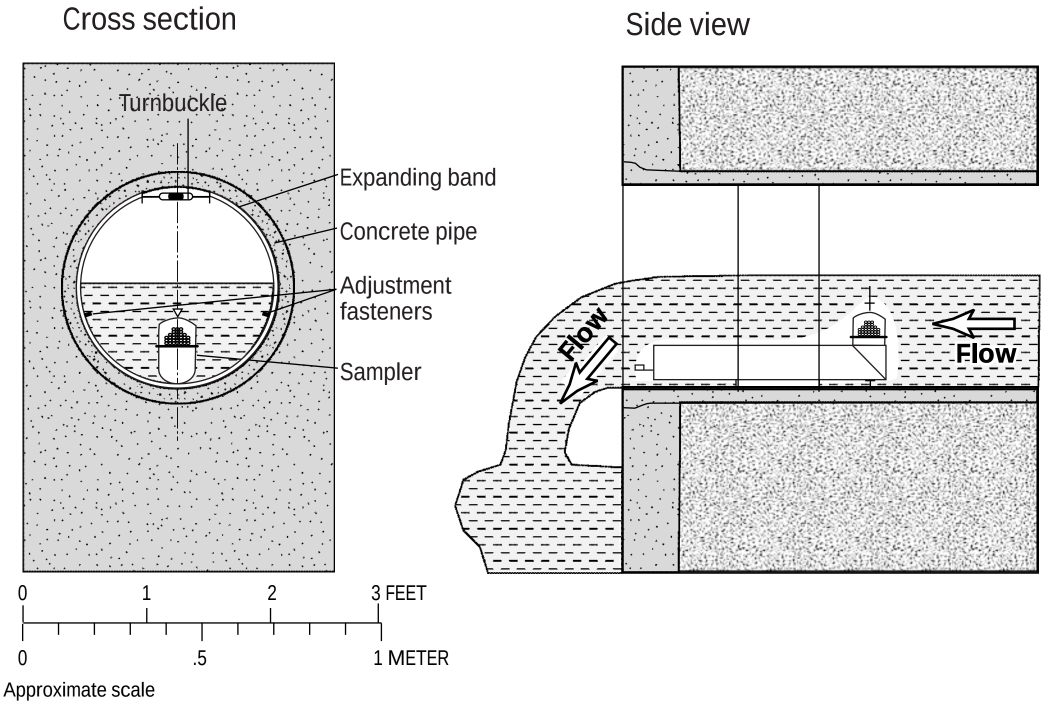


Figure 10. Road washoff material collector for a catch basin and an “in the pipe sampler” (modified from Dudley, 1995).

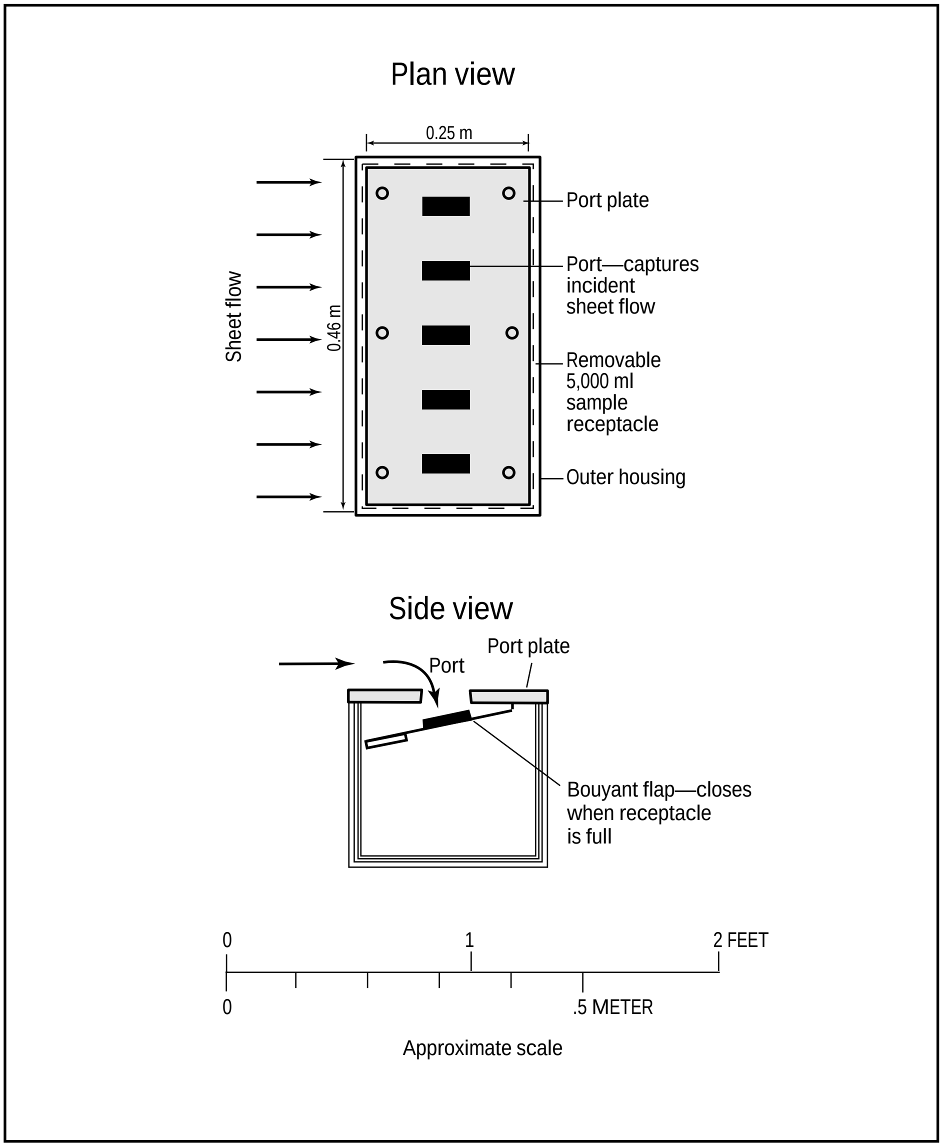


Figure 11. Sheet-flow sampler for a road surface (modified from Stein and others, 1998).

- Emplace multiple samplers to address the problems of small-scale spatial variability and the potential for problems with individual passive samplers.

Site conditions often preclude sampling arrays that meet these guidelines. It is therefore incumbent upon the investigator to clearly document site-specific conditions and to implement QA/QC measures to quantify the performance of sampling efforts.

Some passive samplers are designed for collection of bedload materials. The samplers described by Pratt and Adams (1981); Clark and others (1981); Ellis and Harrop (1984); and Sansalone and others (1998) would be suitable for collection of bedload and suspended sediments. However, research is needed to determine the capture efficiency and other measures of performance for these devices so that the comparability and representativeness of data for highway and urban runoff studies could be assessed. For example, Graczyk and others (2000) compared SSCs of 41 paired samples collected by a single-stage sampler and an automatic pumping sampler and found that mean and median differences (single-stage sampler

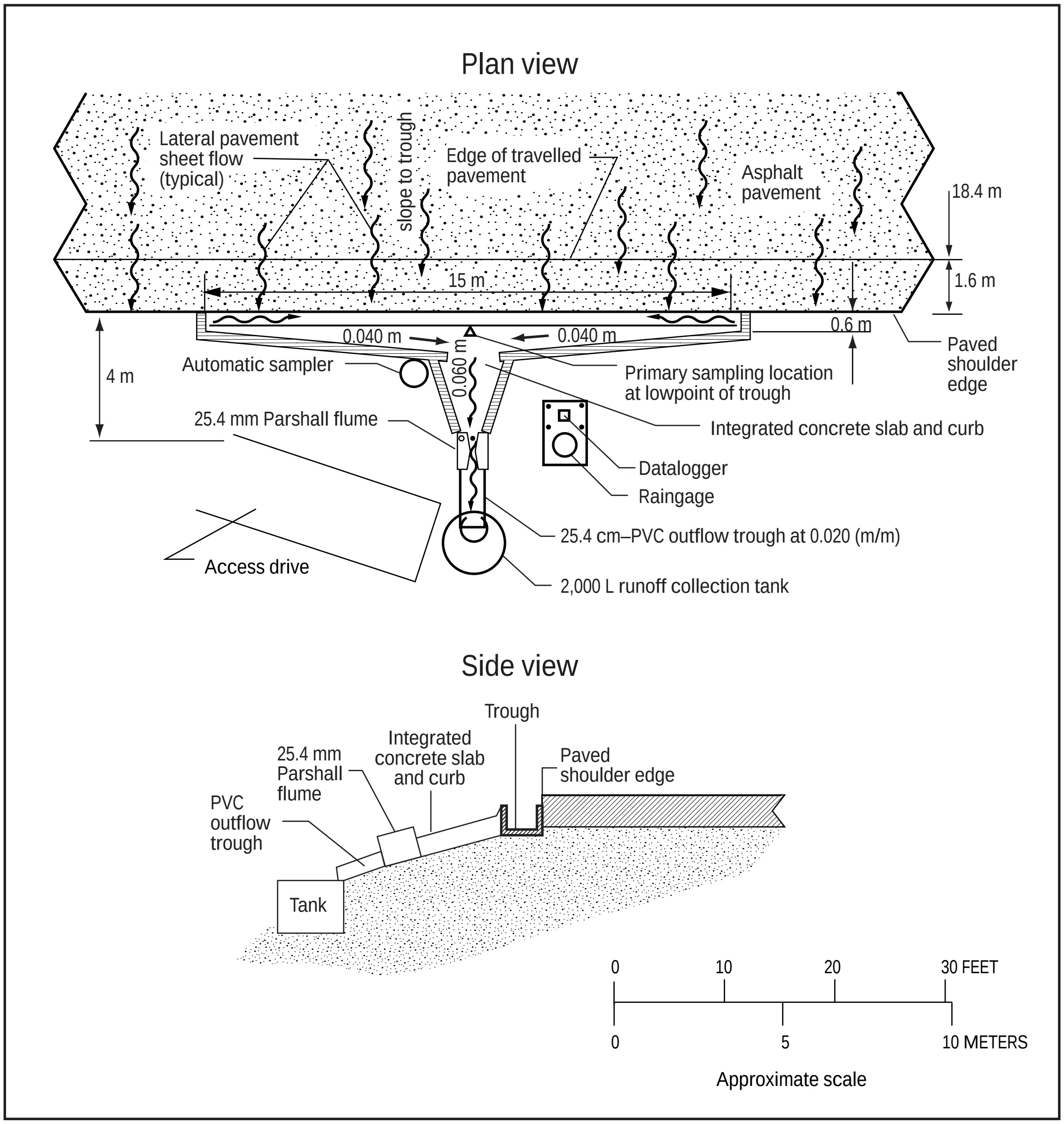


Figure 12. Sheet-flow collection trough for a road (modified from Sansalone and others, 1998).

concentration—automatic pumping sampler concentration) were reasonably similar (14 and 5 mg/L, respectively), but the individual differences had a standard deviation of 133 mg/L and ranged from about -300 mg/L to about 600 mg/L. Therefore, on average, the single-stage samplers may provide representative data but individual sample concentrations collected may vary substantially from samples collected with an automatic pumping sampler (Graczyk and others, 2000).

Indirect Methods for Measuring Sediment

Indirect methods for measuring sediment may be useful as a supplementary and (or) surrogate means to monitoring sediment in runoff. These methods include analysis of available bottom material, measurement of turbidity, and other indirect methods. Each method has benefits and design limitations, which must be recognized and quantified if representative data are to result.

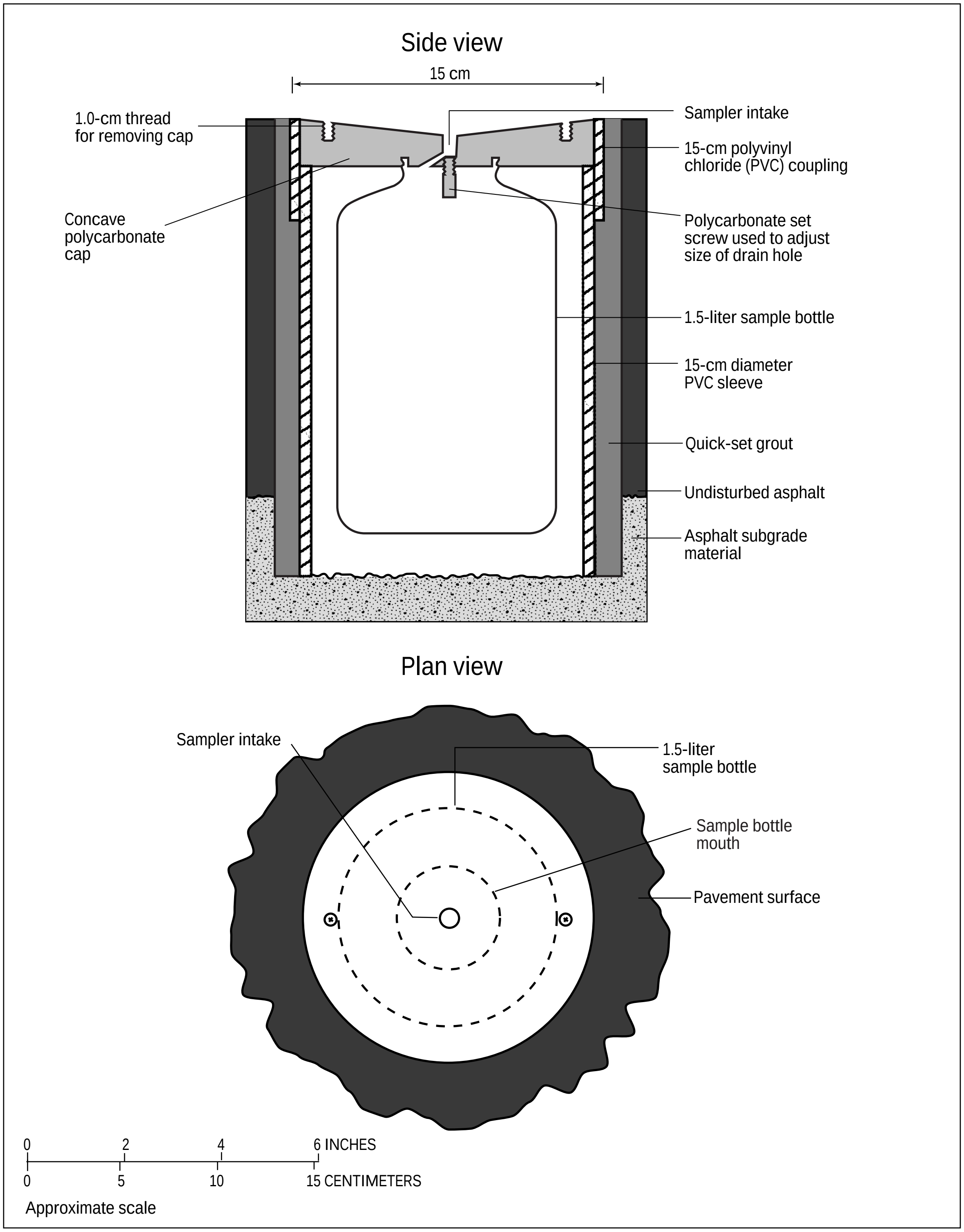


Figure 13. Street-runoff sampler (modified from Waschbusch and others, 1999).

Bottom Material

Bottom material is the sediment mixture remaining on the bottom of the channel (Edwards and Glysson, 1999). More specifically for highway- and urban-runoff studies, it is the sediment retained on the road, in drainage structures, in structural BMPs, or near drainage outfalls in receiving waters between storms. Repeated analysis of the PSD of bottom material provides information about the sediments transported during runoff events at various flow rates. However, bottom-material samples may not include fine material that moved through the system as washload.

Many of the bed-material samplers designed for fluvial systems may also be suitable for bottom material sampling in runoff conveyances. Edwards and Glysson (1999) describe the samplers developed by the Federal Interagency Sedimentation Project for collecting bed sediments in natural waters. Radtke (1997) lists these and several other bed-material samplers. Yuzyk (1986), Ashmore and others, (1988), Diplas and Fripp (1991), Yuzyk and Winkler (1991), ASTM (1994), Environment Canada (1994), Shelton and Capel (1994), International Standards Organization (1997b), and Edwards and Glysson (1999) provide bed-material sampling guidelines for subsequent physical and (or) chemical analyses. Kobriger and Geinopolos, (1984) discuss bottom-material sampling in a study of sources and migration of highway runoff pollutants. Materials and methods for collection of bottom-material samples need to be evaluated carefully, especially if these materials will also be used for chemical analysis. As with other methods designed for use in natural (fluvial) systems, the design and implementation of these methods need to be evaluated and QA/QC data need be documented so that the comparability and representativeness of data obtained for highway- and urban-runoff studies may be assessed.

Turbidity

Turbidity is a measure of the light attenuation caused by interference from suspended materials and dissolved materials that produce color. Suspended materials that affect turbidity include organic matter (anthropogenic materials, leaves, and aquatic biota), and natural and anthropogenically derived particulates. Color-producing dissolved materials include iron (as ferric humate) and colloids from the decomposition of organic debris. Turbidity is measured either by a turbidimeter or by an optical backscatterance sensor (OBS) (Downing and others, 1981). Turbidity has been a common surrogate used to estimate SSCs in fluvial systems (Brown and Ritter, 1971; Brown, 1973; Reed, 1978; Beschta, 1980; Smith, 1986; Gippel, 1995; Lewis, 1996 and Schoellhammer and Buchanan, 1998). Turbidity also has been measured in many highway- and urban-runoff studies, including those by Irwin and Losey, (1978), Cramer and Hopkins (1981), McKenzie and Irwin (1983); Dupuis and others (1985), Schiffer (1989); Spangberg and Niemczynowicz (1992); and Barrett and others (1996).

Turbidity can be measured to provide real-time estimates of SSCs in flowing waters. To date, several researchers (Reed, 1978; Lewis, 1996; and Eychaner, 1997; Buchanan and Schoellhamer, 1998; Schoellhamer and Buchanan, 1998) have used continuous turbidity data from turbiditimeters or OBS as a surrogate for SSCs. Spangberg and Niemczynowicz (1992) used turbidity measurements to estimate sediment runoff from a parking lot on a 10-second interval. They found substantial variations—related to variations in flow—at time scales on the order of about one minute. In many highway- and urban-runoff studies, however, turbidity is at best a qualitative indication of sediment concentration because measured turbidity depends on many factors, including the PSD of sediments, the quality and maintenance of the probe, the effects of degree of fouling (trash, sediment, and biota) and temperature on the probe. Laboratory analysis of turbidity and SSC data for 1,135 runoff samples collected in a highway drainage pipe in eastern Massachusetts (Smith, 2000) indicates that the relation between measured values is qualitative over the full range of measured sediment concentrations. For example, at a measured turbidity of 100 nephelometric turbidity units (NTU), the SSC ranged from about 70 to 2,000 mg/L, and at a turbidity of 1,000 NTU the SSC ranged from about 700 to 3,000 mg/L (fig. 14). These data do not include the additional variability of measuring turbidity in a harsh field environment that would further reduce the reliability of any quantitative relation developed between turbidity and SSC.

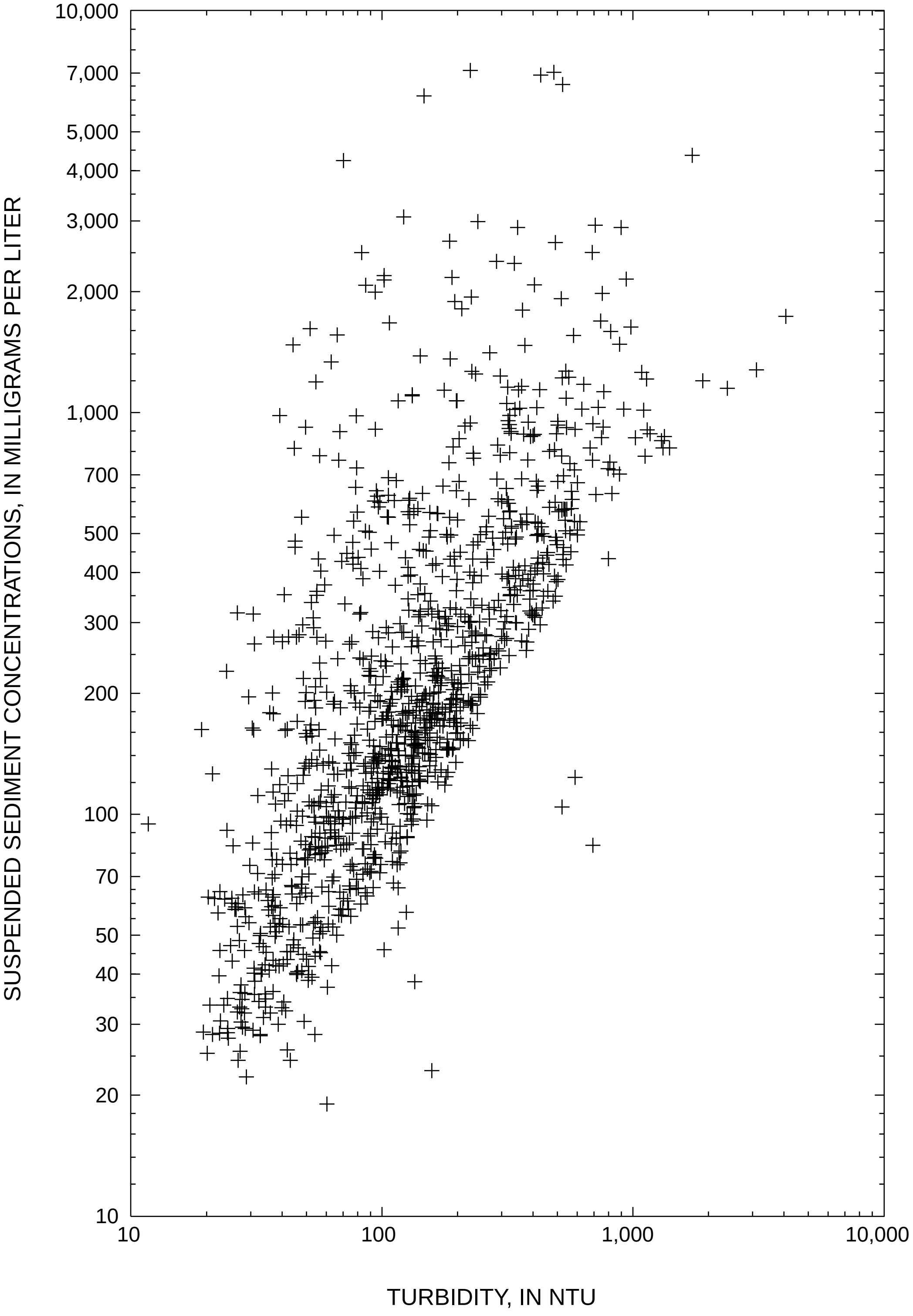


Figure 14. The relation of suspended-sediment concentration to turbidity in highway-runoff samples collected along I-93 in Boston, Massachusetts, 1999–2000 (data from Smith, 2000).

Turbidity as an optical measurement is easily fouled by oil and grease, biofilm, and other materials found in highway runoff. Also, field measurements are affected by temperature, color, bubbles, and larger particles, which may disproportionally influence turbidity in the small field of view of the instrument.

Calibration and maintenance of in-situ turbidimeters and OBS, can be expensive and time consuming. Each instrument must be calibrated periodically on-site with standards. The accuracy of these instruments often tends to vary in one direction, or “drift,” as the sensor becomes fouled with sediment or biota. In spite of these problems, Lewis (1996), and Buchanan and Schoellhamer (1998) recently demonstrated improved accuracy in measuring continuous turbidity data to calculate suspended-sediment discharges in fluvial systems. Highway and urban conveyances, however, can be more challenging because of intermittent flows; large variations in the concentrations and PSDs of sediment, and because of the difficult monitoring environment. As with other sediment monitoring methods, use of turbidity data needs to be evaluated and QA/QC data need be documented so that the comparability and representativeness of data obtained for highway- and urban-runoff studies may be assessed.

Other Indirect Methods

Skinner and others (1986), Ficken (1986), and Skinner and Szalona (1991) describe other surrogate measurement techniques to infer SSCs. These include a transmissometer, x-ray particle size analyzer, ultrasonic suspended-solids meter, radioisotope gage, vibrating U-tube fluid density tube, vibrating straight tube, and the plummet gage. They report limited successes with these technologies in estimating SSCs in fluvial systems, and none is currently being deployed by the USGS in large-scale monitoring programs. Wren and others (2000) describe emerging technologies as surrogates for measuring SSCs. A suite of emerging technologies for the measurement of suspended sediment, bed material, and bedload, is described by Gray and Schmidt (1998). New technologies that measure suspended sediment and (or) bed topography include acoustic (Kuhnle and others, 1998; Mueller, 1998; Derrow and others, 1998; Garcia and Admiraal, 1998), optic (Muste and Kruger, 1998; Schmidt, 1998a, 1998b), fluid density (William Fletcher, Design Analysis Associates, Inc., written commun., 2000; Dirk de Hoop, Hope Hydrology, written commun., 2000), satellite (Chavez, 1998), laser techniques (Yogi Agrawal, Sequoia Scientific, Inc., written commun., 1998), and electro-mechanical techniques (Jobson, 1998). These technologies are being developed for fluvial systems and show some promise to automate and (or) improve the quality of sediment data collection in that environment. These techniques may also be applicable for future highway- and urban-runoff studies including the monitoring of BMP structures and receiving waters. Currently, the difficult highway- and urban-monitoring environment may preclude use of these devices, but future technical developments may improve the potential utility of these methods. Mineral magnetic techniques, however, may be useful for source identification and may be used to follow the transport and sequencing of surface sediments through a stormwater conveyance systems (Beckwith and others, 1990). As with other methods designed for use in natural (fluvial) systems, the design and implementation of these methods need to be evaluated and QA/QC data need to be documented so that the comparability and representativeness of data obtained for highway- and urban-runoff studies may be assessed

SAMPLE-PROCESSING METHODS

Appropriate sample processing methods are determined by the characteristics of the water sampled and by the analytical and interpretive methods used for data reduction. Water-quality data for highway and urban runoff are generally reported as event mean concentrations (EMC) to provide summary values that can be used to compare measurements from individual runoff periods at a site or from populations of storms between sites. Theoretically, the EMC for suspended sediments is the cumulative storm load (mass) of suspended sediment divided by the total runoff volume for the storm period (event) (Driscoll and others, 1991). An EMC may be determined by collecting a bulk sample, by physically compositing a number of discrete samples, or by mathematically calculating a flow-weighted composite value from analysis of multiple discrete samples taken during the runoff period. The composite sample can be obtained manually from discrete stormwater samples by methods described by Gray and Fisk (1992), or automatically by methods described by Heaney and Huber (1979).

Each sample type has certain pre-analysis processing requirements that may affect measured sediment concentrations. Large bulk samples require homogenization and subsampling to produce an aliquot suitable for laboratory analysis and (or) for concurrent analysis of other water-quality constituents. When discrete samples are physically composited, the resulting bulk volume must also be homogenized and representatively subsampled to produce an aliquot suitable for laboratory analysis and (or) for concurrent analysis of other water-quality constituents. Discrete samples, however, need not be homogenized and subsampled unless laboratory analysis for concurrent analysis of other water-quality constituents is necessary. This requirement can be avoided by collection of duplicate discrete samples for analysis of sediment and other water-quality constituents.

Homogenization

Homogenization is necessary when subsamples will be extracted from an aliquot for analysis. Also, large bulk-samples collected by passive samplers such as described by Clark and others (1981) need to be homogenized and subsampled to obtain volumes that are feasible for laboratory analysis. The objectives of a homogenization process are to provide a uniform distribution of sediment concentrations and PSDs in each subsample extracted. Homogenization is accomplished by imparting kinetic energy to the solution to uniformly suspend all particles in solution. The presence of particles larger than medium sands (about 0.25 mm, table 4) increases difficulties associated with obtaining representative subsamples. Additionally, it may be impossible to evenly distribute several sediment grains throughout a sample container for representative subsampling.

Before 1976, USGS guidelines on manual sample splitting required compositing the water sample into a large, clean jug or bottle, and shaking it for uniform mixing (USGS, 1976). In 1976, the 14-liter churn splitter, which utilizes a large plunger to mix a composite water sample was introduced to facilitate the withdrawal of a representative subsample of a water-sediment mixture (Capel and Larson, 1996; Wilde and others, 1998). Demonstrating the comparability of the homogenization process among different samples is important to establish that sediment subsamples are representative and that sediments included in each subsample used for chemical analysis are comparable. It is therefore incumbent upon the investigator to use consistent homogenization protocols, to clearly document site-specific conditions (such as the range of concentrations and PSDs) and to implement QA/QC measures to quantify the performance of this sample processing method.

Subsampling Water-Sediment Mixtures

Samples of water-sediment mixtures are sometimes subsampled, or split into multiple parts to enable different analytical determinations on the subsamples. The validity of data obtained from subsamples depends on the comparability of selected constituent concentrations in the subsample to those in the original sample. Subsamples tend to have larger constituent variances than the original, and may also be biased. Subsampling should be avoided unless it is necessary to achieve the ends of the sampling program. Currently, the 14-liter churn splitter is commonly used to collect subsamples for analysis of sediment concentrations (Capel and Larson, 1996; Wilde and others, 1998). The cone splitter, developed to split water samples for suspended sediment and other water-quality constituents into ten equal and representative aliquots, was introduced for wide-scale use in 1980 (Capel and Nacionales, 1995; Capel and Larsen, 1996). Results of tests on the sediment-splitting efficiency of the churn and cone splitters were published in 1997 (USGS, 1997). The churn splitter was approved for providing subsamples when the original sample's sediment concentration is less than 1,000 mg/L at mean particle sizes less than 0.25 mm. At SSC concentrations of 10,000 mg/L or more, the bias and precision of sediment concentrations in churn splitter subsamples are considered unacceptable (USGS, 1997; Wilde and others, 1999b). The cone splitter was approved for providing subsamples at sediment concentrations up to 10,000 mg/L at mean particle sizes less than 0.25 mm. The test data suggest that the cone splitter's acceptable concentration range exceeds 10,000 mg/L, and may approach 100,000 mg/L at PSDs less than 0.25 mm.

The usefulness of data obtained from subsamples depends on their comparability of selected constituent concentrations to those in the original sample. Demonstrating the comparability of the subsampling process is important to establish that sediment subsamples are representative and comparable. It is therefore incumbent upon the investigator to select consistent subsampling protocols, to clearly document site-specific conditions (such as the range of concentrations and PSDs) and to implement QA/QC measures to quantify the performance of this sample processing method.

SAMPLE-ANALYSIS METHODS

Representative analysis of concentrations and physical characteristics of sediment in highway and urban runoff is an integral step toward assuring data quality. Methods for determining the physical characteristics of sediment that are pertinent to the study of highway and urban runoff include PSD, specific gravity, settling velocity, and the organic content of sediment.

Measurement of Sediment Concentration

Virtually all solid-phase concentration values determined in the United States are obtained by one of two analytical methods: the suspended-sediment concentration (SSC) method (American Society for Testing and Material, 2000) and the total suspended solids (TSS) method (American Public Health Association and others, 1995). Analytical methods used to produce SSC and TSS data differ; however, the terms are often used interchangeably to describe the concentration of solid-phase material suspended in a water-sediment mixture, usually expressed in milligrams per liter (G.E. Granato, USGS, oral commun., 1999; James, 1999). Extensive review of highway- and urban-runoff water-quality literature indicate that these studies commonly do not define the analysis method, but almost all describe the total concentration of suspended solid-phase material in terms of TSS, regardless of the method used (G.E. Granato, USGS, written commun., 2000). For example, the draft report, “Proposed Sediment Total Maximum Daily Load for Stekoa Creek, Georgia” (USEPA, Region 4, written commun., 2000) uses “regional TSS data” that are compiled from USGS records; the TSS data referred to are actually SSC data. Buchanan and Schoellhamer (1998) refer to sediment data collected as “suspended-solids concentration data” for San Francisco Bay monitoring efforts. These data would more appropriately be referred to as SSC, because the total water-sediment mass and all sediment are measured in the analysis (Alan Mlodnosky, USGS, oral commun., 1999).

Use of SSC and TSS in load calculations can produce substantially different results (Glysson and others, 2000, 2001; Gray and others, 2000, 2001a; Gordon and others, 2001). Although these methods are often expected to produce comparable results, recent research indicates that there are systematic differences between methods (Glysson and others, 2000, Gray and others, 2000).

The SSC method (ASTM, 2000) uses standardized procedures and equipment to measure all of the sediment and the net weight of the water-sediment mixture to calculate concentration. Three analytical methods are used to produce SSC data: Evaporation, filtration, and wet-sieving filtration of the entire sample volume received by the laboratory. The evaporation method is applicable for all concentrations; if the dissolved-solids concentration exceeds about 10 percent of the sediment concentration, an appropriate correction factor must be applied to the suspend-sediment concentration value derived by the evaporation method because these solids are included in the analysis. The filtration method is used only on samples with concentrations of sand-size material (diameters greater than 0.062 mm) less than about 10,000 mg/L and clay-size material concentrations of about 200 mg/L or less. No dissolved solids correction is needed. The wet-sieve-filtration method yields a concentration for the total sample, a concentration of the sand-size particles, and a concentration for the silt- and clay-size particles. A dissolved-solids correction may or may not be needed, depending on the type of analysis done on the fine frac tion and the dissolved-solids concentration of the sample. These three methods are virtually the same as those used by USGS sediment laboratories and described by Guy (1969). USGS sediment laboratories, however, use the Whatman grade 934AH, 24-millimeter-diameter filter for purposes of standardization. Each method includes retaining, drying at 103˚ to 105˚C, and weighing all of the sediment in a known mass of a water-sediment mixture. The USGS analyzes sediment samples using methods described by Guy (1969), Matthes and others (1991), Knott and others (1992, 1993), and USGS (1998a; 1998b; 1999a). Most of these methods were developed by the Federal Interagency Sedimentation Project, were approved by the Technical Committee (Glysson and Gray, 1997), and are used by most Federal agencies that analyze fluvial sediment data.

According to Gray and others (2000), all three SSC test methods have analytical uncertainties (precision and bias) on the order of plus or minus:

- 6 to 40 percent at low concentrations (about 10 mg/L),
- 2 to 20 percent in midrange concentrations (from 100 to about 1,000 mg/L), and uncertainties decrease proportionally with increasing concentrations (greater than 1,000 mg/L).

Tests of SSC quality-control samples by sediment laboratories participating in the USGS National Sediment Laboratory Quality Assurance Program (Gray and others, 2000; 2001a; 2001b) provide estimates of bias and variance associated with sediment data. The median concentration bias for all participating laboratories is -1.83 percent, and the 25th and 75th percentile values are -4.39 and 0.00 percent, respectively (Gray and others, 2000). The bias primarily reflects a loss of some sediment, such as through a filter or an inability to weigh accurately very small amounts of sediment. Gordon and others (1999) show that the concentration bias is largest at smaller concentrations, and very small at concentrations exceeding about 2,000 mg/L.

The TSS analytical method (American Public Health Association and others, 1995) originated as an analytical method for wastewater samples. The fundamental difference between SSC and TSS analytical results stems from preparation of the sample for subsequent filtering, drying, and weighing. In contrast with the SSC analytical method, the TSS method requires analysis of a subsample extracted from the original. The standard method requires a subsample, or aliquot volume of 100 mL, unless more than 200 mg of residue is expected to collect on the filter, in which case a proportionally smaller volume is removed. The standard specifies that a subsample be extracted from the original water sample by pipette while the entire sample volume is being mixed with a magnetic stirrer. The subsample is filtered, and the filter and contents are removed and dried at 103˚ to 105˚C, and weighed. No dissolved-solids correction is required and the standard provides no indication of the size of particles used in the testing for the method. The percentage of sand-size and finer material cannot be determined using the TSS method.

In practice, TSS data are produced by a number of variations to the processing methods described in the American Public Health Association and others (1995). For example:

- For the collection of TSS samples from the Chesapeake Bay Program, field staff pump water from a specified depth into a plastic gallon container. The container is vigorously shaken, and 200–1,000 mL of the water-sediment mixture is poured for field filtering and subsequent analysis. (Mary Ley, Interstate Commission on the Potomac River Basin, the State of Maryland, and the Commonwealth of Virginia, written commun., 2000).
- A State government laboratory in Virginia produces TSS data by vigorously shaking the sample and pouring the sample into a crucible for subsequent analysis. All of the sample is poured into the crucible unless “there is a lot of suspended material,” in which case only part of the sample is poured (Lori Sprague, USGS, written commun., 1999).
- One laboratory analyzed TSS quality-control samples using Method 2540D of the American Public Health Association and others (1995), with the following variation: The sample is shaken vigorously and a third of the desired subsample volume is decanted to a secondary vessel. This process is repeated twice to obtain a single subsample for subsequent filtration, drying, and weighing.

The reduction in TSS data comparability by variations in protocols used is not limited to lack of consistency in processing and analytical methods. According to James (1999), there is generally no agreed upon definition of TSS in regard to stormwater runoff, in part because the settleable part of TSS is not reported in most stormwater studies.

If a sample contains a substantial percentage of sand-size material, stirring, shaking, or otherwise agitating the sample before obtaining a subsample will rarely produce an aliquot representative of the sediment concentration and PSD of the original sample. This is a by-product of the rapid settling properties of sand-size material, compared to those for silt- and clay-size material, given virtually uniform densities as described by Stokes' Law. Aliquots obtained by pipette might be withdrawn from the lower part of the sample where the sand concentration tends to be enriched immediately after agitation, or from a higher part of the sample where the sand concentration is rapidly depleted. Additionally, the physical characteristics of a pipette used to withdraw an aliquot can introduce bias in the subsample (Gray and others, 2000).

The physical characteristics of a pipette used to withdraw an aliquot, or subsample, can introduce additional errors in subsequent analytical results. The tip opening of pipettes recommended for use is about 3 mm in diameter (Kimble-Contes, Inc., 2000). The upper limit of sand-size particles, which is expressed as the median diameter, is 2 mm (Folk, 1980). A natural sediment particle's long axis is almost always larger than its median diameter and can be substantially larger. Hence, a single coarse-grained sand particle or multiple sand-size particles, particularly when present in large concentrations, may clog a 3-millimeter tip pipette under suction.

Subsampling errors are hardly limited to use of a pipette to withdraw a sample. Methods that include pouring of a subsample can introduce additional errors in subsequent analytical results. This is because, based on Stokes' Law, subsamples obtained by pouring a sand-rich water-sediment mixture likely will be deficient in sand-size material due to settling in the original sample. Fine-material concentrations will not normally be altered by the removal of an aliquot.

Bias in results produced by the SSC and TSS analytical methods tends to become apparent when sand-size material exceeds about a quarter of the sediment mass in the sample (Gray and others, 2000). This has important ramifications with respect to transport calculations. Solid-phase concentrations tend to increase with discharge for a stream, as does the percentage of sand-size material in transport. High flows tend to be inordinately influential in mass transport. Bias in TSS data would probably be largest at higher flows, and therefore transport calculations based on TSS data are prone to be biased. Glysson and others (2000; 2001) indicate that transport estimates using TSS data can be orders of magnitude in error. Gray and others (2000) show an example of a stream at low flow where instantaneous-value sediment discharges calculated from SSC data are more than an order of magnitude larger than those calculated from TSS data at similar flow rates. Glysson and others (2000; 2001) conclude that there appears to be no simple, straightforward way to relate TSS and SSC data unless pairs of TSS and SSC results are available for a site.

Part of the problem may be attributable to the origin of the TSS method and subsequent changes in the types of water for which it is recommended for use. The American Public Health Association and others (1971) intended the Total Suspended Matter Method (a precursor to the TSS method) to be suitable for "wastewaters, effluents, and polluted waters." In 1976, the American Public Health Association and others deemed the Total Suspended Matter Method as suitable for "residue in potable, surface, and saline waters, as well as domestic and industrial wastewaters in the range up to 20,000 mg/L." Gray and others (2000) conclude that the TSS analytical method is being misapplied to natural-water samples, and that the TSS method is fundamentally unreliable for that purpose. Additionally, the percentage of sand-size and finer particles can not be determined as a part of the TSS method, whereas it can be determined as a part of the SSC method.

The USGS (2000) policy on the collection and use of TSS data establishes that TSS concentrations and resulting load calculations of suspended material in water samples collected from open channel flow are not appropriate. The TSS analytical method can result in unacceptable large errors and is fundamentally unreliable to determine concentrations of suspended material in open channel flow. Therefore, based on these issues, the USGS standard for determining concentrations of suspended material in surface-water samples continues to be the SSC method of analysis (USGS, 2000).

These findings are directly relevant to sediment-load estimates in runoff from highways and urban areas. Highway and urban runoff tends to be rich in sand-size material (table 3); hence, TSS analytical results from samples collected may be substantially biased. As described previously, load estimates using TSS data can deviate by orders of magnitude from those calculated from SSC data.

To examine the applicability of TSS data in highway and urban runoff, analyses of paired SSC and TSS samples collected by the USGS from studies of highway sediments along I-93 in Boston, Mass. (Smith, 2000), and along I-894 in Milwaukee, Wisc. (Waschbusch, 2000), were examined (fig. 15). As with the natural water samples examined by Glysson and others (2000) and Gray and others (2000), results from the TSS analytical method have a substantial negative bias when compared to the SSC method. These data sets (Smith, 2000; Waschbusch, 2000) also indicate that the sand-size fractions can be substantial, and that the grain-size distributions vary considerably between samples within a storm and also vary considerably among storm-runoff periods (fig. 16). These TSS data are not representative of sediment loads from highways and cannot be quantitatively adjusted to produce SSC estimates because of the large variability in grain-size distributions from storm to storm. Analyses of these data sets, obtained from a coastal site and an interior sites in the conterminous United States, indicate substantial differences between TSS and SSC in highway-runoff data that are consistent with those reported by Glysson and others (2000) and Gray and others (2000). It is therefore incumbent upon the investigator to select consistent subsampling protocols, to clearly document site-specific conditions (such as the range of concentrations and PSDs) and to implement QA/QC measures to quantify the performance of the sample-analysis methods used.

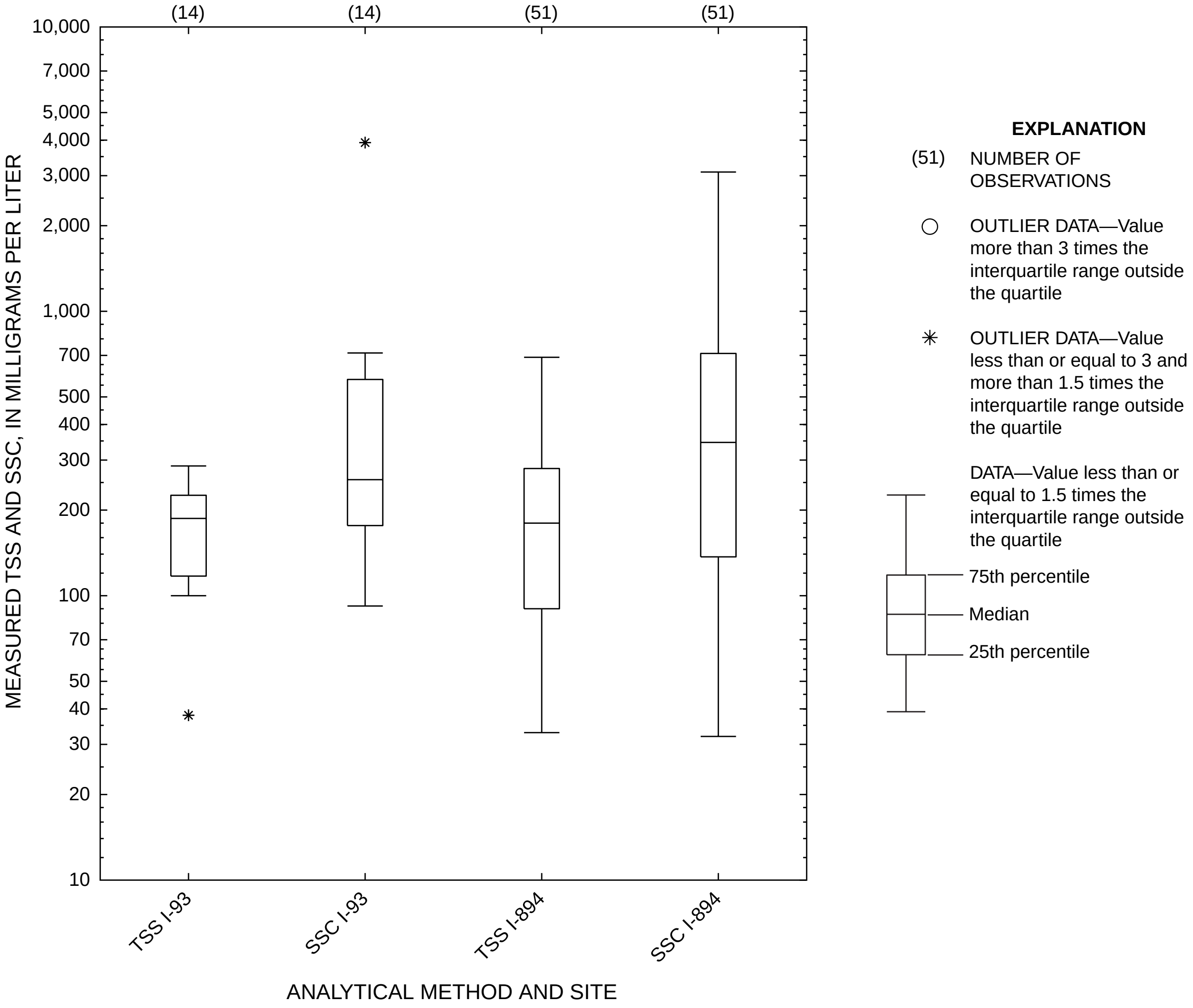


Figure 15. Distribution of measured total suspended solids (TSS) and suspended-sediment concentration (SSC) in highway-runoff samples collected along I-93 in Boston, Massachusetts, and I-894 in Milwaukee, Wisconsin, 1999–2000. (Data from Smith, 2000, and R.J. Waschbusch, USGS, written commun., 2000, respectively.)

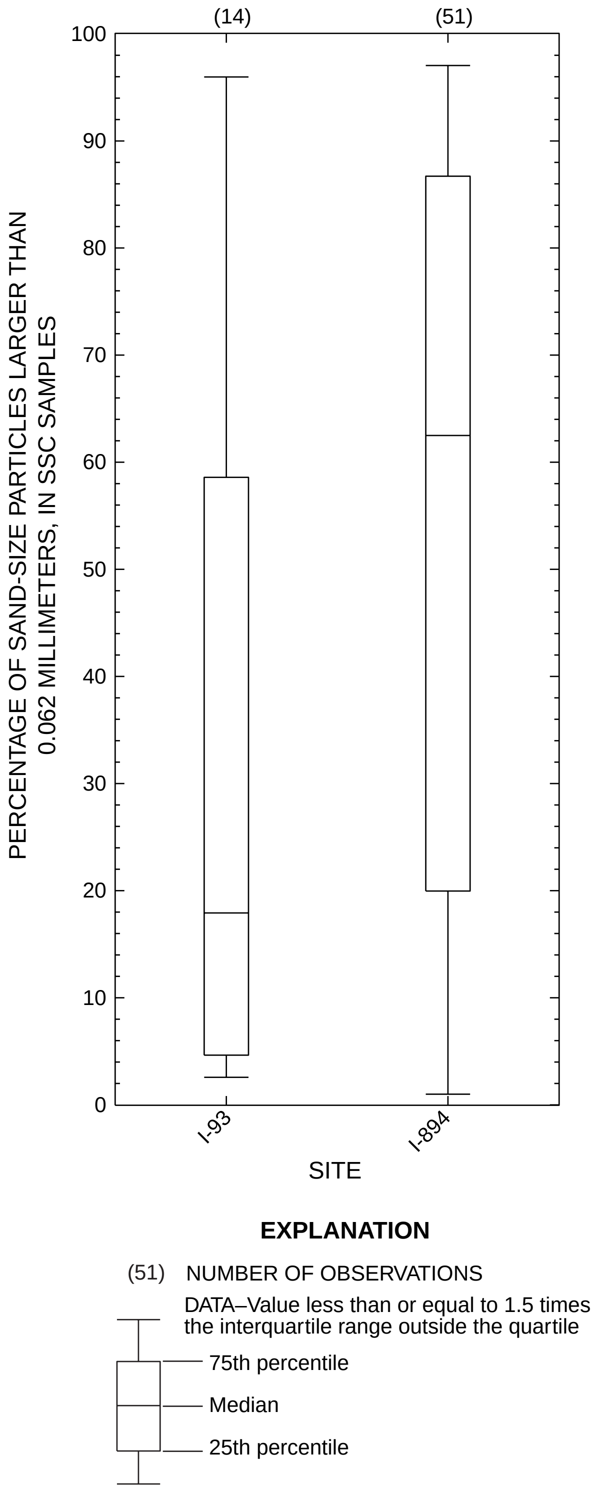


Figure 16. Distribution of the percentage of sand-size particles measured in suspended-sediment concentration (SSC) in highway-runoff samples collected along I-93 in Boston, Massachusetts, and I-894 in Milwaukee, Wisconsin, 1999–2000. (Data from Smith, 2000, and R.J. Waschbusch, USGS, written commun., 2000, respectively.)

Perhaps the broadest implication of this systematic problem in the TSS analysis method is for interpretation of the performance of sediment-removal BMPs. For example, figure 17 demonstrates the effect of the analysis method on the calculated removal efficiency of catch basins and oil-grit separators. These devices have a median removal efficiency of about 50 percent when the SSC analysis is used because these BMPs are relatively effective for removing sand-size particles. When the proportion of SSC associated with fine sediments (diameters of less than 0.063 mm) are calculated, this "efficiency" compares well with the TSS efficiency calculated using the TSS analysis (fig. 17). These efficiencies are less than the efficiencies calculated using the SSC analysis because these devices do not effectively retain fine-grained sediments. When the TSS analysis method is used, these artifacts will have several important consequences for the assessment, design, and maintenance of BMPs, including:

- the variability in grain-size distributions for different periods of storm runoff and site to site may confound meaningful analysis of BMP effectiveness;
- the necessary volume of sediment-retention structures may be underdesigned; and
- maintenance schedules for sediment removal from these structures may not be adequate because sedimentation rates may be greater than expected.

These problems may arise if decisions are based on expected TSS capture efficiencies because the TSS values do not reflect the actual sediment retention of larger grain sizes, which are characterized by the SSC method. Problems in analysis, interpretation, and design using the TSS method would be exacerbated in areas where sand is used for winter maintenance.

Particle-Size Distribution

Particle-size distribution (PSD) is the percentage measured by mass, volume, or number of particles in a range of specific sizes, such as those shown in table 4. The American Society for Testing and Materials (ASTM) (ASTM, 1997a; 1997b) has identified information about the PSD to be a necessary component of data sets for environmental sediments.

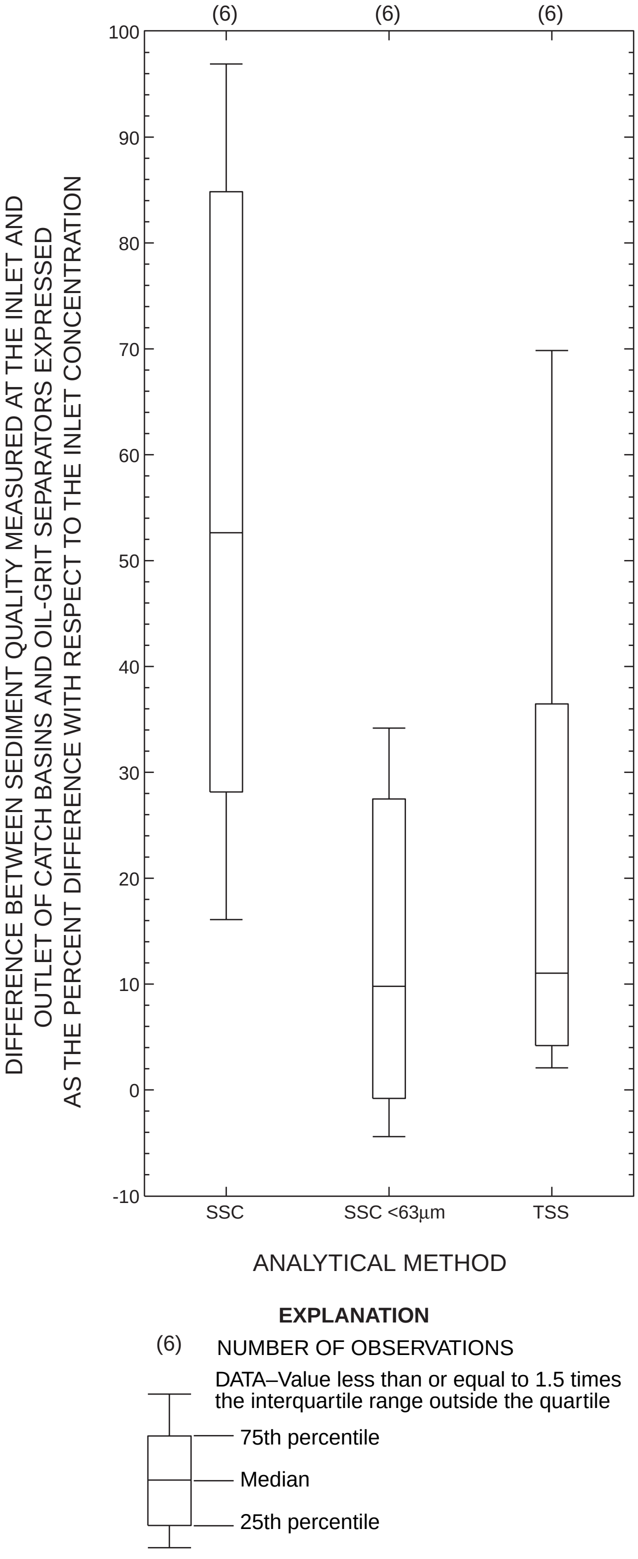


Figure 17. Distribution of differences in sediment measured at the inlet and outlet of catch basins and oil-grit separators in highway-runoff samples collected along I-93 in Boston, Massachusetts (data from Smith, 2000).

Particle-size analysis is useful for study of the chemistry (Breault and Granato, 2001), transport, and fate of sediment in highway and urban runoff, BMPs, and receiving waters (Kobriger and Geinopolos, 1984). Particle-size analysis may be a measure of sample integrity because the representativeness of individual samples collected may be compared to the grain-size distributions measured for each site. For example, an unusually high sediment concentration may be caused by relatively few sand-size particles in a sample in which the materials at a site are predominantly fine grained, because one medium-size sand grain has the equivalent mass of about 1,000 medium-size silt grains given equal densities. Traditional manual methods used for determining particle size are dry sieve, wet sieve, visual-accumulation (VA) tube, bottom withdrawal (BW) tube, pipet, and microscopy (Guy, 1969; International Standards Organization, 1997a; Percival and Lindsay, 1997; ASTM, 1999). Electronic methods used for determining particle size include the electrical sensing-zone principal (Coulter Counter), x-ray sedimentation (Sedigraph), laser time of transition (Brinkman Particle Size Analyzer), laser diffraction spectroscopy, and light-optically based image analysis (Matthes and others, 1991; Percival and Lindsay, 1997; Jongedyk, 1999). Each method has different effective size ranges, effective analysis concentrations, and sediment quantity requirements (Guy, 1969; Percival and Lindsay, 1997). For example, sieve analysis has a lower limit of about 0.062 mm, whereas pipet analysis is most effective in the range between 0.002 and 0.062 mm (Guy, 1969; Matthes and others, 1991). Each method is also based on design assumptions that may affect the interpretation of results. For example, grain sizes produced by the pipet and Sedigraph methods are based on the assumption that all sediments in the sample have the specific gravity (and therefore the effective fall velocity) of similar shaped quartz particles (Percival and Lindsay, 1997). It is therefore incumbent upon the investigator to select consistent PSD analysis protocols designed for the concentrations, size range, and other characteristics typical of highway- and urban-runoff sediments. It is also necessary to clearly document the methods used to implement QA/QC measures to quantify the performance of PSD methods (Matthes and others, 1991; Knott and others, 1992; 1993).

Specific Gravity

Specific gravity is the ratio of the unit weight of the sediment to the unit weight of water at 4˚C. It is a unitless measure of density determined by direct measurement of the weight and volume of the sediment sample (Guy, 1969). The ASTM (ASTM, 1997a) has identified specific gravity as a necessary component of data sets for characterization of environmental sediments. Knowledge of specific gravity of runoff sediments provides information about the settleability of these sediments. For example, Whipple and Hunter (1981) measured substantial differences among the settling rates of different fractions in urban-runoff samples. As previously mentioned, knowledge of the specific gravity may affect interpretation of PSD analysis. It may also provide information about the relative contribution of inorganic and organic components in runoff sediments because the organic fraction is usually less dense than the inorganic (soil) fractions (Butler and others, 1996a). Typically, mineral species (inorganics) have specific gravities that are generally between about 2.5 and 3.5, (Dunn and others, 1980), whereas the organic fraction of stormwater solids are between about 1.1 to 2.5 (Butler and others, 1996a).

Other Sediment Measurements

Other sediment measurements of potential interest for highway and urban runoff and the design and maintenance of structural BMPs include those of settling velocity, the organic content of sediment, particle shape, and specific surface area. The settling velocity is a primary measure that incorporates a number of factors (grain size and shape, and specific gravity) germane to the treatability of solids in runoff. Methods for determination of settling velocity are described by Guy (1969) and Clesceri and others (1998). As presented previously, the organic content of suspended sediments affects the average specific gravity and could thereby affect the interpreted PSD (Guy, 1969). Particle shape represents the aspect ratios of individual sediments and affects settling velocities and PSD measurements (Vanoni, 1975; ASTM, 1997a). The specific surface area is a function of the shape and texture of the sediments and is an important characteristic of the sediment's ability to act as a carrier of contaminants (Horowitz and Elrick, 1987; Sansalone and others, 1996; Percival and Lindsay, 1997; Sansalone and others, 1998).

DATA-QUALITY CONSIDERATIONS

Data quality, comparability, and utility are important considerations when collecting, processing, and analyzing sediment samples and interpreting sediment data for studies of highway and urban runoff. Results from a sediment study must also be readily transferable from electronic databases, and useful to resource managers and regulators. To meet these objectives, supporting ancillary information must be available that documents the methods and procedures that are used and describes QA/QC procedures that are employed.

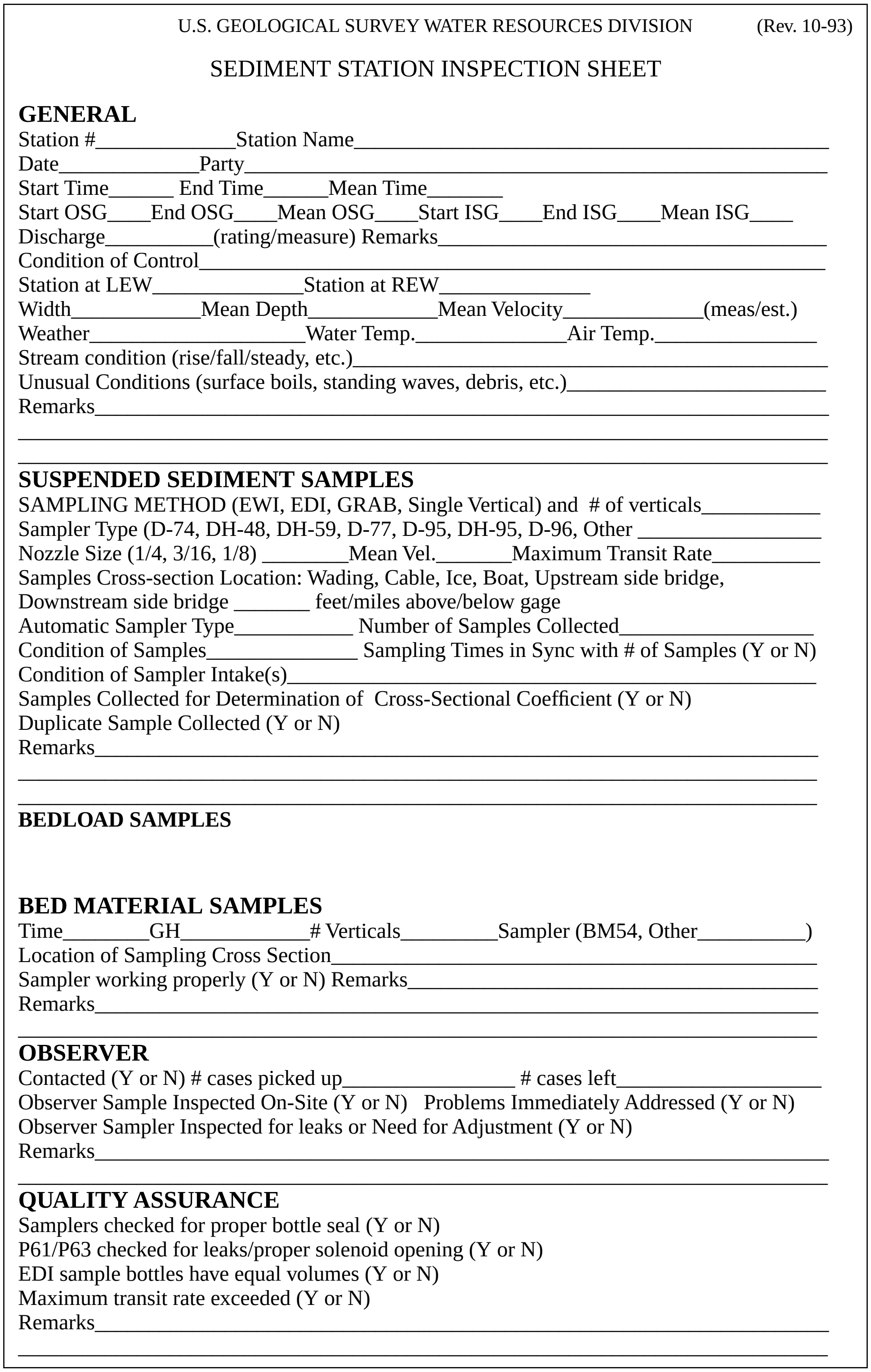
Documentation of Methods

Techniques for the collection, processing, and analysis of sediments in highway and urban runoff and in fluvial systems are continually being developed and refined. New techniques and improvements of existing techniques serve to enhance the accuracy and cost-effectiveness of monitoring programs. This evolution of the science, however, makes it increasingly difficult to compare data over time. This is of particular concern to long-term and broad-scale monitoring and assessment programs that draw upon the expertise of a wide range of scientists. The exclusive use of published and proven procedures would help alleviate this concern, but could impede scientific advancement. Studies designed to compare the results of new and existing methods and the practice of thoroughly documenting and describing all techniques employed, however, can help resolve these problems (USGS, 1991, ITFM, 1995a; 1995b).

Many of the data elements necessary to document methods and procedures used are discussed in Glysson (1989), USGS (1991), ASTM (1997a), and Edwards and Glysson (1999), and are include on sediment-station inspection sheets developed by the USGS (1991). Standard sediment-station field inspection forms were designed to record who visited the site, the date and time of each visit, site conditions, the status of equipment and instrumentation, records of instrument calibration, and other information pertinent to the operation of the station that are necessary for data verification (USGS, 1991). One example of a modified sediment station inspection sheet (Robert Holmes, USGS, written commun., 1994) is provided to illustrate information necessary for documentation of local, regional, and national data sets (fig. 18). The general elements necessary to document the station and field conditions include: station information (linked to detailed location and site characteristics data in the USGS national water data bases), the date and time sediment data are collected, and climatic and hydrologic conditions. Elements necessary to document sample collection methods include the type of sampler, the location in the channel where samples are collected, and the number of and condition of samples collected. When bed-material samples are collected, sampling methods for these samples must be documented as well. Information about the observer is also necessary, especially if sampling is conducted for regulatory programs, which may require chain-of-custody information (USEPA, 1992; Granato and others, 1998). Information about field quality-assurance steps also are recorded appropriately on the field inspection sheet. Inspection sheets also represent checklists to improve the consistency and comparability of data-collection efforts. For example, if sample water is spilled during transport to the laboratory, field sheet records and practices, such as marking the bottle's water level, may facilitate analysis and interpretation of data. These field sheets should have sufficient space to record remarks describing field conditions such as trash accumulation at the sampling sites, malfunctioning equipment, and other factors that may affect the validity, comparability, or representativeness of samples. These field sheets may be customized to address the data-quality objectives of an individual study and to address site-specific conditions (USGS, 1991). For example, a water-quality field inspection form designed for use of automated data-collection methods and automatic pumping samplers at a highway-runoff monitoring station is presented in figure 19 (Smith, 2000). All sediment data as well as methods and procedures used in data collection and analysis should be stored in an electronic database(s) with several hard copies stored in alternative locations to avoid the loss of valuable information.

Quality Assurance and Quality Control

In sediment data-collection programs, quality assurance/quality control (QA/QC) efforts are an integral component of all sample collection processing, and analysis operations. Quality-assurance protocols for water-quality data collection have improved substantially since the early 1980s. The guidelines developed by Edwards and Glysson (1999) serve as protocols for sediment data collection by most Federal agencies that collect these data as part of their mission. These guidelines also are consistent with the Wilde and others (1999a) protocols for collection of water samples. Knott and others (1993) provide a quality-assurance plan for field collection, laboratory processing, and office analysis of sediment data. Protocols for collecting stream-water and bed-sediment samples for the National Water-Quality Assessment Program (Shelton, 1994; Shelton and Capel, 1994) are consistent with Edwards and Glysson (1999). Among the protocols relevant to sediment data developed by the International Standards Organization (ISO) are Methods for Measurement of Suspended Sediment (International Standards Organization, 1993), Guidance on Sampling Rivers and Streams (International Standards Organization, 1990b), Guidance on Sampling of Bottom Sediments (International Standards Organization, 1995), and Determination of Turbidity (International Standards Organization, 1990a). Standards relevant to sediment by the ASTM include Terminology for Fluvial Sediment (ASTM, 1998c), Standard Guide for Sampling Fluvial Sediment in Motion (ASTM, 1998a), Standard Guide for Core-Sampling Submerged, Unconsolidated Sediment (ASTM, 1995), Standard Guide for Elements of a Complete Data Set for Non-Cohesive Sediments (ASTM, 1997a), Standard Guide for the Selection of Maximum Transit Rate Ratios and Depths for the U.S. Series of Isokinetic Suspended-Sediment Samplers (ASTM, 1998b), Standard Guide for Monitoring Sediment in Watersheds (ASTM, 1997b), and Standard Guide for Collection, Storage, Characterization, and Manipulation of Sediments for Toxicological Testing (ASTM, 1994).



U.S. GEOLOGICAL SURVEY WATER RESOURCES DIVISION (Rev. 10-93)

SEDIMENT STATION INSPECTION SHEET

GENERAL

Station #_____________Station Name____
Date_____________Party____
Start Time______ End Time______Mean Time_______
Start OSG____End OSG____Mean OSG____Start ISG____End ISG____Mean ISG____
Discharge__________(rating/measure) Remarks____________________________________
Condition of Control____
Station at LEW______________Station at REW______________
Width____________Mean Depth____________Mean Velocity_____________(meas/est.)
Weather____________________Water Temp._______________Air Temp.________________
Stream condition (rise/fall/steady, etc.)____
Unusual Conditions (surface boils, standing waves, debris, etc.)________________________
Remarks____
____
____

SUSPENDED SEDIMENT SAMPLES

SAMPLING METHOD (EWI, EDI, GRAB, Single Vertical) and # of verticals___________
Sampler Type (D-74, DH-48, DH-59, D-77, D-95, DH-95, D-96, Other _________________
Nozzle Size (1/4, 3/16, 1/8) ________Mean Vel._______Maximum Transit Rate__________
Samples Cross-section Location: Wading, Cable, Ice, Boat, Upstream side bridge,
Downstream side bridge _______ feet/miles above/below gage
Automatic Sampler Type___________ Number of Samples Collected__________________
Condition of Samples______________ Sampling Times in Sync with # of Samples (Y or N)
Condition of Sampler Intake(s)____
Samples Collected for Determination of Cross-Sectional Coefficient (Y or N)
Duplicate Sample Collected (Y or N)
Remarks____
____
____

BEDLOAD SAMPLES

BED MATERIAL SAMPLES

Time________GH____________# Verticals_________Sampler (BM54, Other__________)
Location of Sampling Cross Section____
Sampler working properly (Y or N) Remarks_______________________________________
Remarks____
____

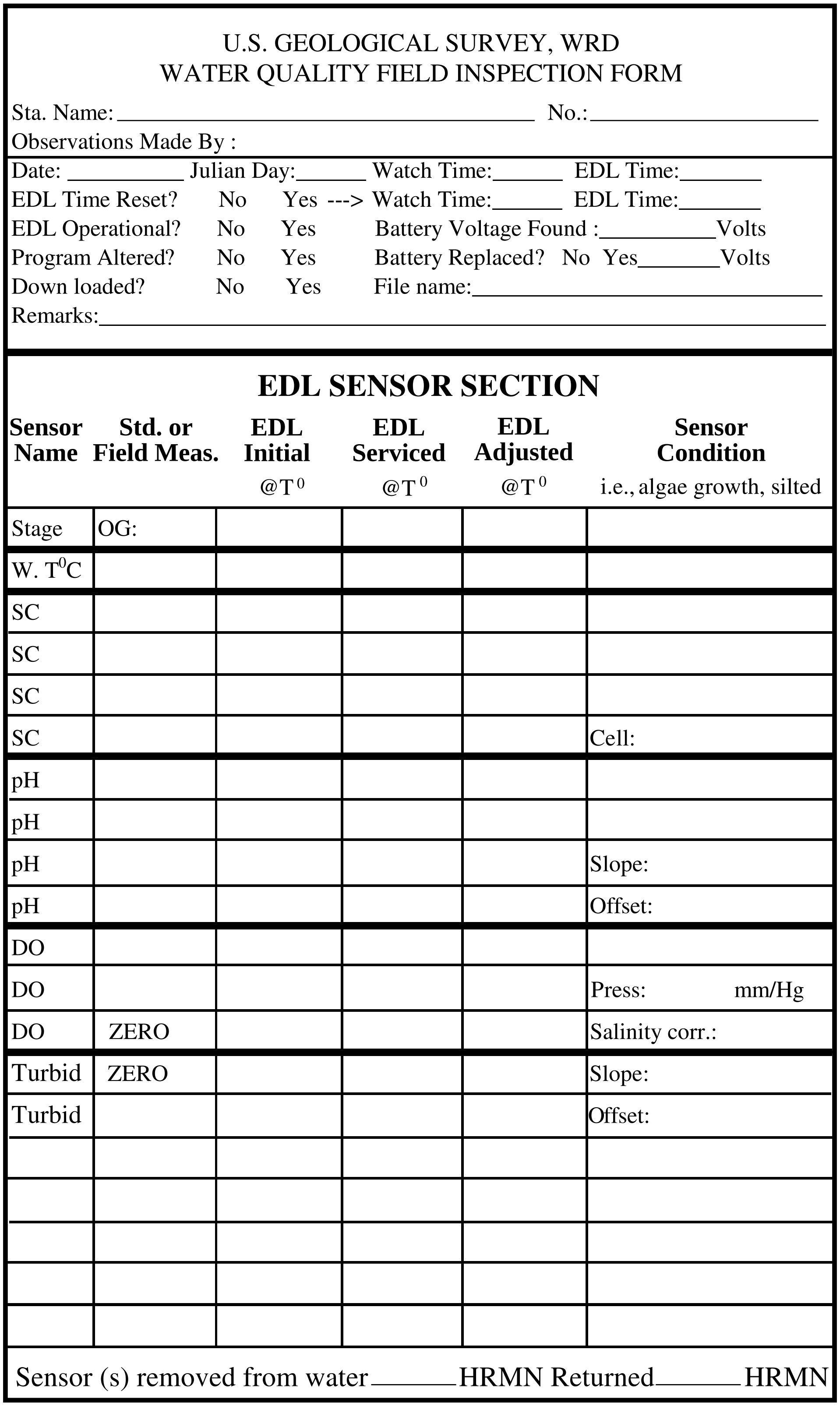
OBSERVER

Contacted (Y or N) # cases picked up________________ # cases left__________________
Observer Sample Inspected On-Site (Y or N) Problems Immediately Addressed (Y or N)
Observer Sampler Inspected for leaks or Need for Adjustment (Y or N)
Remarks____
____

QUALITY ASSURANCE

Samplers checked for proper bottle seal (Y or N)
P61/P63 checked for leaks/proper solenoid opening (Y or N)
EDI sample bottles have equal volumes (Y or N)
Maximum transit rate exceeded (Y or N)
Remarks____
____

Figure 18. Field inspection sheet to record measurements and stream conditions observed during a visit to a sediment-measurement site (modified from Robert Holmes, USGS, written commun., 1994).



U.S. GEOLOGICAL SURVEY, WRD
WATER QUALITY FIELD INSPECTION FORM

Sta. Name:____________________________________ No.:____________________

Observations Made By :

Date: __________ Julian Day:______ Watch Time:______ EDL Time:_______

EDL Time Reset? No Yes ---> Watch Time:______ EDL Time:_______

EDL Operational? No Yes Battery Voltage Found :__________Volts

Program Altered? No Yes Battery Replaced? No Yes_______Volts

Down loaded? No Yes File name:______________________________

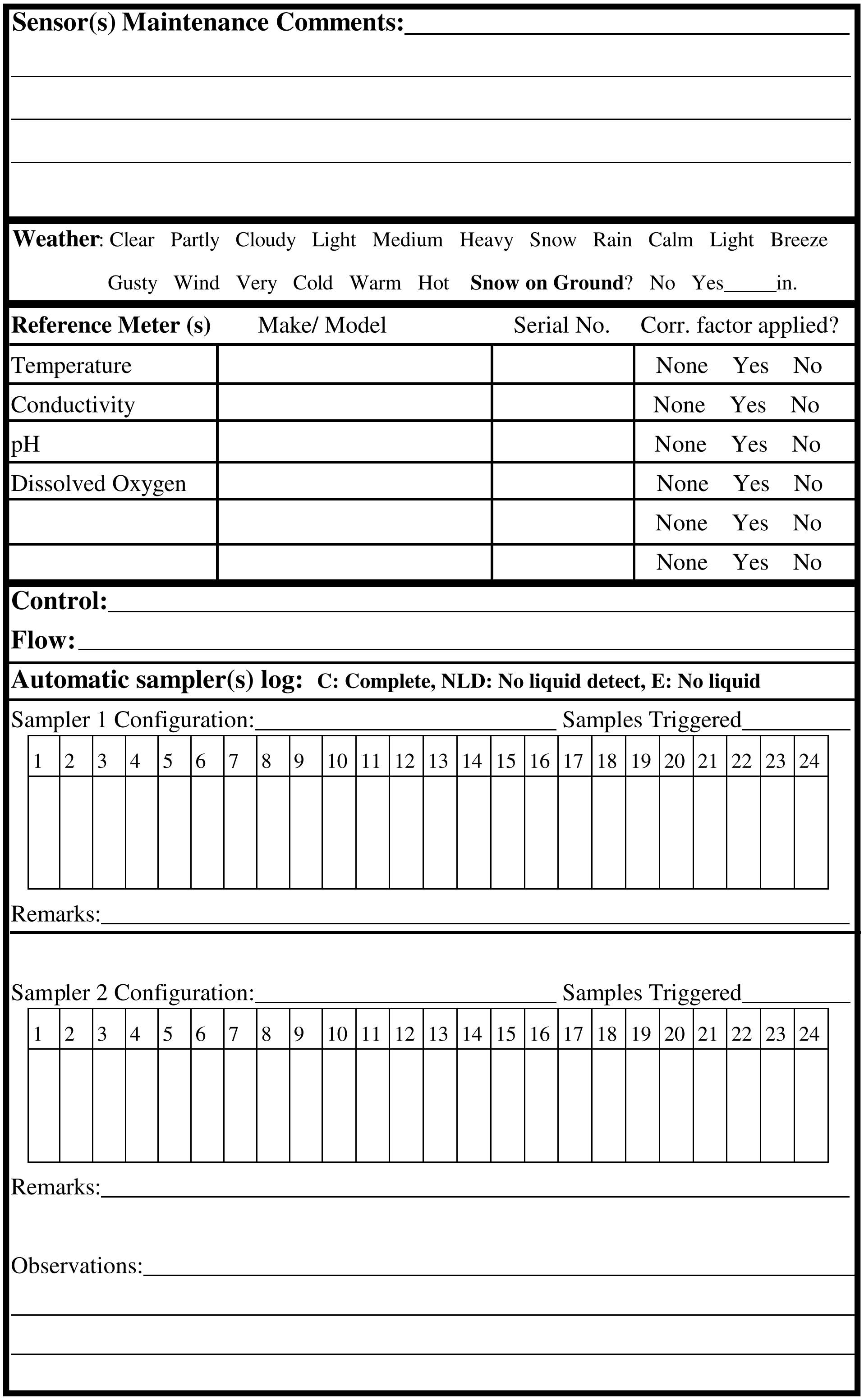
Remarks:____

EDL SENSOR SECTION

Sensor Name	Std. or Field Meas.	EDL Initial @T ^{0}	EDL Serviced @T ^{0}	EDL Adjusted @T ^{0}	Sensor Condition i.e., algae growth, silted
Stage	OG:				
W. T^{0}C					
SC					
SC					
SC					
SC					Cell:
pH					
pH					
pH					Slope:
pH					Offset:
DO					
DO					Press: mm/Hg
DO	ZERO				Salinity corr.:
Turbid	ZERO				Slope:
Turbid					Offset:

Sensor (s) removed from water______HRMN Returned______HRMN

Figure 19. Field inspection sheet customized for automatic data collection at a highway-runoff monitoring station (Smith, 2000).



Sensor(s) Maintenance Comments:

Weather: Clear Partly Cloudy Light Medium Heavy Snow Rain Calm Light Breeze
Gusty Wind Very Cold Warm Hot **Snow on Ground**? No Yes_____in.

Reference Meter (s)	Make/ Model	Serial No.	Corr. factor applied?
Temperature			None Yes No
Conductivity			None Yes No
pH			None Yes No
Dissolved Oxygen			None Yes No
			None Yes No
			None Yes No

Control:

Flow:

Automatic sampler(s) log: C: Complete, NLD: No liquid detect, E: No liquid

Sampler 1 Configuration:_________________________ Samples Triggered_________

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24

Remarks:

Sampler 2 Configuration:_________________________ Samples Triggered_________

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24

Remarks:

Observations:

Figure 19. Field inspection sheet customized for automatic data collection at a highway-runoff monitoring station (Smith, 2000)—*Continued.*

QA/QC efforts need to be established at the beginning of a project to ensure that sediment measurements are accurate and representative of the hydrologic system investigated (Guy 1969; Matthes and others 1991; Knott and others 1992 and 1993; and USGS, 1998a; 1998b; 1999a). QA/QC programs are especially important for all phases of stormwater-flow and water-quality investigations (Clark and Whitfield, 1993; Brown and others, 1995; and Jones, 1999). An effective QA/QC program for sediment data-collection programs would include:

- Frequent and routine site visits by trained/experienced field personnel;
- Redundant methods for measuring precipitation and stormwater flow (Church and others, 1999);
- Technical training for project personnel;
- Frequent review by project personnel of field and laboratory sediment data;
- Quality audits, in the form of periodic internal reviews; and
- Quality audits, in the form of periodic external reviews.

Field instrumentation must be maintained operational and in good working order to ensure the integrity of the data collected, and derivative data must be reviewed on-site or immediately in the office following the site visit. The site must be inspected for debris accumulation, natural corrosion of equipment, vandalism, and other potential problems. Debris can affect measurements by blocking sample-collection intakes and by affecting necessary flow measurements (Church and others, 1999). Frequent maintenance and calibration of equipment and instrumentation is necessary because of the difficult monitoring environment. Field inspection sheets also are part of quality-assurance efforts and these inspection sheets should be archived with project records, and at the least, use of these forms should be mentioned in the QA/QC documentation in project reports (Guy, 1969; Matthes and others, 1991; Knott and others, 1992 and 1993; USGS, 1998a).

Periodically, it is necessary to do a more detailed review using the entire data record, field notes, and other available information to detect errors or anomalous data. For example, a comparison between flow, turbidity, and measured sediment concentrations for a given runoff period could indicate a bias in one or the other measurement system if the relation for this storm departed from normal values for the site in question. Analysis of field records, including calibration records, adjustments to measured values, and other information, when compared to the data record, may indicate systematic bias, long-term drift, or an abrupt change in the performance of the instrumentation. Quality audits, in the form of periodic internal reviews, are necessary to monitor and implement the project QA/QC program (Jones, 1999). Internal audits establish that the project has a QA/QC plan and that it is being implemented and documented. Also, periodic internal reviews serve as a method to provide technical feedback from subject-matter experts to examine and address problems and (or) potential problems in the data-collection program. Internal reviews should ensure that trained/experienced personnel are available for frequent and routine site visits, that appropriate and robust monitoring systems are in place and collecting data, and that project personnel are examining and interpreting data using appropriate methods on a timely basis. These internal reviews could take place at the proposal stage of the project and then again when the project is about 10-, 40-, and 70-percent complete, or at fixed intervals, such as quarterly or semiannually.

Quality audits, in the form of periodic external reviews, are also necessary to monitor and implement the project QA/QC program (Jones, 1999). External audits should examine project plans, project data, project records, and QA/QC documentation to ensure that study objectives are being met, and to ensure that study objectives will meet the goals of the monitoring project. External reviews should ensure that the project information is properly documented and that the documentation is accessible. Within the USGS, external quality audits include periodic reviews by technical specialists at different levels in the chain of command above the local organizational unit and by technical specialists from discipline offices such as the Office of Surface Water, the Office of Ground Water, the Office of Quality Water, and the Branch of Quality Systems.

To ensure that the sediment data produced or used for highway- and urban-runoff studies are of a known quality and are sufficient to provide long-term comparability and consistency, sediment laboratory quality-assurance programs are needed (USGS, 1998a; Gordon and Newland, 2000; Gordon and others, 2000). It is therefore necessary to document the name and location of the laboratory, methods used, and the performance of the laboratory in one or more quality-assurance programs. The parameters that are typically evaluated as indicators of quality include accuracy, precision, bias, detection limits or performance range, and interference. In analytical chemistry, these performance parameters can be addressed by the use of internal standards and spiked, blind, and blank samples (Jones, 1999).

SUMMARY

This report addresses technical issues pertinent to the methods for the collection, processing, and analysis of water samples for concentrations and physical characteristics of sediment in highway and urban runoff, best management practice (BMP) structures, and receiving waters. The report focuses on sediment-transport issues related to highway use, as opposed to highway construction. Information presented in this report is also applicable for many issues related to sediment in urban runoff from stormwater. Many technical issues associated with sample collection, processing, and analysis must be addressed in order to produce valid (useful for intended purposes), current, and technically defensible data for local, regional, and national information needs. All aspects of sediment data-collection programs need be evaluated and quality-assurance and quality-control (QA/QC) data need be documented so that the comparability and representativeness of data obtained for highway- and urban-runoff studies may be assessed.

The erosive capacity of runoff from highways and urban areas can be substantial because runoff from paved areas, ditches, and storm drains can be hydraulically supercritical and turbulent. The area contributing to surface runoff is usually small, water-surface slope is relatively steep, runoff is concentrated, and surface roughness is low. The mode of transport can be described from the origin of the material as bed-material load and wash load, or operationally (as measured by sediment samplers) as suspended load and bedload. As particle-size distributions (PSDs) increase to include sand-size material, a vertical gradient tends to form with larger particles concentrating nearer the bed. Although some coarser sediment can move as bedload, most highway drainage systems are designed to carry water and maintain sediments in suspension so that the volumetric capacity of the highway conveyance structures is not diminished. Sediment in highway runoff comprises particles derived from atmospheric dust, pavement degradation, vehicle rust, tire degradation, trash, rocks, natural soils, biological materials, or chemical precipitates that are transported by, suspended in, or deposited in flowing water. The rapid response of flow volume and velocity to changes in precipitation of highway and urban runoff drainages complicates the sampling and analysis of sediment in these systems. Therefore, it is necessary to use methods that are suitable to this harsh monitoring environment and to support data collected using QA/QC for these methods.

Representative sample collection for measurement of sediment in highway and urban runoff involves a number of interrelated issues. Temporal and spatial variability in runoff can be large, based on a combination of factors including volume and intensity of precipitation, rate of snowmelt, and features of the drainage basin such as drainage area, slope, infiltration capacity, channel roughness, and storage characteristics. The remoteness or inaccessibility of sites makes it difficult to monitor runoff manually, and it can be difficult to get personnel to the site before the onset of runoff. Costs associated with deployment of trained and properly equipped personnel in addition to uncertainties related to the location and timing of runoff, can be prohibitive for manual sampling of storm-runoff periods. The difficulty in collecting a relatively large number of samples during storm runoff and the dangers to field personnel operating in adverse conditions (including traffic, weather, reduced visibility, and rapid changes in discharge) reduces the practicality of manual sampling efforts. In contrast, automatic samplers can be deployed before and samples can be retrieved after storm runoff, reducing logistics and increasing the safety for field personnel. Automatic pumping samplers typically collect water from the water column by suction and control the sampling rate using the pump speed. Passive sampling devices typically are installed in the flow path and control the sampling rate by placement, orientation, and design of the water intake. Each type of sampler has benefits and design limitations, which must be recognized and quantified to produce representative data. Indirect sediment-measurement methods also may be useful as supplementary and (or) surrogate means for monitoring sediment in runoff. These methods include analysis of available bottom materials, turbidity, and other indirect sediment-measurement methods. All these methods have benefits and design limitations, which must be recognized and quantified to produce representative data.

Appropriate sample processing methods are determined by the characteristics of the water sampled and by the analytical and interpretive methods used for data reduction. Water-quality data for highway and urban runoff are generally reported as event-mean concentration EMC to provide summary values that can be used to compare measurements from individual runoff periods at a site or to compare, between sites, measurements from populations of storms. An EMC may be determined by collecting a bulk sample, by physically compositing a number of discrete samples, or by mathematically calculating a flow-weighted composite from analysis of multiple discrete samples taken during the runoff period. Each sample type has certain pre-analysis processing requirements that may affect measured sediment concentrations. Each sample type has certain pre-analysis processing requirements that typically include homogenization and subsampling. Homogenization methods are designed to produce representative subsamples for the analysis process. Subsampling methods are designed to enable different analytical determinations to be made on the subsamples. Processing artifacts can be substantial if the methods used are not appropriate for the concentrations and PSDs present in the samples collected.

Representative analysis of concentrations and physical characteristics of sediment in highway and urban runoff involves a number of complex issues. The two analytical methods most commonly used to determine sediment concentration in a water sample are the suspended-sediment concentration (SSC) method and the total suspended solids (TSS) method. The terms SSC and TSS are often used interchangeably in the literature to describe the concentration of solid-phase material suspended in a water-sediment mixture. The SSC analytical procedure, entails measurement of the entire mass of sediment and the net weight for the entire sample, whereas only a part of the water-sediment mixture (a subsample) is typically analyzed in the TSS method. Although these methods are commonly expected to produce comparable results, recent research indicates systematic differences between the methods. Two studies comparing laboratory analysis results for TSS and SSC found that TSS analysis does not represent the larger grain-size fractions, and therefore, consistently tends to underrepresent the true sediment concentrations. Furthermore, these studies determined that relations between TSS and SSC concentrations are not transferable among sites, even when grain-size distribution information is available. An analysis of data from a coastal and an interior highway in the United States indicates that TSS underrepresents the true sediment concentration, and that relations between TSS and SSC concentrations are not transferable from site to site even when grain-size distribution information is available. TSS data may be fundamentally unreliable and published TSS data may not represent sediment concentrations and loads from highways. When the TSS analysis method is used, these artifacts may have important consequences for the assessment, design, and maintenance of sediment removal BMPs, including consideration that the variability in grain-size distributions from storm to storm and site to site will confound meaningful analysis of BMP effectiveness, that the necessary volume of sediment retention structures may be underdesigned, and that maintenance of these structures may not be adequate because sedimentation rates are greater than expected. These common problems arise if decisions are based on expected TSS capture efficiencies because the TSS values do not reflect the actual sediment retention of larger grain sizes, which are characterized by the SSC method. Further research, however, may be necessary to quantity the scope of this issue in different highway and urban settings.

Data quality, comparability, and utility are important considerations for the collection, processing, and analysis of sediment samples and interpretation of sediment data for highway- and urban-runoff studies. Results from a sediment study must also be readily transferable and useful to resource managers and regulators. To meet these objectives, supporting ancillary information must be available that documents the methods and procedures that are used and describes QA/QC procedures that are employed for highway-runoff studies. Valid, current, and technically defensible protocols for collecting, processing, and analyzing sediment data for the determination of highway-runoff quality therefore need to be documented with study results.

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Chapter 6. A Synopsis of Technical Issues of Concern for Monitoring Trace Elements in Highway and Urban Runoff

By Robert F. Breault *and* Gregory E. Granato

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A Synopsis of Technical Issues of Concern for Monitoring Trace Elements in Highway and Urban Runoff

By Robert F. Breault *and* Gregory E. Granato

Abstract

Trace elements, which are regulated for aquatic life protection, are a primary concern in highway- and urban-runoff studies because stormwater runoff may transport these constituents from the land surface to receiving waters. Many of these trace elements are essential for biological activity and become detrimental only when geologic or anthropogenic sources exceed concentrations beyond ranges typical of the natural environment. The Federal Highway Administration and State Transportation Agencies are concerned about the potential effects of highway runoff on the watershed scale and for the management and protection of watersheds. Transportation agencies need information that is documented as valid, current, and scientifically defensible to support planning and management decisions. There are many technical issues of concern for monitoring trace elements; therefore, trace-element data commonly are considered suspect, and the responsibility to provide data-quality information to support the validity of reported results rests with the data-collection agency.

Paved surfaces are fundamentally different physically, hydraulically, and chemically from the natural surfaces typical of most freshwater systems that have been the focus of many trace-element-monitoring studies. Existing scientific conceptions of the behavior of trace elements in the environment are based largely upon research on natural systems, rather than on systems typical of pavement runoff. Additionally, the logistics of stormwater sampling are difficult because of the great uncertainty in the occurrence and magnitude of storm events. Therefore, trace-element monitoring programs may be enhanced if monitoring and sampling programs are automated. Automation would standardize the process and provide a continuous record of the variations in flow and water-quality characteristics.

Great care is required to collect and process samples in a manner that will minimize potential contamination or attenuation of trace elements and other sources of bias and variability in the sampling process. Trace elements have both natural and anthropogenic sources that may affect the sampling process, including the sample-collection and handling materials used in many trace-element monitoring studies. Trace elements also react with these materials within the timescales typical for collection, processing and analysis of runoff samples. To study the characteristics and potential effects of trace elements in highway and urban runoff, investigators typically sample one or more operationally defined matrixes including: whole water, dissolved (filtered water), suspended sediment, bottom sediment, biological tissue, and contaminant sources. The sampling and analysis of each of these sample matrixes can provide specific information about the occurrence and distribution of trace elements in runoff and receiving waters.

There are, however, technical concerns specific to each matrix that must be understood and addressed through use of proper collection and processing protocols. Valid protocols are designed to minimize inherent problems and to maximize the accuracy, precision, comparability, and representativeness of data collected. Documentation, including information about monitoring protocols, quality assurance and quality control efforts, and ancillary data also is necessary to establish data quality. This documentation is especially important for evaluation of historical trace-element monitoring data, because trace-element monitoring protocols and analysis methods have been constantly changing over the past 30 years.

INTRODUCTION

Trace elements that are considered contaminants have been a focus of highway- and urban-runoff studies because stormwater runoff may be a source of trace elements that are regulated for the protection of aquatic life (Gupta and others, 1981; Driscoll and others, 1990; Makepeace and others 1995; Young and others, 1996). In highway- and urban-stormwater literature, the term metal is usually used to describe a trace element that has adverse effects on aquatic biota at relatively low concentrations. The trace elements included in these studies, however, commonly were measured at concentrations that were above the detection limits for laboratory analysis-techniques used in runoff studies during the 1960's, 1970's, and early 1980's (Gupta and others, 1981; Athayde and others, 1983).

Trace element concentration, transport and fate are difficult to quantify, especially in stormwater-runoff studies. Determination of accurate trace element data in runoff studies is made difficult by the complexity of the physical and chemical processes involved and the difficult monitoring environment. Storms occur at random, and when they do occur the intensity of precipitation and the resultant volume and quality of runoff can vary by orders of magnitude within a storm and between storms (Spangberg and Niemczynowicz, 1992; Granato and Smith, 1999). Highway runoff is a complex mixture. It can include constituents from atmospheric deposition, vehicles, the highway, and many other sources. The physicochemical processes that influence the quality of highway runoff also are complex (Bricker, 1999). Large variations in values of explanatory variables (such as traffic volume, antecedent conditions, and precipitation characteristics) that characterize runoff quality and quantity within a storm, between storms, from season-to-season, and from year-to-year may preclude quantitative interpretation of cause and effect relations (Driscoll and others, 1990). Furthermore, the logistics of stormwater sampling are demanding (USEPA, 1992a).

Highway-runoff contaminants of concern include trace elements, inorganic salts, solids, organic compounds, and pathogens that accumulate on the road surface as a result of local and regional atmospheric deposition and regular highway operation and maintenance activities (Smith and Lord, 1990; Lopes and Dionne, 1998; Buckler and Granato, 1999). Historically, trace elements have been the prime focus of most state- and federal-highway runoff studies and include, but are not limited to, the elements cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), lead (Pb), manganese (Mn), nickel (Ni), and zinc (Zn). Trace elements washed off the highway during rain storms, snow storms, or periods of snow-melt may have adverse effects on ecosystems and receiving waters if effective measures are not taken for attenuation of potential contaminants (Buckler and Granato, 1999).

The Federal Highway Administration (FHWA) and State Transportation Agencies (SDOT) have conducted an extensive program of water-quality monitoring and research since the early 1970's. SDOTs and the FHWA are increasingly concerned about potential effects of highway runoff at the watershed scale and responsibilities for management and protection of watersheds (Driscoll and others, 1990; Bank, 1996). The increasing environmental emphasis on non-point sources of contamination such as highway runoff as a component of total maximum daily loads (TMDLs) for watersheds will further increase the need for reliable information with which to make planning and management decisions (Rossman, 1991; Shoemaker and others, 1997). Historically, data from State and Federal studies have been combined to:

- characterize the quality of highway runoff;
- determine contaminant loads for highway-runoff constituents;
- assess the effects of highway stormwater discharges on ecosystems and receiving waters;
- identify the sources and mechanisms that determine the quantity of contaminants in highway runoff;
- develop information for the design and operation of best management practices (BMPs); and
- develop models and monitoring data to meet regulatory needs (Granato and others, 1998).

Information that is documented as valid, current, and scientifically defensible is needed by transportation agencies to support necessary planning and management decisions for these diverse objectives.

Problem

Since the 1970's, requirements for documentation of study-site characteristics, methods and materials used, quality assurance and quality control (QA/QC) information, and other ancillary information for runoff quality studies have been increasing (Granato and others, 1998). During the same period, the accuracy, precision, and detection limits of analytical techniques and instrumentation commonly employed to measure trace elements have improved (van Loon, 1985; Thompson and Walsh, 1989; Garbarino and Struzeski, 1998). In addition, field and laboratory studies have demonstrated that sample collection and processing methods can have a substantial effect on measured concentrations of trace constituents (Kennedy and others, 1974; Patterson and Settle, 1976; Shiller and Boyle, 1987; Horowitz and others, 1992; Benoit, 1994; Taylor and Shiller, 1995; Bloom, 1995; Benoit and others, 1997; Dupuis and others, 1999). These factors have led to substantial disagreements within the scientific and regulatory communities about the validity of existing data, have contributed to the current lack of standardization for trace-element monitoring methods, and have made it difficult to interpret and assess historical and current trace-element data. Therefore, trace-element data are considered suspect, and the responsibility to provide published data-quality information to support the validity of reported results rests with the data-collection agency.

Purpose and Scope

The purposes of this report are to examine the technical issues associated with the monitoring of the trace-element chemistry of highway and urban runoff, to discuss trace element monitoring artifacts, and to discuss matrixes of potential use for monitoring trace elements. These issues are discussed in terms of the information requirements for a regional or national synthesis of trace-element-monitoring data. The primary focus of the report will be the sampling of trace elements in stormwater flow—specifically, runoff on the pavement, in drainage structures, in structural BMPs, and at discharges to receiving waters—and in other matrixes potentially affecting trace elements measured in runoff and receiving waters. Ground-water trace-element-monitoring programs are not discussed because these programs are complicated further by the unique physical and chemical characteristics of the subsurface at each individual sampling well (Puls and Barcelona, 1989; Miller, 1993; Lapham and others, 1997).

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BACKGROUND

The terms trace element, trace metal, toxic metal, or heavy metal are commonly used to describe the largest class of inorganic elements (Elder, 1988; Hem, 1992). Historically, the term "trace" is an operational definition that denotes an inorganic constituent that could not be precisely measured with the techniques available at the time when trace elements were classified (Hem, 1992). For example, trace elements are constituents that are found in the structure of minerals or adsorbed to a solid's surface at concentrations less than 0.1 percent and(or) found in natural waters at concentrations less than about 1.0 mg/L (Hem, 1992; table 1.). These definitions, however, are not absolute; for example, despite the fact that aluminum (Al) is the third most abundant element in the earth's outer crust, it is present at very low concentrations in most fresh waters because of the chemical properties of the element (table 1). The term toxic metal is also an operational definition. Many metals are actually essential for biological activity and become "toxic" only when geologic or anthropogenic sources exceed concentrations typical of the natural environment (Elder, 1988). For example, the U.S. Environmental Protection Agency (USEPA) issued a policy establishing site-specific aquatic life criteria that are equal to natural background (non-anthropogenic) concentrations at sites where these concentrations exceed national water-quality criteria (Davies, 1997).

Trace elements have a variety of both natural sources (such as weathering of rock and soil) and anthropogenic sources (such as ore processing and combustion of fossil fuels) (Forstner and Wittmann, 1981; Salomons and Forstner, 1984; van Loon, 1985; Horowitz, 1991). Although the crustal abundance, average soil abundance, and natural fresh-water concentrations listed in table 1 are only qualitative order-of-magnitude estimates, these values indicate that many of the trace elements measured in highway runoff have natural as well as anthropogenic sources within the local environment. Therefore, the constituents of interest must be measured in a complex matrix of major elements, trace elements, and organic chemicals. The presence of, and the large spatial and temporal variability of these geological, biological, and anthropogenic sources make the interpretation of trace-element data more difficult than the interpretation of data for anthropogenic organic compounds (Forstner and Wittmann, 1981; Salomons and Forstner, 1984; van Loon, 1985; Horowitz, 1991). For example, natural concentrations of Zn range from less than 5 to about 2,900 parts per million in soils of the conterminous United States (Shacklette and Boerngen, 1984). Particulates in road runoff are derived in part from these natural materials. The relative abundance of major and trace elements in local rocks and soils is expected to affect the geochemistry of highway runoff and receiving waters and, therefore, the potential effect of contaminants on the local aquatic environment (Gupta and others, 1981; Bricker, 1999; Buckler and Granato, 1999). Construction materials, vehicles, and roadway-maintenance activities also are substantial sources of trace-element contamination to surface water and ground water near highways and urban areas (Gupta and others, 1981; Makepeace and others, 1995; Barrett and others, 1993). For example, sanding, salting, traffic activities, vehicular wear, pavement degradation, and littering result in the release of exhaust, oil, grease, rust, hydrocarbons, rubber particles, and other materials that contain trace elements (Gupta and others, 1981; Sansalone and Buchberger, 1997).

The chemistry of natural waters is the product of many sources of constituents including atmospheric deposition, weathering and erosion of soil and rocks, and geochemical processes that determine the solubility and form of constituents in the solid, colloidal and dissolved phases entrained in flowing waters (Hem, 1992, Bricker, 1999). Many factors determine the partitioning of trace elements that are mobilized and transported from the highway, through drainage systems, into structural BMPs, and potentially into receiving waters and aquatic biota. Partitioning of trace elements is defined as the processes by which trace elements are transferred among the different physical, chemical, and biological phases of an aquatic environment. Transfer among these phases is usually multi-directional; that is, trace elements rarely remain in one phase permanently (Elder, 1988). The important characteristics of the mixture that effect the partitioning of trace elements include pH, ionic strength, temperature, hardness (base cations), anions, suspended sediment, oxidation-reduction potential (redox), and in some cases, the presence of other trace elements (Bricker, 1999).

Table 1. Characteristics of selected major and trace elements of potential interest to studies of urban and highway runoff

[**Elemental Groups:** Sources: Chang (1984); Hem (1992). M, Major element; T, Trace element; m, metal; n, nutrient; o, other. **Essential Element:** Sources: Chang (1984); Forstner and Whittmann (1981); van Loon (1985); Chapman (1992). Y, yes; U, unidentified. **Natural Abundance:** Sources: **Crust:** Lide and Frederikse (1997). **Soils:** Shacklette Boerngen (1984). **Fresh waters:** Brownlow (1979); Drever (1988); Appelo and Postma (1993). Crustal Abundance is the estimated abundance in the continental earth crust; Soil Abundance is the average from analysis of about 1300 soil samples taken throughout the conterminous United States; Fresh Water Abundance is an order of magnitude estimate of the elemental abundance in unpolluted fresh waters of the United States based on older literature values. ppm, parts per million; mg/kg, milligrams per kilograms; mg/L, milligrams per liter; ~ , about; --, not available. **USEPA water quality criteria:** Source: USEPA (1999). USEPA, USEPA. P, Priority Toxic Pollutants; F, Fresh water; S, Salt water; H, Human Health for consumption of water. **Potential highway source(s):** Source: Bourcier, Hinden, and Cook (1980); Falahi-Ardakani (1984); Kobriger and Geinopolos (1984); Hodge and Stallard (1986); Smith and Lord (1990); Hildemann, Markowski, and Cass (1991); Armstrong (1994); Hee (1994); Granato (1996); Helmers (1996); Farago, Thornton, Kazantzis, and Simpson (1997); Pearce, Brothwood, Fuge, and Perkins (1997)

Element name (abbreviation)	Elemental groups	Essential element	Natural abundance (ppm)			USEPA water-quality criteria	Potential highway source(s)
			Crust (mg/kg)	Soils (mg/kg)	Fresh waters		
Aluminum (Al)	Mm	Y	$8.23x10^{4}$	$7.2x10^{4}$	$\sim10^{-2}$	F	Auto exhaust, brakes
Antimony (Sb)	To	Y	$2x10^{-1}$	$6.6x10^{-1}$	$\sim10^{-3}$	PH	Auto exhaust, brakes
Arsenic (As)	To	Y	$1.8x10^{0}$	$7.2x10^{0}$	$\sim10^{-3}$	PFSH	
Barium (Ba)	Tm	Y	$4.25x10^{2}$	$5.8x10^{2}$	$\sim10^{-3}$	H	Auto exhaust, brakes, fuel
Beryllium (Be)	Tm	Y	$2.8x10^{0}$	$9.2x10^{-1}$	--	PH	
Bismuth (Bi)	Tm	Y	$8.5x10^{-3}$	--	--	FSH	
Boron (B)	Mo	Y	$1.0x10^{1}$	$3.3x10^{1}$	$\sim10^{-1}$		Auto exhaust, deicers
Bromide (Br)	Mo	Y	$2.4x10^{0}$	$8.5x10^{-1}$	$\sim10^{-2}$		Auto exhaust, deicers, fuel
Cadmium (Cd)	Tm	Y	$1.5x10^{-1}$	--	--	PFSH	Auto wear, insecticide application, lubricants, tire wear
Calcium (Ca)	Mm	Y	$4.15x10^{4}$	$2.4x10^{4}$	$\sim10^{1}$		Auto exhaust, brakes, deicers
Carbon (C)	Mo	Y	$2.00x10^{2}$	$2.5x10^{4}$	$\sim10^{2}$		Auto exhaust, fuel
Cerium (Ce)	Tm	U	$6.65x10^{1}$	$7.5x10^{1}$	$\sim10^{-5}$		Catalytic converters
Chloride (Cl)	Mo	Y	$1.45x10^{2}$	--	$\sim10^{1}$	F	Brakes, deicers
Chromium (Cr)	Tm	Y	$1.02x10^{2}$	$5.4x10^{1}$	$\sim10^{-3}$	PFSH	Auto exhaust, auto wear, brakes
Cobalt (Co)	Tm	Y	$2.5x10^{1}$	$9.1x10^{0}$	$\sim10^{-4}$		Auto exhaust
Copper (Cu)	Tm	Y	$6.0x10^{1}$	$2.5x10^{1}$	$\sim10^{-3}$	PFSH	Auto exhaust, auto wear, brakes, deicers
Fluoride (F)	Mo	Y	$5.85x10^{2}$	$4.3x10^{2}$	$\sim10^{-1}$		Deicers
Gold (Au)	Tm	Y	$4x10^{-3}$	--	$\sim10^{-6}$		
Iodine (I)	To	Y	$4.5x10^{-1}$	$1.2x10^{0}$	$\sim10^{-3}$		
Iron (Fe)	Mm	Y	$5.63x10^{4}$	$2.6x10^{4}$	$\sim10^{-2}$	FH	Auto exhaust, auto rust and wear, brakes, deicers
Lead (Pb)	Tm	Y	$1.4x10^{1}$	$1.9x10^{1}$	$\sim10^{-3}$	PFSH	Auto exhaust, bearing wear, deicers, lubricants, tire wear
Lithium (Li)	Tm	Y	$2.0x10^{1}$	$2.4x10^{1}$	$\sim10^{-2}$		Auto exhaust
Magnesium (Mg)	Mm	Y	$2.33x10^{4}$	$9.0x10^{3}$	$\sim10^{0}$		Auto exhaust, brakes, deicers
Manganese (Mn)	Mm	Y	$9.5x10^{2}$	$5.5x10^{2}$	$\sim10^{-2}$	F	Engine wear, fuel additive
Mercury (Hg)	Tm	Y	$8.5x10^{-2}$	$9.0x10^{-2}$	$\sim10^{-5}$	PFSH	

Table 1. Characteristics of selected major and trace elements of potential interest to studies of urban and highway runoff—*Continued*

Element name (abbreviation)	Elemental groups	Essential element	Natural abundance (ppm)			USEPA water-quality criteria	Potential highway source(s)
			Crust (mg/kg)	Soils (mg/kg)	Fresh waters		
Molybdenum (Mo)	Tm	Y	$1.2x10^{0}$	$9.7x10^{-1}$	$\sim10^{-4}$		Brakes
Nitrogen	Mn	Y	$1.9x10^{1}$	--	$\sim10^{0}$	FH	Auto exhaust, deicers, roadside fertilizer
Nickel (Ni)	Tm	Y	$8.4x10^{1}$	$1.9x10^{1}$	$\sim10^{-3}$	PFSH	Auto exhaust, wear, asphalt, deicers, fuel, lubricants
Palladium (Pd)	Tm	Y	$1.5x10^{-2}$	--	--		Catalytic converters
Phosphorus (P)	Mn	Y	$1.05x10^{3}$	$4.3x10^{2}$	$\sim10^{-1}$		Auto exhaust, fuel, lubricants
Platinum (Pt)	Tm	Y	$5x10^{-3}$	--	--		Auto exhaust, catalytic converters
Potassium (K)	Mm	Y	$2.09x10^{4}$	$1.5x10^{4}$	$\sim10^{0}$		Auto exhaust, deicers
Rhodium (Rh)	Tm	U	$1x10^{-3}$	--	--		Catalytic converters
Selenium (Se)	To	Y	5x10-2	$3.9x10^{-1}$	$\sim10^{-4}$	PFSH	Auto exhaust
Silicon (Si)	Mo	Y	$2.82x10^{5}$	$3.1x10^{5}$	$\sim10^{1}$		Auto exhaust, brakes, deicers
Silver (Ag)	Tm	Y	7.5x10-2	--	$\sim10^{-4}$	PFSH	
Sodium (Na)	Mm	Y	$2.36x10^{4}$	$1.2x10^{4}$	$\sim10^{1}$		Auto exhaust, deicers
Strontium (Sr)	Tm	Y	$3.70x10^{2}$	$2.4x10^{2}$	~10-2		Auto exhaust, deicers
Sulfur (S)	Mo	Y	$3.5x10^{2}$	$1.6x10^{3}$	$\sim10^{-4}$	FS	Auto exhaust, deicers, fuel, roadway beds
Tellurium (Te)	Tm	Y	$1x10^{-3}$	--	--		
Titanium (Ti)	Tm	Y	$5.65x10^{3}$	$2.9x10^{3}$	$\sim10^{-2}$		Studded tires
Tin (Sn)	Tm	Y	$2.3x10^{0}$	$1.3x10^{0}$	--		Brakes
Tungsten (W)	Tm	U	$1.25x10^{0}$	--	$\sim10^{-5}$		Studded tires
Vanadium (V)	Tm	Y	$1.20x10^{2}$	$8.0x10^{1}$	$\sim10^{-3}$		Auto exhaust, deicers
Zinc (Zn)	Tm	Y	$7.0x10^{1}$	$6.0x10^{1}$	$\sim10^{-3}$	PFSH	Auto exhaust, brakes, tire wear, lubricants

For simplicity, the aquatic environment can be viewed as a four-phase system (fig. 1) consisting of water, suspended material, bottom material, and biota (Chapman and others, 1982; Elder, 1988; Chapman, 1992). The phase to which a particular trace element will partition depends upon the chemical and physical environmental conditions and the chemistry of the trace element of interest. For example, trace elements tend to partition toward the water phase (dissolved) when conditions of low pH, low Eh (a measure of the redox condition), low particulate loads, and high concentrations of organic matter are prevalent (Elder, 1988). In contrast, high pH and Eh, increased particulate loads, and high hydraulic energies are conditions that favor partitioning of trace elements to the particulate phase (suspended). Low hydraulic energies and high concentrations of organic matter (>0.5 percent), moderate to high sedimentation rates, and the presence of sulfide favor the partitioning of trace elements to bottom sediment (Morse, 1995). Many complex chemical and physical conditions control partitioning of trace elements to organic matter, plants, and animals (Elder, 1988).

The mobilization, transport, and fate of trace elements from highway surfaces are affected by the abundance and chemical and physical properties of solids carried by runoff. Concentrations of suspended solids and grain size distributions in runoff vary at individual sites and between different sites (Gupta and others, 1981; Athayde and others, 1983; Driscoll and others,

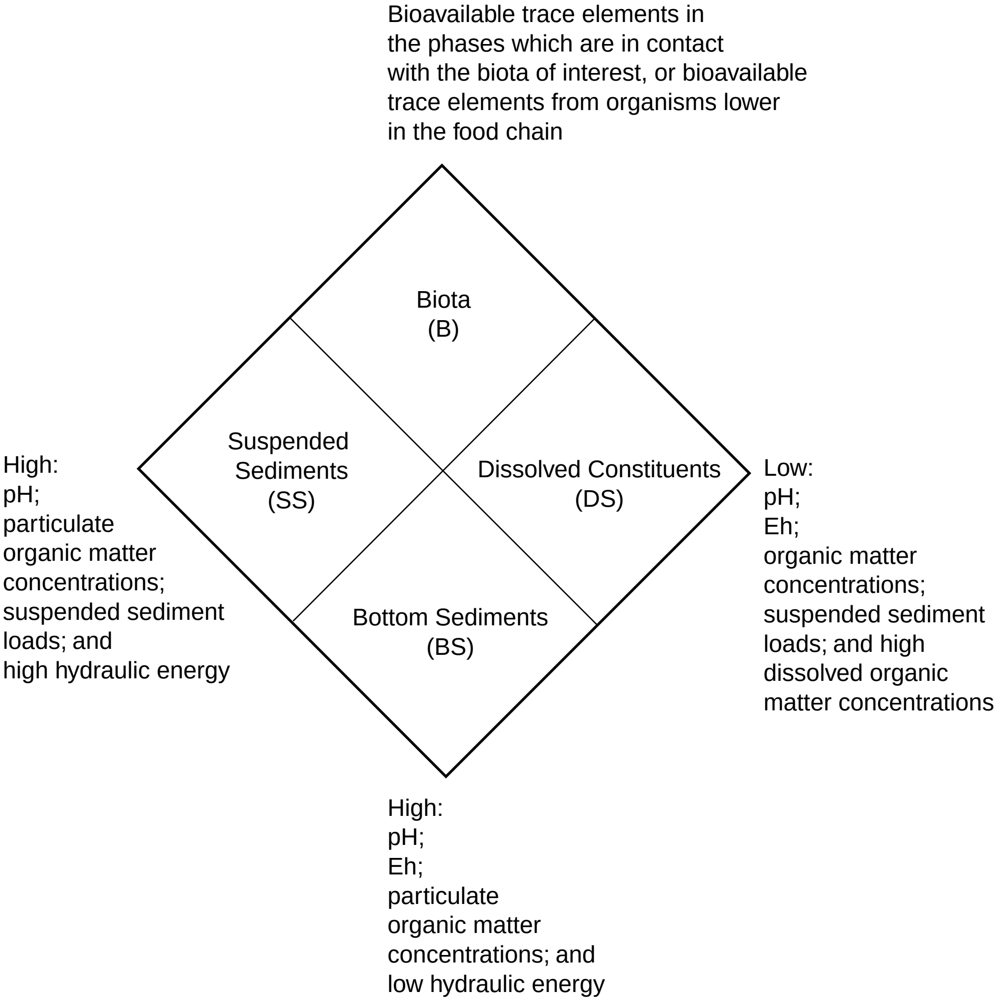


Figure 1. The four phases of aquatic ecosystems that may receive trace elements from nonpoint runoff and the environmental conditions that favor partitioning into each phase (modified from Elder, 1988).

1990; Smith and Lord, 1990). Trace-element transport can be enhanced by sorption onto Fe- and Mn-hydrous oxide coatings on silt and clay particles, and by sorption onto colloidal material including humic substances, viruses, oxides, bacteria, algae, and fecal pellets (Thibodeaux, 1996). These colloids range in size from less than 0.001 micrometer (μm) to about 1000 μm (Hem, 1992). Surface complexation of trace elements onto particulate matter (silts and clays) and colloidal surfaces has little effect on the colloid surface chemistry (because trace elements are present in low concentrations) but significantly enhances trace-element transport (Thibodeaux, 1996). Sorbed trace elements tend to accumulate in bottom sediment. Accumulation in bottom sediment, however, is not necessarily equivalent to permanent removal or to complete export from an aqueous ecosystem. Trace elements accumulated in bottom sediment may repartition into one of the other phases by way of physical, chemical, or biological processes.

The effects of trace-element chemistry on trace-element partitioning—in terms of the ratio of dissolved to total trace-element concentrations in natural fresh water systems—was studied by Martin and Meybeck (1979) and Meybeck and Helmer (1989). They found that the partitioning of many trace elements between the dissolved (water) and particulate matter phases (suspended and bottom) was highly dependent on the solubility of the trace element of interest (table 2). For example, about 50 percent of antimony (Sb) was associated with particulate matter, indicating that Sb is relatively soluble compared to other trace elements. On the other hand, mercury (Hg) appears to be the least soluble because more than 99.9 percent of Hg is associated with particulate matter (table 2). In receiving waters that approach geochemical equilibrium, many trace elements are expected to be associated with particulate matter (Drever, 1988). Although generally true for large rivers with sufficient contact time and favorable geochemical conditions, this generalization must be used with caution when applied to the study of the chemistry of highway- and urban-runoff.

Paved surfaces are fundamentally different physically, chemically, and hydraulically from the receiving waters that have been the focus of most trace-element-monitoring studies. Existing scientific conceptions of the behavior of trace elements in the environment are based largely upon research on natural systems approaching geochemical equilibrium, not on systems typical of pavement runoff. For example, in contrast to the behavior of trace elements in natural systems (table 2), more than 90 percent of some trace elements have been found in the dissolved phase (water) of freshly weathered pavement runoff from highways and urban areas (Yousef and others 1985a; 1985b; Morrison and others, 1990; Revitt and others, 1990; Legret and others, 1995; Sansalone and Buchberger, 1997). Physical mobilization, pulverization, and

Table 2. Ratio between natural dissolved and total elemental concentrations in rivers

[Modified from Meybeck and Helmer, 1989. The higher the percentage, the greater the partitioning into the dissovled phase. Arranged vertically in order of decreasing solubility. >, greater than]

>99 percent	>90–99 percent	>50–90 percent	>10–50 percent	>5–10 percent	>1–5 percent	>0.5–1 percent	>0.1–0.5 percent	>0.05–0.1 percent
Chloride	Bromide	Sodium	Antimony	Copper	Nickel	Gallium	Titanium	Scandium
	Sulfur	Strontium	Magnesium	Phosphorus	Silicon	Lead	Gadolinium	Mercury
		Carbon	Nitrogen		Rubidium	Lutetium	Lanthanium	
		Calcium	Boron		Uranium		Holmium	
		Lithium	Molybdenum		Cobalt		Ytterbium	
			Arsenic		Cadmium		Terbium	
			Fluoride		Manganese		Erbium	
			Barium		Thorium		Samarium	
			Potassium		Vanadium		Chromium	
					Cesium		Iron	
							Europium	
							Cerium	
							Zinc	
							Aluminum	

transport of roadway dirt and dust, lubricants, hydraulic fluids, and other materials on paved surfaces and vehicles is enhanced by the erosive power of precipitation and the kinetic energy of moving vehicles (Irish and others, 1996). Hydraulically, the impervious nature of the pavement and drainage-system designs (which favor rapid turbulent flow to quickly remove water and to keep sediment in suspension) are also responsible for the relatively high mobilization and transport of dissolved and solid phases in highway runoff in comparison to flows in natural systems. Vehicles are composed of trace-element-laden components exposed to high temperatures, pressures, and kinetic energy during combustion of fuel, lubrication of moving parts, and braking. Also, tires and pavement contribute trace elements and organic ligands through road wear. These materials, temperatures, and pressures are generally not found in natural aquatic environments. For example, the combustion of fuel produces carbon dioxide and water in an engine at high temperatures and pressures as well as unburned organic residues and trace elements (from gasoline, lubricants and the engine itself). These trace elements are entrained with the water vapor, carbon dioxide and residues from the engine and the exhaust system. As the water of combustion condenses, it forms a hot acidic solution that contains hundreds of hydrocarbon compounds (Hoekman, 1992) as well as anions, including bromide (Br), chloride (Cl), sulfate (SO_4), and nitrate (NO_3) (Hildemann and others, 1991; Laxen and Harrison, 1977). These organic and inorganic compounds in exhaust particulates and aerosols washed out from the atmosphere, vehicles, the road surface, dust, and dirt can complex trace elements in pavement runoff.

Complexation of trace elements increases their mobility and transport into the natural environment. For example, Breault and others (1996) demonstrated that Cu was 84-99 percent dissolved (as organometalic complexes) in whole-water samples from an urban river spiked with Cu to a total concentration of about 12.6 µg/L, which is a concentration comparable to that in pavement runoff (Driscoll and others, 1990; Makepeace and others, 1995). Conversely, existing scientific conceptions of the behavior of trace elements in the natural environment would predict that less than 10 percent of the Cu would be measured in the dissolved phase (table 2). Furthermore, the concentration and type of complexing agent and geochemical conditions will control the phase of the aquatic ecosystem to which the trace element will partition. For example, adsorption of trace elements to sediment may be either increased or reduced, depending on whether complexing agents are available in solution or adsorbed to the sediment surfaces (Elder, 1988).

Another important factor that distinguishes the chemistry of highway runoff from that of natural fresh waters is the magnitude of variation in the ionic strength of pavement runoff caused by seasonal use of deicing chemicals. The range of specific conductance (a measure of ionic strength) in fresh water is from about 1 to about 1,500 microsiemens per centimeter (Granato and Smith, 1999). In comparison, the specific conductance of highway runoff varies from about 3 to more than 60,000 µS/cm. These values represent a Cl concentration range from about 1 to 20,000 mg/L (these measurements approximate the range between distilled water and a dilute brine solution; Granato and Smith, 1999). Similarly, the range of Cl concentrations measured in urban-runoff studies was reported to be 0.30–25,000 mg/L (Makepeace and others, 1995). At high conductance, the associated salinity can shift pH, saturate available ion-exchange sites on sediment with major ions, and form trace-element Cl complexes that increase trace-element mobilization measured in the dissolved phase (Granato and others, 1995). Conversely, high salinities also may cause flocculation of fine particulates and organometallic complexes (Burton, 1976), which may in turn cause these trace elements to be deposited with the flocculated particulates in highway sediment near discharge points. Conductance, and therefore salinity, varies by orders of magnitude within storms, between storms, and from season to season; this variation further complicates measurement and interpretation of trace-element highway-runoff data.

TRACE-ELEMENT MONITORING

Currently, any trace-element data that is not supported by quality-assurance and quality-control (QA/QC) documentation that demonstrates the validity of those data is viewed as suspect. Data may be suspect because artifacts of the monitoring process can substantially affect the measured concentrations of trace elements and(or) the representativeness of samples collected. In several studies, the problem of sample contamination is identified as an issue that may overshadow all other potential problems that result from the use of different sampling, processing, preservation, and analytical procedures, as well as problems that are associated with spatial and temporal variability of trace elements (Brewer and Spencer, 1970; Bruland, 1983; Shiller and Boyle, 1987; Horowitz and others, 1994; Taylor and Shiller, 1995; Benoit and others, 1997). Dupuis and others (1999) raised the issue for evaluation of available highway-bridge-runoff data, but determined that no highway-runoff studies to date have addressed the issue of sampling artifacts (errors in the actual concentration of trace elements present). Sample collection, handling, and processing materials can contribute and(or) sorb trace elements within the time scales typical for collection, processing and analysis of runoff samples. The relative effect of potential contamination and(or) attenuation of trace elements in runoff samples is a function of the concentration of major and trace elements, organic chemicals, and sediment in solution. Sampling artifacts are especially important when measured concentrations are at or near analytical detection limits. Historically, measured concentrations of trace elements in highway and urban runoff have ranged from less than detection limits to several orders of magnitude greater than detection limits within and between studies (Athayde and others, 1983; Driscoll and others, 1990; Barrett and others, 1993; Makepeace and others, 1995). Without sufficient supporting documentation, however, it is impossible to determine how sampling artifacts affect data in these ranges. For example, contamination introduced during sampling can mask temporal differences at the same location as well as spatial differences among different sampling locations. Trace elements such as uranium (U), and thallium (Tl) that are not commonly used in sampling materials and(or) are not generally prevalent in the environment may not be affected, or may be minimally affected by contamination; however, common highway-runoff constituents such as Al, Cr, Fe, Ni, Pb, and Zn may be substantially affected (Shiller and Boyle, 1987; Windom and others, 1991; Benoit, 1994; Benoit and others 1997). Therefore, great care is required to collect and process samples in a manner that will minimize potential contamination and variability in the sampling process.

Clean Monitoring Methods

Historically, anthropogenic sources in developed areas were thought to produce trace-element concentrations high enough to obscure the effects of contamination from most sample collection and processing procedures. Benoit and others (1997), however, compared sampling artifacts of silver (Ag), Cd, Cu, and Pb from a rural stream and an urban stream in an industrial area in Connecticut. That study showed that even for the urban-stream samples, skipping even one step of the clean collection and processing protocol introduced substantial contamination (fig. 2). Lack of process control increased contamination by up to three times for each of several steps. Some steps reduced potential contamination by only about 20 percent, whereas others led to reductions of two to three orders of magnitude. In particular, when sample bottles were not cleaned properly, measured Cd concentrations were 15 times greater than when ultraclean bottles were used (Benoit and others, 1997).

The so-called "clean/ultra-clean" sampling, processing, preservation, and analytical techniques were developed during the 1970s, 1980s, and 1990s to address concerns about the validity of existing data and to produce reliable trace-element data (Patterson and Settle, 1976; Trefrey and others, 1986; Shiller and Boyle, 1987; Flegal and Coale, 1989; Windom and others, 1991; Nriagu and others, 1993; Benoit, 1994; Horowitz and others, 1994; Taylor and Shiller, 1995; Benoit and others, 1997). These techniques have led to marked reductions in sample contamination and to an associated decrease in the reported concentrations of ambient trace elements in marine and freshwater systems. In fact, during the past

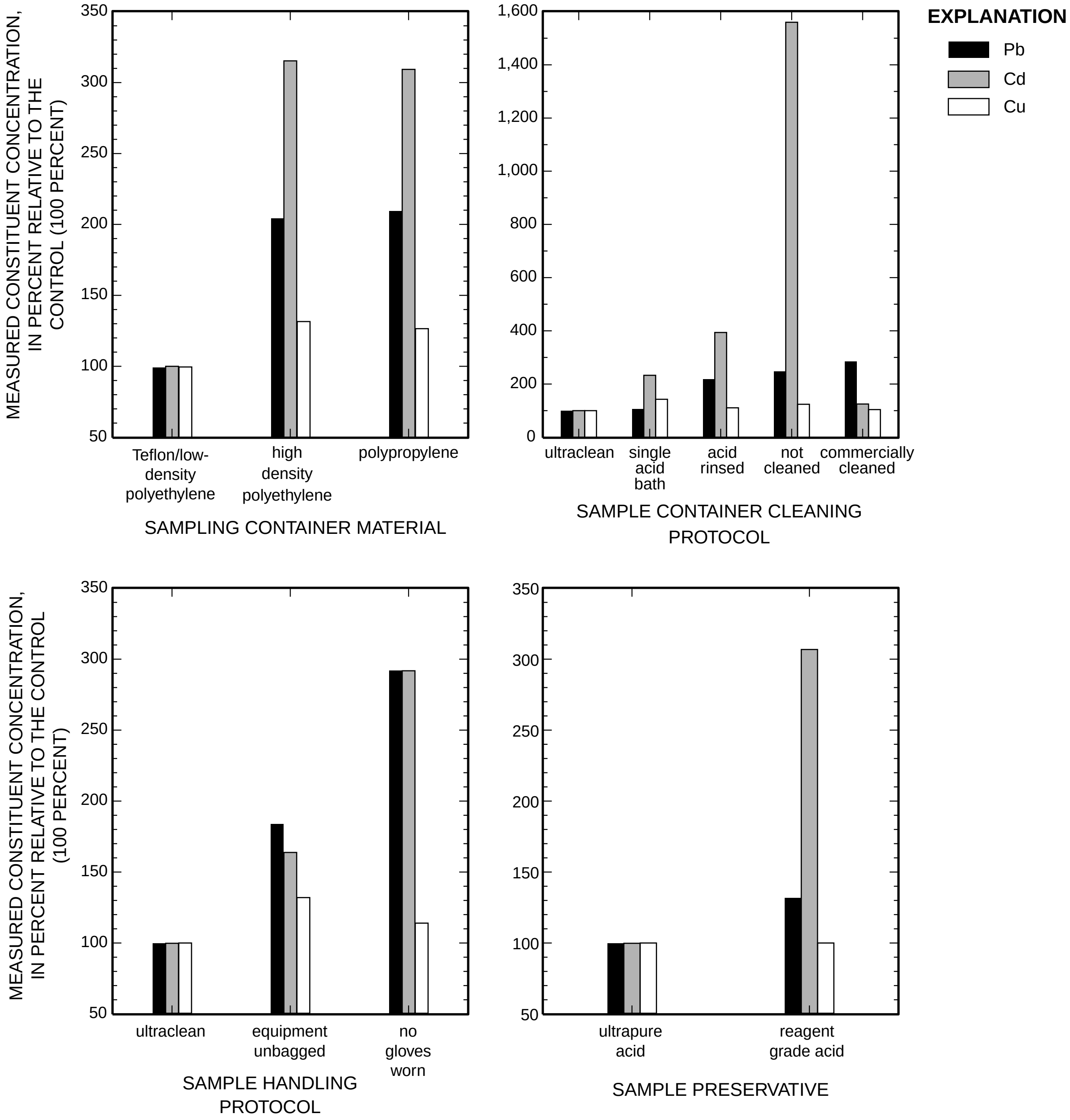


Figure 2. Potential contamination introduced in different components of the sample-handling process (data from Benoit and others, 1997).

10 years, reported concentrations in samples collected by clean methods have declined from tens of parts-per-billion (µg/L) to parts-per-billion to the parts-per-trillion (ng/L) range for many trace elements in natural systems (Shiller and Boyle, 1987; Windom and others, 1991; Benoit, 1994; Nriagu and others, 1996).

These rigorous sample collection and processing methods, also known as "clean hands-dirty hands" techniques, are used to minimize the contamination introduced during the collection of samples for analysis of trace elements (Wilde and Radtke, 1999). The basic strategy is to handle all containers while wearing non-contaminating gloves and to change gloves whenever they have touched something that is not "clean." To perform the clean hands-dirty hands procedure correctly, a field crew should consist of at least two persons, each with rigorously defined roles. "Clean-hands" is the person who collects and processes the water sample using sampling and processing equipment that has been cleaned in a controlled environment and transported to the field inside two or more airtight bags. "Dirty-hands" is the person who handles all sampling equipment that could be in contact with any potential source of contaminants. These methods were developed and tested by a number of researchers (Fitzgerald and Watras, 1989; Bloom, 1995; Benoit and others, 1997) and have been accepted as protocols for regional and national water-quality-monitoring programs (Horowitz and others, 1994; Wilde and Radtke, 1999). For example, Benoit and others (1997) demonstrated that the use of gloves and prebagged equipment was critical for the success of these protocols (fig 2). Strict adherence to the clean hands-dirty hands protocols, however, is sometimes considered excessive for some trace-element-monitoring programs; departures from these protocols are accepted if sufficient quality-control data is collected to establish that the modified (relaxed) protocols meet data-quality objectives. Details of these protocols and related QA/QC measures are described by Wilde and Radtke (1999).

Samples collected for the analysis of trace elements must be preserved in order to mitigate the effect of chemical reactions in sample storage containers as well as sorptive losses to the sample container (Batley, 1989; Radtke, 1999). Samples are typically preserved by chilling and(or) adding chemicals. For example, sample pH is adjusted to about 2 standard units by the addition of nitric acid, which is expected to fix the sample chemistry during storage (Radtke, 1999). Chemicals used as preservatives for trace-element samples must be analyzed and certified as being free of the constituents of interest to ensure a minimum of contamination (Benoit and others, 1997; fig 2). Ideally, the procedures for preservation and storage should be started the moment the sample has been collected. Once treated, samples can be stored for extended time periods (sometimes weeks to months), but in some cases, data quality was improved by analysis sooner rather than later during the holding period (Batley, 1989; Kramer, 1994).

Clean Monitoring Materials

Monitoring of trace elements in environmental studies also is complicated by several factors related to the materials used for collection, processing and storage of trace-element samples (Radtke and Wilde, 1998). Substantial gains or losses of trace elements can occur by means of adsorption or desorption from the surfaces of collection, processing and storage containers. For example, the chemical composition, surface roughness, cleanliness, permeability, wall thickness, and closure integrity of the container can affect the quality of stored samples (Moody and Lindstrom, 1977; Sansalone and Buchberger, 1996). Other factors that affect interactions of trace elements with sample collection, processing, and storage materials include the characteristics of the constituent of interest, characteristics of the monitoring matrix, and external factors such as temperature, contact time, access of light, and the degree of agitation (Massee and others, 1981, Sansalone and Buchberger, 1997).

Numerous articles and reports have been published about the use of plastic as the ideal material for sampling equipment and sample containers. The suitability of any individual plastic, however, depends on the type of material and on the cleaning procedure (Moody and Lindstrom, 1977). Different types of plastics have been evaluated for desorption (Moody and Lindstrom, 1977) and adsorption of trace elements onto container surfaces (Good and Schroder, 1984). Good and Schroder (1984) found that polypropylene, polyethylene and polyester/polyolefin would not be suitable as collection or storage vessels for water samples to be analyzed for Cu, Fe, molybdenum (Mo), Pb, and vanadium (V), all of which showed adsorption losses. Consequently, these plastics should not be used in the collection, processing, and analysis of samples for the determination of these trace elements at low levels. Materials such as rubber and Viton also should be avoided, as they may contain leachable trace elements (Bloom, 1995). The plastic Teflon is commonly considered the most suitable material for trace-element sampling (Moody and Lindstrom, 1977; Benoit and others 1997) in terms of its non-reactive chemical properties (fig. 2)

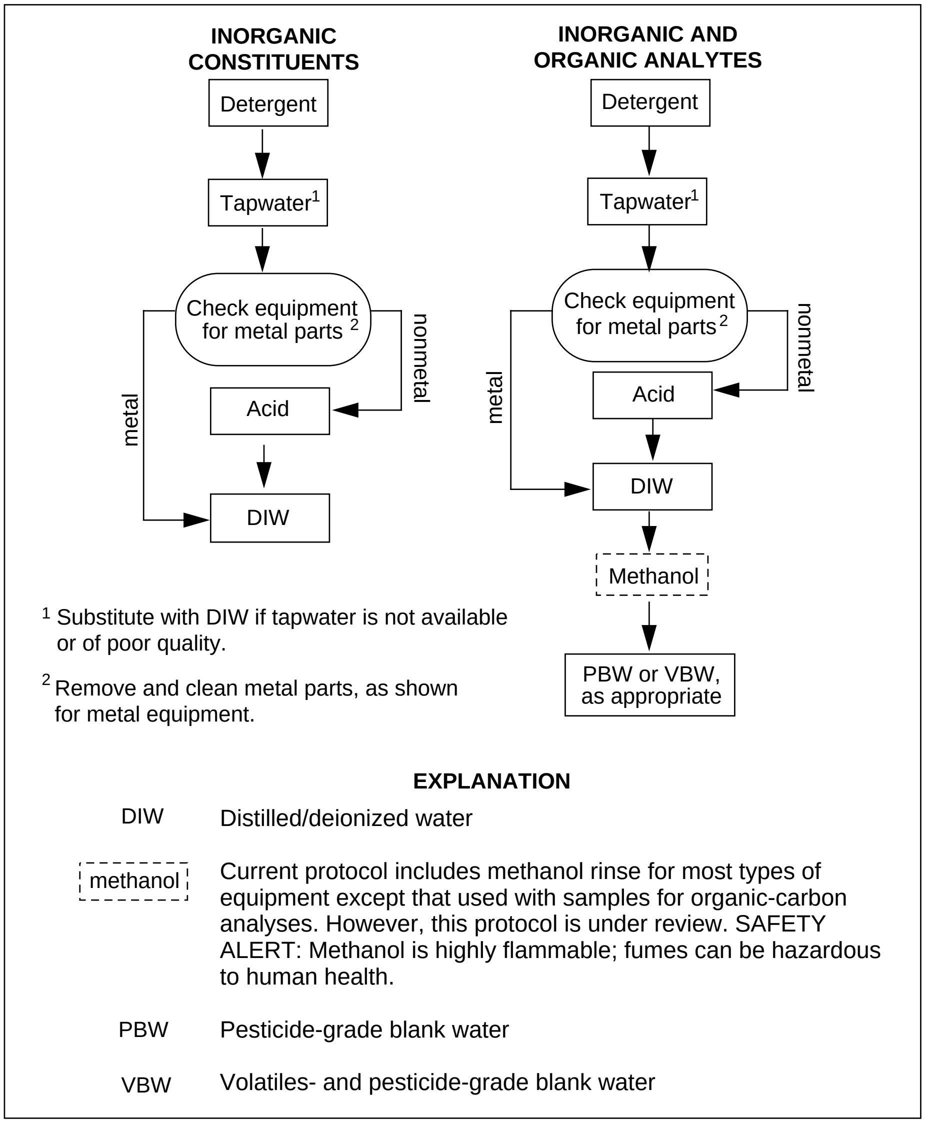
Regardless of the material selected for use in trace-element sampling, procedures for cleaning are necessary to reduce trace-element contamination to concentrations below analytical detection limits. Cleaning instructions suitable for materials used in the collection, processing and storage of trace-element-monitoring samples have been published (Moody and Lindstrom, 1977; Bloom, 1995; Benoit and others 1997; Horowitz and Sandstrom, 1998). Briefly, protocols include a wash and rinse to remove gross contaminants and a subsequent cleaning with a suitable acid and(or) deionized water to remove the remaining trace elements (fig. 3). The protocols used for cleaning will determine the potential for contamination from equipment and materials (Benoit and others, 1997; fig. 2). Data-quality objectives dictate the cleaning protocols and QA/QC that are necessary (Granato and others, 1998; Jones, 1999).

Spatial and Temporal Variability

Spatial variability between highway monitoring sites including the environmental setting, local land use, traffic characteristics, highway and drainage design characteristics, and many other features are also recognized as potential explanatory factors for variations in measured concentrations (Gupta and others, 1981; Driscoll and others, 1990; Young and others, 1996). For example, runoff from curbed highways tends to have higher constituent concentrations and loads than that from flush-shouldered highways, because the curbed highway-drainage design structures tend to trap sediment on the paved surface (Gupta and others,1981; Driscoll and others, 1990; Young and others, 1996). Spatial variability among potential sites along a single highway also is a concern. For example, one would expect the acceleration, deceleration, and braking of vehicles to cause increased constituent loadings at a site near an interchange than at a comparable site within a long straight section where vehicles are traveling at constant speed (Gupta and others, 1981; Driscoll and others, 1990; Legret and Pagotto, 1999).

The distribution of sediment, as well as major and trace elements, can be highly variable within a cross-section of the water column in natural waters. Therefore, methods for depth and width integration of samples are commonly recommended (Edwards and Glysson, 1999; Hem, 1992; Shelton, 1994; Averett and Schroder, 1994; Webb and others, 1999). Automatic point samplers generally do not provide depth or width integration (Horowitz, Rinella, and others, 1989). The small cross-sectional areas of drainage pipes, rapid mixing, and turbulent flows characteristic of many runoff drainage systems, however, may preclude the need for depth and width integration. Flow and concentrations of water-quality constituents change rapidly in storm flows. Therefore, depth and width integration methods may not be suitable for runoff studies because the concentration is changing while the sample is being collected within the cross section. It is, however, important to recognize the potential for this spatial variability within the water column, to choose sites where the potential for stratification is minimized, where possible, to promote vertical and horizontal mixing upstream of the sampling point, and (if possible) to test the hypothesis that the point sample is representative of the cross section.

Temporal variability also is an important consideration for trace-element monitoring studies. Long-term trends (such as the effects of the ban on leaded gasoline) can affect the comparability of data from different studies (Young and others, 1996; USEPA, 1999). Seasonality also is a major issue for runoff studies. For example, Driscoll and others (1990) analyzed data from more than 990 storm events at 31 sites in 11 states and concluded that winter "snow" storms were significantly different from non-winter storms. Long-term nationwide experience with both hydrologic and water-quality studies indicates that, if possible, studies should span several years to quantify seasonal and interannual variations in weather (Averett and Schroder, 1994).



[1] Substitute with DIW if tapwater is not available or of poor quality.

[2] Remove and clean metal parts, as shown for metal equipment.

EXPLANATION

DIW	Distilled/deionized water
methanol	Current protocol includes methanol rinse for most types of equipment except that used with samples for organic-carbon analyses. However, this protocol is under review. SAFETY ALERT: Methanol is highly flammable; fumes can be hazardous to human health.
PBW	Pesticide-grade blank water
VBW	Volatiles- and pesticide-grade blank water

Figure 3. General sequence for cleaning equipment before sampling for inorganic and organic analytes (modified from Horowitz and Sandstrom, 1998).

Stormwater Monitoring Logistics

Trace-element data collection and interpretation efforts are further compounded by the logistics of sampling stormwater in the highway environment. Storms can occur any day of the week at all hours, and the arrival and magnitude of each storm is a source of great uncertainty. For example, Thiem and others (1998) employed a meteorologist to predict the occurrence of design storms for a highway study in Rhode Island but still mobilized the sampling crew when storms did not materialize, and missed storms that were not predicted accurately. To sample a complete event on very small, impervious catchments, it often is necessary to initiate sample collection within minutes of the onset of precipitation and to collect a relatively large number of subsamples. This is necessary because concentrations of dissolved and suspended solids change rapidly in response to changes in rainfall intensity and other factors. To generate meaningful event mean concentrations (EMCs), it is necessary to record the runoff flow (Church and others, 1999) and either to calculate an EMC from the analysis of a number of discrete samples

(Driscoll and others 1990), or to composite one EMC sample using an accepted compositing protocol (USEPA, 1992a). Therefore, storm sampling should be conducted within the framework of an automated monitoring and automatic sampling program to standardize the process and to provide a record of the variations in flow and water-quality characteristics (Driscoll and others 1990; USEPA, 1992a; Spangberg and Niemczynowicz, 1992; Church and others, 1999; Granato and Smith, 1999).

Quality Assurance and Quality Control

A QA/QC program that includes steps to minimize contamination as well as measures of gains and losses of each constituent of interest throughout the sampling and analysis process is necessary to document the accuracy, precision, and comparability of data collected. Quality assurance is designed to prevent systematic error (Jones, 1999). If the monitoring project is extensive (multiple sites or long study periods), the QA program should be documented and published (for example, Mueller and others, 1997). The QA program should be documented in the same report as the study results for less extensive monitoring projects. The QA program also should include a schedule of intraoffice quality reviews and documentation for all methods, field personnel, and analytical laboratories used in the data collection process (FHWA, 1986). Documentation allows others to interpret the data and to verify that appropriate practices were followed in the design and execution of the study.

Quality control (QC) includes the steps used to check that QA is effective and to evaluate bias and variability. QC techniques include preparation and analysis of equipment blank samples to ensure that equipment is clean, replicate samples to assess sample variance and analytical precision, and samples spiked with analytes to evaluate analyte degradation and recovery (Jones, 1999). The field and ambient-atmosphere blank samples described by Jones (1999) also are important for highway and urban runoff studies because samples are collected in environments exposed to airborne particulates suspended by local winds and vehicular turbulence along the roadway (Smith, K.P., USGS, written commun., 2000).

The fundamental trace-element-monitoring concepts covered herein are generally considered applicable for most trace-element monitoring matrixes. It is necessary to use methods and materials that will minimize sampling artifacts, to characterize real sources of variability, and to document these efforts within the context of a defined QA/QC program. These and many other factors, however, need to be addressed and documented in detailed sampling plans that define the data-quality objectives that are developed for each matrix of interest (Granato and others, 1998; Jones, 1999).

SAMPLING MATRIX

The objective(s) of an individual study often determine which matrixes and therefore, which materials and methods are used for trace-element monitoring at a given site. If data are to be used in a regional or national synthesis, the matrixes, materials, and methods used also must be considered in this broader context. For example, a need for information about the speciation of trace elements among the dissolved, suspended-sediment, bottom-sediment, and tissue matrixes will dictate that each matrix be sampled, processed, and analyzed using appropriate materials and methods. Historically, study objectives have affected the suitability of a given data set for regional or national synthesis (Driscoll and others, 1990; Granato and others, 1998).

For simplicity, the aquatic environment may be divided into four phases including biota, dissolved constituents, suspended sediment, and bottom sediment (fig. 1). In practice, however, the boundaries between these phases are not easy to define and the wide spectrum of geochemical conditions encountered often precludes the definitive physical and chemical characterization of aqueous systems. For example, trace elements in bacteria or algae in highway runoff may be measured as a component of biota, dissolved, suspended sediment, or bottom sediment, depending upon the methods used and the site selected. Operational definitions to describe these four phases are therefore used to establish sampling matrixes without reference to the character of individual aquatic environments being studied. The techniques that are established for collecting, processing, and analyzing each matrix should not be considered absolute, but rather as common methods and guidelines chosen by investigators to provide relatively comparable and scientifically defensible data. Therefore, an understanding of operational definitions and careful selection of the appropriate sample matrix is necessary to meet the objectives of the monitoring program.

Whole Water

Whole-water samples are unfiltered samples from the water column, which include suspended materials and the water matrix. Three recognized methods—"total", "total recoverable," and "acid soluble"—are used for analysis of dissolved and sediment-associated trace elements in whole water samples. These methods differ in the amount of sediment-associated trace elements that may be solubilized prior to analysis (USEPA, 1992c). The total technique is designed to dissolve 95 percent of the constituent of interest in the whole water sample, so that the analysis measures most of the target constituents in the sample, including sediment-grain matrix constituents (Fishman and Friedman, 1989). The total-recoverable technique is designed to dissolve constituents associated with sediment surfaces, but less than 95 percent of the constituents present (Fishman and Friedman, 1989). The acid soluble method is a less rigorous digestion technique than the total-recoverable method, but research shows that it commonly yields similar results (USEPA, 1992c). In practice digestion techniques are defined by standard methods that prescribe reagents, concentrations of reagents, temperature, and contact time rather than an exact percent recovery (for example American Public Health Association-American Water Works Association-Water Pollution Control Federation, 1989; Hoffman and others, 1996). Furthermore, these standard methods may solubilize different percentages of the constituent of interest in samples with differing water chemistry, sediment chemistry, and sediment concentrations.

Benefits

If the information gained from analysis of constituent concentrations in whole-water matrix samples will meet the data-quality objectives of a given study, use of this matrix precludes many of the problems that are of concern when sampling trace element concentrations in individual matrixes (dissolved (filtered) water and(or) suspended sediment). In a national synthesis of highway or urban runoff, it is important to be able to predict the total concentration and load of trace elements generated by a given highway or land use on the basis of local climate, site characteristics, and other explanatory variables such as average daily traffic (Granato and others, 1998). For highway- and urban-runoff water-quality studies, therefore, the whole-water matrix may be the most robust sampling matrix because speciation among the dissolved (water) and solid (sediment) matrixes is not a factor. This is an important consideration in stormwater studies, because the chemistry and kinetics that control speciation of trace elements depend on

- concentration and geochemistry of the solids suspended in solution;
- geochemistry of the solution (pH, ionic strength, redox, and major ions);
- biological activity in the sample;
- chemistry of, concentration of, and competition between trace elements; and
- sample temperature;

all of which are variable within and between storms and are a function of the time between collection and processing of each sample. Avoiding these contact-time issues by use of the whole-water sampling matrix allows for fully automatic sample collection so that sampling crews can be dispatched to gather the samples that have been collected (usually during normal business hours when visibility and safety are maximized).

Whole-water sampling also has logistical benefits in comparison to sampling other matrixes. Once whole-water samples are collected, composited and(or) split (if necessary), and preserved, there are no additional field-processing steps to introduce bias. Whole-water samples are relatively uncomplicated and inexpensive to collect, process, and analyze, because there is no physical separation (or associated labor, equipment, and material costs) of water from sediment. Use of whole-water samples requires less contact between the sample and processing equipment than does phase separation (the dissolved- or suspended-sediment matrix), which minimizes the potential pathways for contamination or attenuation of measured constituents. Analysis of whole-water samples also is cost effective because one analysis defines the total contribution of all matrixes in the sample. Solids control using structural BMPs is currently the most practicable method to address non-point runoff contamination (Young and others, 1996). Therefore, at present, whole water samples also are necessary to provide information for the design of structural BMPs, because concentrations of sediment and associated trace elements in samples collected at the inflow and outflow are directly comparable (based upon sedimentation and the contact time issues to be discussed).

By law (40 CFR 122.45), analysis of whole-water samples is required for monitoring effluents and for monitoring within the Non-Point Discharge Elimination System (NPDES) permit process because it is recognized that the partitioning of trace elements in effluents may be different than in receiving waters (USEPA, 1992c). Whole-water samples, therefore, are most comparable to the bulk of historical highway- and urban-runoff data and are specified for use in nonpoint source monitoring studies (Gupta and others 1981; Athayde and others, 1983; Driscoll and others, 1990; USEPA, 1992a). Driscoll and others (1990) compiled precipitation, flow, and water-quality data from more than 990 individual storm events from 31 highway sites in 11 states during the 1970s and early 1980s. They determined that median event mean concentrations (EMCs) in whole-water samples of total suspended solids (TSS), Cu, Pb, and Zn were about 93,000; 39; 234; and 217 µg/L, respectively. The coefficients of variation (COVs) for these sample populations are about 1.2, 0.9, 2.0, and 1.4 for suspended solids, Cu, Pb, and Zn, respectively. These COVs indicate that measured concentrations may vary by more than plus or minus two orders of magnitude. The National Urban Runoff Program (NURP) data base of urban loading sites (sites without upstream BMPs), which includes total recoverable whole-water EMCs from 2,300 separate storm events from 81 sites in 22 different cities, also was conducted in the late 1970s and early 1980s (Athayde and others, 1983). The NURP was advanced for its time in that it included a substantial QA/QC component and that detection-limit issues were addressed. The median EMCs for all the urban NURP sites are about 70,000, 30, 110, and 150 µg/L for TSS and total recoverable Cu, Pb, and Zn in whole-water samples, respectively. The coefficients of variation for these populations are about 1.0, 1.0, 0.8, and 0.8 for suspended solids, Cu, Pb, and Zn, respectively, indicating that measured concentrations in urban runoff also may vary by more than plus or minus two orders of magnitude. In more recent studies, investigators find that concentrations of Cu may be higher than historical values (possibly a consequence of the use of metallic brake pads on vehicles), concentrations of Pb are substantially lower than historical values (possibly from the reduction of Pb in gasoline; Callendar and Van Metre, 1997), and Zn concentrations are generally equivalent to the historical values (Marsalek and others, 1997; Sansalone and Buchberger, 1997; Dupuis and others, 1999; Legret and Pagotto, 1999).

Technical Concerns

Although the whole-water sampling matrix would seem to be a simple and universal solution for runoff-monitoring studies, some technical concerns must be understood and evaluated. Suspended sediment is an integral part of the whole-water matrix. When the suspended-sediment distribution in the water column is highly heterogeneous, therefore, proper techniques for suspended-sediment sampling are critical for the collection of representative whole-water samples (Webb and others, 1999).

Many of the constituents reported as "total" are actually "total recoverable." Because differences in measured constituents between methods may be substantial (especially in mineral-rich areas of the country), it is important to establish the digestion method with appropriate documentation, especially in the context of a regional or national monitoring program. The total recoverable method may yield results comparable to the total method if the digestion proceeds to the point at which the natural mineral substrate is being dissolved. Measured concentrations of trace element are dependent on the geochemical composition of the particulate matter in whole-water samples for all total recoverable digestion procedures (Hoffman and others, 1996; Garbarino and Hoffman, 1999). Differences in measured concentrations, therefore, may be accentuated by regional differences in the amount of natural minerals that are solubilized during digestion, because solubilization is a function of the mineralogy of the solids.

Potential differences in performance among water-quality laboratories are an issue with whole-water samples because the digestion, separation of residuals, and analysis is not always a trivial matter. The results of an interlaboratory comparison (fig. 4) involving about 40 professional water-quality laboratories indicates that laboratory performance can be highly variable. Most of the reported concentrations

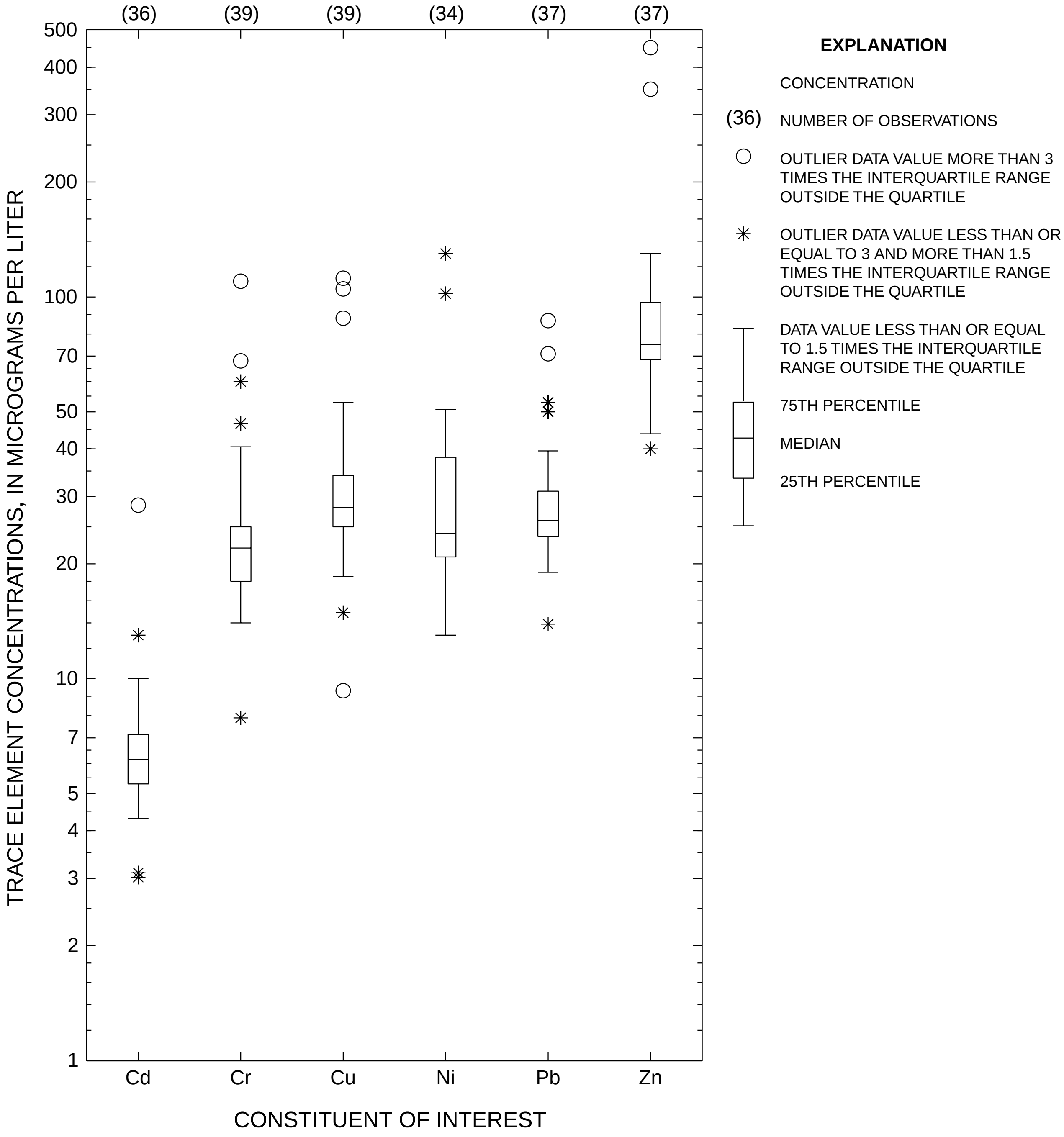


Figure 4. The distribution of total-recoverable trace-element concentrations measured in a natural-water matrix standard reference solution of a whole-water sample (excluding far outliers of 0.5 micrograms per liter for Cd and 38,160 micrograms per liter for Zn) by laboratories participating in the USGS interlaboratory evaluation program. Data from Long and Farrar (1994).

range from 63 percent to 180 percent of the most probable value (MPV; the median of interlaboratory determinations) and a substantial number of outliers differ by an order of magnitude from the MPV (Long and Farrar, 1994). This variability in interlaboratory analytical results is noteworthy in light of the fact that all of the MPVs are at least an order of magnitude above the detection limits for the analysis of whole-water samples (Garbarino and Struzeski, 1998), and that these laboratories, by participating in an interlaboratory comparison, have some components of a QA/QC system (Jones, 1999) in place. Therefore, the digestion method and laboratory performance must be properly documented through a QA/QC program to ensure comparability of data from sample to sample and among data collected from different studies.

Differences in digestion procedures may also affect measured trace element concentrations. For example, whole-water sample digestions have been historically prepared in laboratories without any special precautions to control the potential for airborne contamination. In developing a new in-bottle digestion method for whole-water samples, Hoffman and others (1996) showed that this newer technique had lower blank concentrations and improved reproducibility when compared to the existing open-beaker method. Therefore, historical whole-water data may be affected by these processing artifacts and may not be directly comparable with more recent data.

Historically, the USEPA has recommended the "total recoverable method" of sample preparation as an indication of bioavailability of trace elements (USEPA, 1986a). There are, however, no universal and robust methods to relate concentrations of total recoverable trace elements to ecosystem effects. Therefore, total recoverable concentrations of trace elements in water samples are at best one of many explanatory variables to be measured in addition to more direct measurements of the ecological effects of runoff on aquatic biota (Buckler and Granato, 1999). Also, use of whole-water samples does not address the issue of speciation, which may provide information about processes that control transport and fate of trace elements that may be useful for understanding and potentially mitigating the adverse effects of trace elements in receiving waters (Horowitz, 1991).

Use of the whole-water matrix may present problems if trace-element concentrations in the dissolved matrix are low, because the water may dilute concentrations of the trace elements in the whole-water sample below detection limits even if the sediment is highly contaminated (Horowitz, 1991; Hem, 1992). If the concentrations of trace elements in samples collected from highways and structural BMPs are to be compared with those in samples from relatively uncontaminated receiving waters (in which many of the trace elements are associated with the suspended solids), detection limits also may pose problems. Trace-element concentrations below detection limits for whole-water samples (Garbarino and Struzeski, 1998) are important at the watershed scale because, annually, substantial loads of trace elements may go undetected (Horowitz, 1991; Hem, 1992). Also, many of the trace elements associated with highway operations (table 1) that were not detected in historical whole-water sample analyses may now be measured because of the lower detection limits associated with improvements in analytical techniques. Knowledge of historical and current method-detection limits, therefore, is needed to compare the results of whole-water analysis.

Three examples are presented to illustrate the potential suitability of whole-water sampling for monitoring highway and urban runoff in terms of the aforementioned detection-limit problems. In a "worst case scenario," it is assumed that all trace elements are associated with sediment and trace-element concentrations in the dissolved phase are zero. Sediment-associated trace-element concentrations are from the analysis of sediment samples from highways, urban areas, and U.S rivers by Kobriger and Gienoplos (1984), K.C. Rice (USGS, written commun., 1999) and Rice (1999), respectively. Hypothetical concentrations of suspended-sediment from one to 1,000 mg/L are used in calculations because this range includes many concentrations reported in highway runoff (Driscoll and others, 1990), urban runoff (Athayde and others, 1983) and stream water in most of the conterminous United States (Smith and others, 1993). Using these assumptions, hypothetical whole-water concentrations of trace elements in highway runoff, urban receiving water, and relatively uncontaminated receiving water-samples are calculated by means of equation 1:

$$C_{ww} = C_{ss} * C_{stm} * U \ , \qquad (1)$$

where

C_{ww} is the hypothetical whole water-concentration of trace elements in micrograms per liter;

C_{ss} is the hypothetical suspended-sediment concentration in milligrams per liter;

C_{stm} is the range of measured trace element concentrations from analysis of sediment samples in milligrams of the trace element (TE) per kilogram of sediment (S); and

U is the unit conversion factor (kg(S)(µg(TE)/1000 mg(S)(mg(TE)).

The amount of suspended sediment required to produce detectible whole-water trace-element concentrations can be examined in terms of current whole-water detection limits (Garbarino and Struzeski, 1998). Figure 5 indicates the relations between sediment concentrations, the range of trace elements measured on potential source sediment, and method detection limits for Cd, Cr, Ni and Zn. More specifically, the calculated concentrations (equation 1) associated with the minimum, 25th percentile, median, 75th percentile, and maximum trace-element concentrations measured in sediment samples are shown in figure 5 as a function of suspended sediment concentrations in the hypothetical whole-water samples. The results of this method applied to concentrations of trace elements associated with fine sediment (grain sizes less than 74 µm) from the highway surface (Kobriger and Gienoplos, 1984) are demonstrated in figure 5*A*. This figure indicates that for Cd, Cr, Ni and Zn, the contribution of sediment would not be detectable until suspended-sediment concentrations are about 7 mg/L, 20 mg/L, 3 mg/L, and less than 1 mg/L, respectively. In comparison, a similar calculation uses measured concentrations of trace elements in the fine fraction (grain sizes less than 64 µm) of 91 urban streambed sediment samples collected by the U.S. Geological Survey's (USGS) National Water Quality Assessment (NAWQA) Program (K.C., Rice, written commun., 1999) in equation 1. Figure 5*B* indicates that minimum suspended sediment concentrations of about 60 mg/L, 25 mg/L, 10 mg/L, and about 2 mg/L are necessary for detection of Cd, Cr, Ni and Zn, respectively. Finally, the third example uses concentrations of trace elements in the fine fraction of streambed sediment samples collected by NAWQA in the conterminous United States (Rice, 1999). Cd, Cr, Ni and Zn would not be detectable until suspended-sediment concentrations were about 125 mg/L, 30 mg/L, 10 mg/l, and 4, mg/L respectively (fig 5*C*).

These examples suggest that that the ability to detect sediment-associated trace elements depends on the constituent of interest and the concentration of suspended sediment in the whole-water sample. Median suspended-sediment concentrations characteristic of "rural" and "urban" highways monitored in the 1970s and 1980s were about 50 and 140 mg/L, respectively (Driscoll and others, 1990) and median sediment concentrations measured by NURP were 101, 67, 69, and 70 mg/L for residential, mixed use, commercial, and open/nonurban land uses, respectively. Therefore, the detection-limit issue is not as critical a concern for highway- and urban-runoff studies as it may be when monitoring relatively uncontaminated receiving waters. These examples also indicate, however, that it may be imprudent to declare that a certain trace element is not present in runoff on the basis of whole-water analysis unless the detection limits and suspended-sediment concentrations also are published. Also, these examples are based only upon the contribution of sediment-associated trace elements and do not include concentrations of dissolved trace elements, which may be substantial given the unique geochemical environment on the road surface.

A.

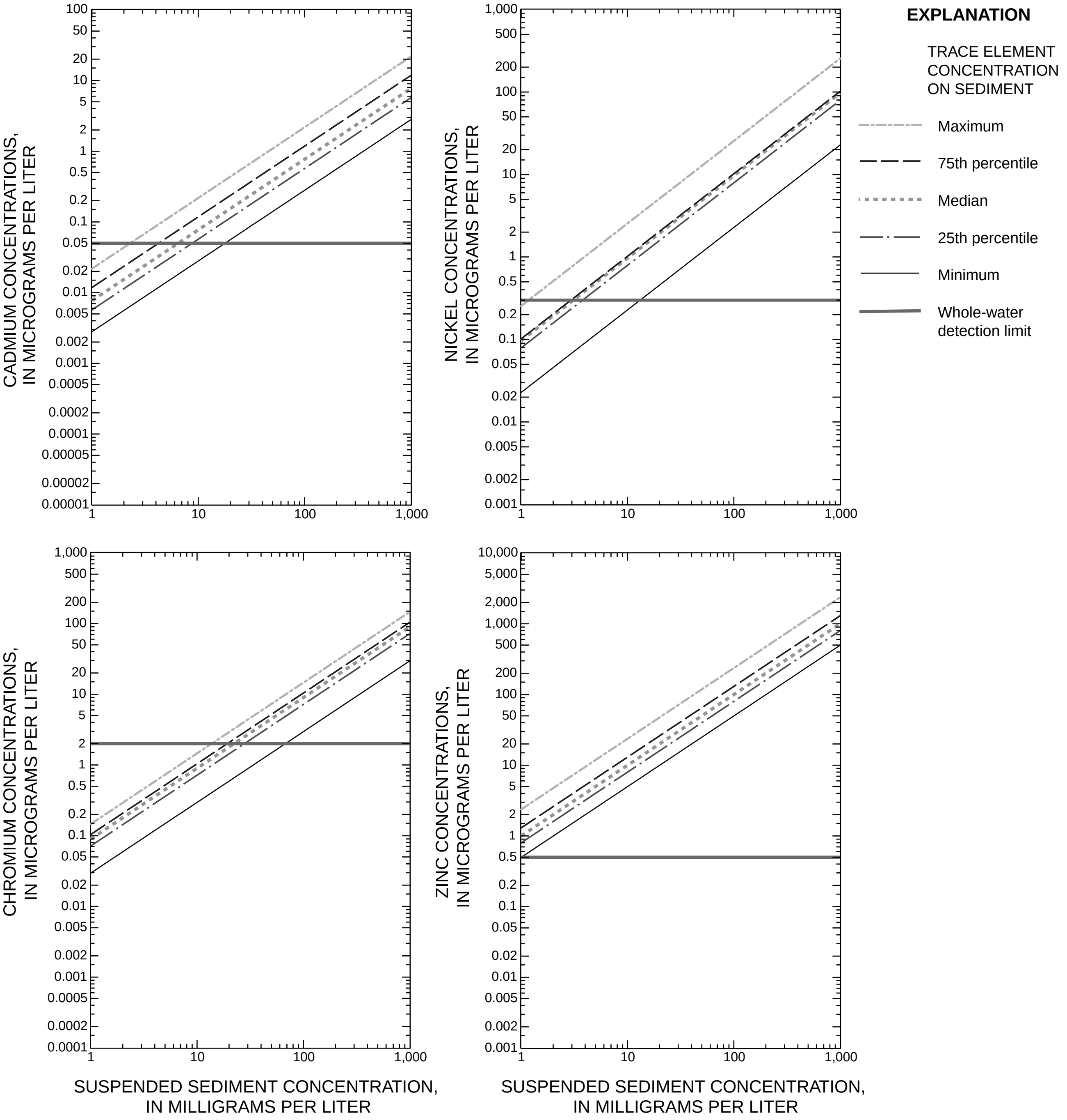
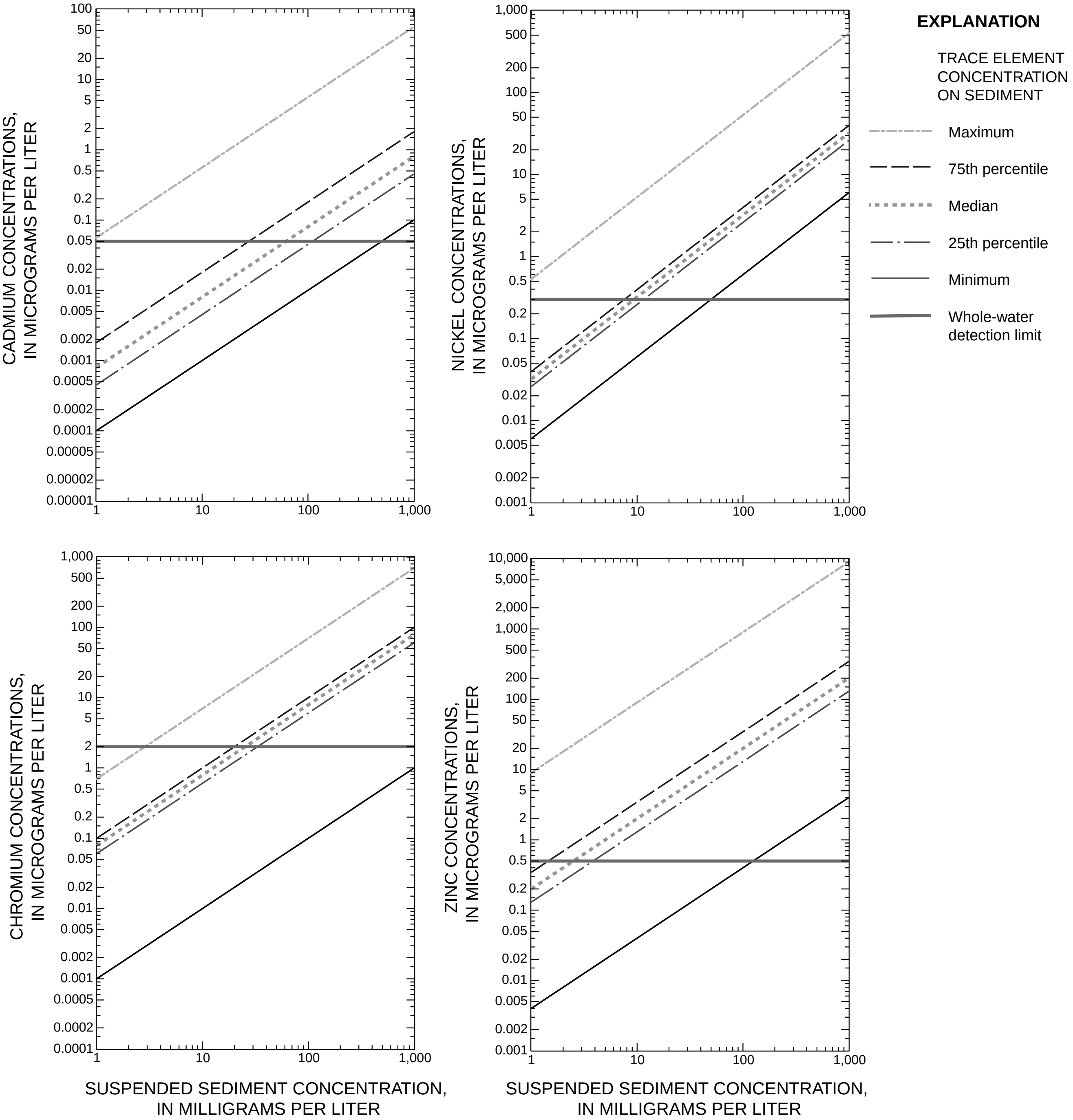


Figure 5. Method detection limits (MDLs) for analysis of whole-water samples (Garbarino and Struzeski, 1998) in comparison to whole-water trace-element concentrations calculated from measured trace-element concentrations in fine-grained (*A*) highway-surface sediments (Kobriger and Geinopolos, 1984) and hypothetical suspended-sediment concentrations in highway runoff; (*B*) urban stream-bed sediments (Rice, K.C., USGS NAWQA Trace Element Synthesis Project, written commun.) and hypothetical suspended-sediment concentrations in urban-stream runoff; and (*C*) stream-bed sediments (Rice, 1999) and hypothetical suspended-sediment concentrations in receiving waters.

B.



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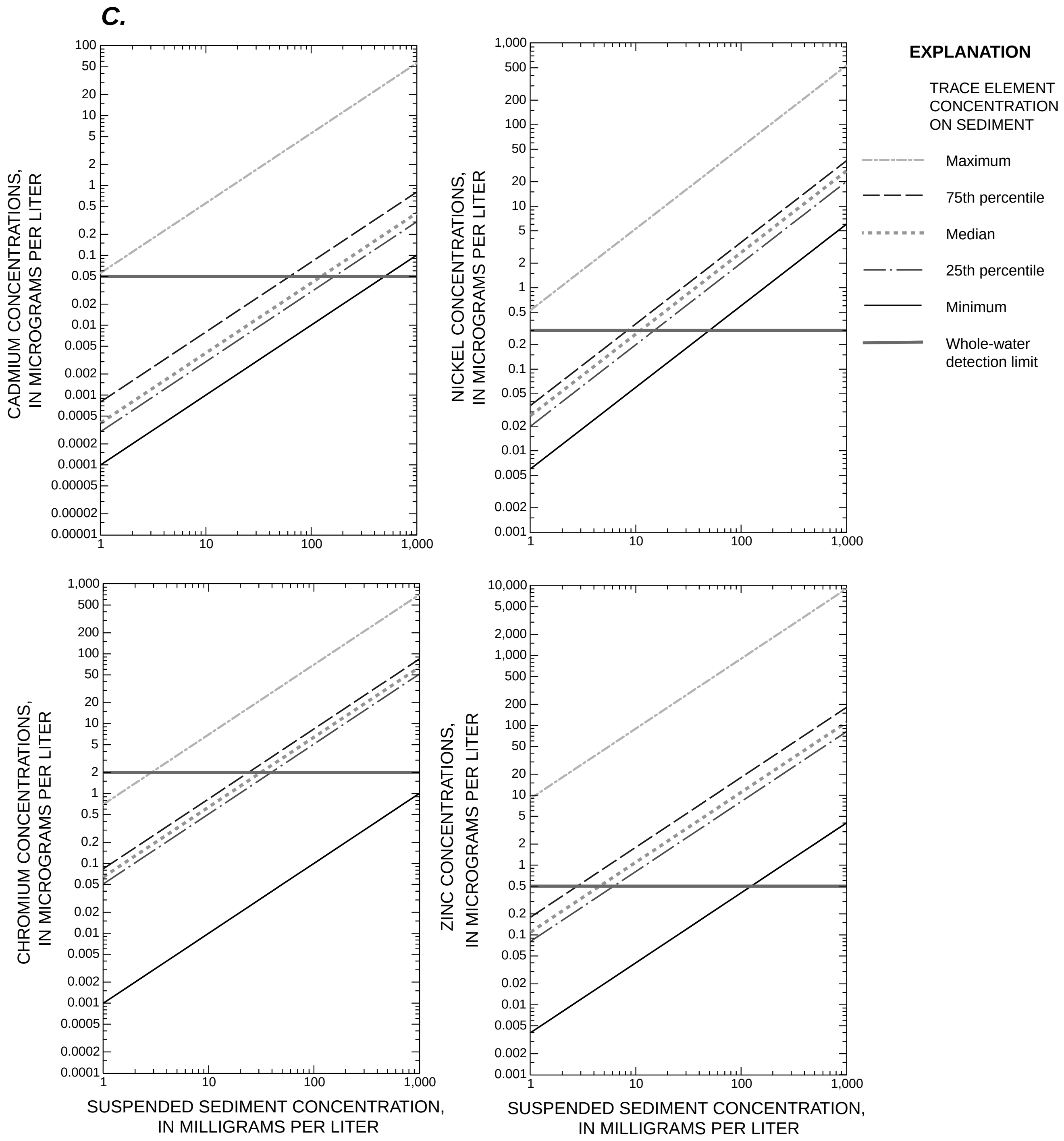

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Dissolved (Filtered Water)

The dissolved phase is, theoretically, the material that forms a uniformly homogeneous solution of water and solute molecules. The solute molecules are surrounded by solvent (water) molecules and do not contact other solute molecules except in collisions during migration through solution (Hem, 1992). Chemically, the theoretical definition of the dissolved phase would include trace elements that exist as neutral atoms, electrically charged ions, neutral or charged complexes (containing two or more associated ions), and multielemental molecules. The amount of each trace element dissolved in solution may be estimated using geochemical models based on the thermodynamics of each constituent in solution (Bricker, 1999), but the information needed to construct such a model is dependent upon water-quality data that can be obtained only from complete analysis of appropriate water samples. Physically, the operational definition of the dissolved phase includes all the material that would never settle out of solution by gravity. Consideration of colloidal particles, however, reveals a fundamental inconsistency in this definition. Colloidal particles (particles having diameters that range from about 0.001 to 1 micrometers) are agglomerations of molecules that are not viewed as chemically dissolved, but that still will not settle from solution, even under favorable conditions (Hem, 1992; Buffle and Leppard 1995a; 1995b).

Difficulties in separating colloids from water have led to the somewhat arbitrary definition of dissolved as those constituents that pass through a 0.45-micron (μm) or a 0.40-μm filter (USEPA, 1983; USGS, 1984; American Public Health Association-American Water Works Association-Water Pollution Control Federation (APHA-AWWA-WPCF), 1989; American Society for Testing and Materials (ASTM), 1995). The USEPA Office of Water has defined the dissolved phase as the standard by which compliance with water-quality criteria should be measured (USEPA, 1996). The use of this operational definition has been codified because it is believed that this "dissolved trace element" definition more closely approximates the bioavailable fraction of trace elements in the water column than does the definition of total recoverable elements (40 CFR Part 131, 1995; Horowitz and others, 1996; Sansalone and Buchberger, 1997). There also are other methods to measure "dissolved" concentrations, such as "exhaustive filtration," which removes colloids from solution by utilizing a filter's tendency to clog to achieve very fine pore sizes (approaching 0.005 micrometers) to remove colloids from solution (Taylor and Shiller, 1995); tangential filtration and centrifugation, which also may be used to separate particulates and colloids from the dissolved phase (Buffle and Leppard, 1995b); and chemical speciation methods such as potentiometry or ion exchange resin removal (Morrison and others, 1984a,b; Morrison and others, 1987; Breault and others, 1996). These methods are much less prevalent than the USEPA standard, so in most cases a reference to a "dissolved constituent" is in reality a reference to an analysis of a filtered water sample.

Benefits

Monitoring the dissolved phase of runoff may provide an abundance of information that is potentially useful for highway and urban runoff studies. Dissolved trace-element concentrations are expected to provide more reliable correlations with toxicity than total-recoverable, or sediment-associated trace-element concentrations (USEPA, 1992c; Stumm and Morgan, 1996). If the dissolved phase is monitored in conjunction with the whole-water and(or) suspended-sediment phases, more detailed information about the partitioning of trace elements of interest (in time and space) can be obtained. The mechanisms that control partitioning (sorption reaction rates), however, are poorly understood and require further study (Davis and Kent, 1990). Repeated sampling of runoff and analysis of the dissolved matrix to evaluate the chemical behavior of trace elements on the pavement, in drainage structures, BMPs, and receiving water may provide information necessary to evaluate the effectiveness of BMPs (including retention) for toxicity reduction of effluent (Sansalone and Buchberger, 1997). Relevant information about the dissolved phase in conjunction with information about the physical and chemical characteristics of suspended solids can provide distribution coefficients between the dissolved, suspended-sediment, and ultimately the bottom-sediment phases. These coefficients may be used to estimate the effects of runoff at unmonitored sites on receiving waters (Yousef and others 1985a, 1985b; Sansalone, Buchberger, and Al-Abed, 1996; Sansalone, and Buchberger, 1997; Radovanovic and Koelmans, 1998; Sigg, 1998).

Monitoring of dissolved trace-element concentrations in runoff samples has been incorporated into recent highway-runoff studies in response to scientific and regulatory information needs and for evaluating the potential toxicity of highway-runoff (Dupuis and others, 1985; Marsalek and others, 1997; Sansalone and Buchberger, 1997). Highway runoff data sets that include analysis of comparable dissolved and whole-water samples indicate that a substantial proportion of the trace elements measured in the whole-water samples may be associated with the dissolved matrix (fig. 6). The relatively high proportion of dissolved trace elements (medians from fig 6 being about 55-, 45-, 52-, 60-, 12-, and 65-percent dissolved for Cd, Cr, Cu, Ni, Pb, and Zn, respectively) would at first seem to contradict the paradigm that almost all trace elements are associated with the suspended-sediment matrix (table 2). Consideration of the unique geochemistry of the highway environment, however, would suggest that a relatively higher proportion of some trace elements may be dissolved in pavement runoff than in river water. For example, data from a very low-flow snowmelt event (Dupuis and others, 1985), which indicated that 100 percent of the Cr, Cu, and Pb was in the dissolved phase, is logical given the fact that this water had relatively high ionic strength but insufficient volume and flow velocity to entrain suspended solids (Dupuis and others, 1985, reported an EMC of 7 mg/L for suspended solids and a corresponding specific conductance of 3,450 µS/cm during this "event"). Although this may be an extreme case, figure 6 indicates that speciation of the individual constituents may be variable and may depend upon the chemistry of the constituent of interest, and potentially many site specific variables. More specifically, table 3 indicates that the relative solubility of trace elements differs from constituent to constituent among available results from highway-runoff studies. Studies of dissolved trace elements also suggest the potential for removal of trace elements by sedimentation. For example, Pb—being the least soluble among these trace elements—may be more efficiently removed using BMPs that employ sedimentation processes than would trace elements with greater relative solubilities.

Study of the dissolved matrix also provides information about trace-element mobilization and transport processes that may be valuable for characterizing highway runoff, evaluating the potential effectiveness of BMPs, and identifying possible environmental effects. Studies indicate that whereas a high proportion of the trace elements in runoff on the pavement are dissolved, geochemical effects such as pH buffering by reaction with suspended and bottom sediment and by the concrete in drainage structures tends to drive speciation toward the solid phase (Revitt and Morrison, 1987; Morrison and others, 1990). Conversely, other biochemical and(or) geochemical conditions that exist in drainage structures and BMPs can reverse this process, thereby increasing concentrations of dissolved trace elements. For example, both Ellis and others, (1987) and Morrison and others, (1990) measured increases in dissolved concentrations of Cd, Cu, Pb, and Zn in "gully-pot liquor" (catch-basin water) between storms that was caused by conditions of low pH and anoxia resulting from decomposition of organic matter in the sump sediment.

Technical Concerns

Although analysis of the dissolved sampling matrix may provide information about the speciation of trace elements, improper sampling, processing, and preservation is of particular concern when using this matrix in trace-element monitoring programs. Recent studies have shown that the currently accepted operational definition of dissolved constituents (passing unspecified volumes of whole water through unspecified 0.45-µm membrane filters) is inadequate due to sampling and processing artifacts (Kennedy and others, 1974; Shiller and Boyle, 1987; Horowitz and others, 1992; Taylor and Shiller, 1995). It is difficult and expensive to process and preserve filtered samples under field conditions without affecting sample integrity (contributing or attenuating trace elements of interest) through the extensive contact with pumps, tubing, filters, and sample bottles used in the filtration process.

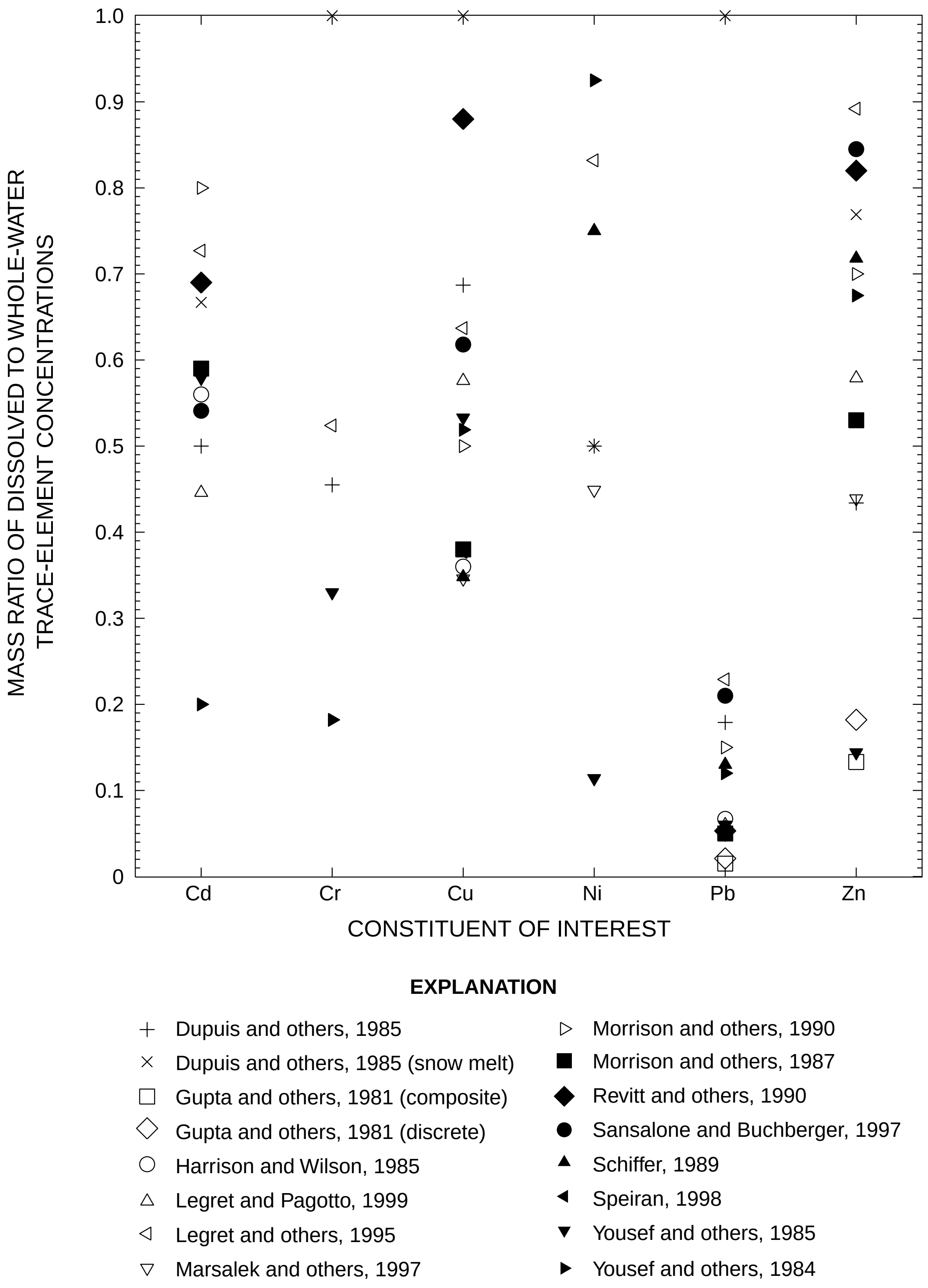

Figure 6. The mass ratio of dissolved to whole-water concentrations measured in pavement runoff.

Table 3. Hierarchy of the relative solubility of trace elements commonly studied in highway runoff

[The percent dissolved of each constituent's total concentration decreases from left to right, the greater than symbol (>) indicates a difference of at least 10 percent between adjacent constituents; ≈, a difference that is less than 10 percent. Cd, cadmium; Cr, Chromium; Cu, Copper; Ni, nickel, Pb, lead; Zn, zinc]

Highway-runoff study	Relative solubility
Dupuis and others, 1985	Cu>Cd≈Ni>Cr>Zn>Pb
Ellis and Revitt, 1982	Cd>Zn≈Cu>Pb
Gupta and others, 1981	Zn>Pb
Harrison and Wilson, 1985c	Cd>Cu>Pb
Laxen and Harrison, 1977	Cd>Zn>Pb
Legret and Paggotto, 1999	Zn≈Cu>Cd>Pb
Legret and others, 1995	Zn>Ni>Cd>Cu>Cr>Pb
Marsalek and others, 1997	Ni≈Zn>Cu
Morrison and others, 1990	Cd>Zn>Cu>Pb
Morrison and Florence, 1990	Cd>Zn>Cu>Pb
Morrison and others, 1987	Cd>Zn>Cu>Pb
Morrison and others, 1984b	Zn> Cd>Cu>Pb
Revitt and others, 1990	Cu>Zn>Cd>Pb
Revitt and Morrison, 1987	Cd≈Zn>Cu>Pb
Sansalone and Buchberger, 1997	Zn>Cu>Cd>Pb
Sansalone and others, 1995	Cr>Cd>Cu≈Zn>Pb
Schiffer, 1989	Ni≈Zn>Cu>Pb
Sperian, 1998	Zn>Cu>Pb
Yousef and others, 1985b (runoff)	Cd≈Cu>Cr>Zn≈Ni>Pb
Yousef and others, 1985b (pond)	Zn≈Cu>Cd≈Ni>Pb≈Cr
Yousef and others, 1984	Ni>Zn>Cu>Cd>Cr>Pb

Laboratory and field evaluations of the filtration process indicate that measured trace-element concentrations in filtered water samples are affected by both environmental and procedural factors (Horowitz and others, 1992). Defining environmental factors, both natural and anthropogenic, include local geochemistry, suspended-sediment concentration, grain-size distribution in suspended sediment, concentration of colloids, and the amount of organic material present in the sample. These factors will be highly variable from storm to storm and site to site, and therefore, these variables need be documented for use of dissolved matrix data (especially for eventual use in a regional or national synthesis). Procedural factors, such as filter pore size, filter type, surface area, method of filtration, and the volume of sample processed also influence the proportion of the total trace-element concentration that will be measured as "dissolved" in the filtrate (Martin and Meybeck, 1979; Horowitz and others, 1992; Karlsson and others, 1994). Filtration-rate reductions commonly are observed as water flows through a filter. These reductions are due to clogging of the filter by organic and inorganic material, which effectively reduces the pore size of the filter and likely increases the quantity of trace-element-rich colloidal material retained by the filter (Kennedy and others, 1974; Wagemann and Brunskill, 1975; Martin and Meybeck, 1979; Hoffman and others, 1981; Ledin, 1993; Nriagu and others, 1993; Karlsson and others, 1994). For example, in a controlled experiment, Horowitz and others (1992) determined that concentrations of dissolved Fe (and other trace elements) in filtrates were affected by pore size, filter diameter, and the total volume processed (fig. 7). In a subsequent study, Horowitz and others (1996) evaluated the performance of different filters commonly used for sampling the dissolved matrix (Shiller and Boyle, 1987; Windom and others, 1991; Nriagu and others, 1993; Benoit, 1994; Horowitz and others, 1994; Taylor and Shiller, 1995; USEPA, 1996) and found that trace-element concentrations appear to be proportional to the surface areas of the filters. Horowitz and others (1996) recommended use of the Gelman filter for minimizing filtration artifacts because of its large surface area and because the necessary QA/QC data (Windom and others, 1991; Horowitz and others, 1994; Horowitz and others, 1996; USEPA, 1996) are available for this filter.

Aspects of the filtration process other than the pore size and type of filter must also must be considered if artifacts are to be reduced or eliminated and concentration data for dissolved constituents are to be considered reliable and comparable. In some studies, trace elements were shown to sorb to the filter during initial processing, and, once all the potential sorption sites were filled, higher concentrations were measured in subsequent aliquots of the filtrate (Horowitz and others, 1994). One should be aware that the presence of

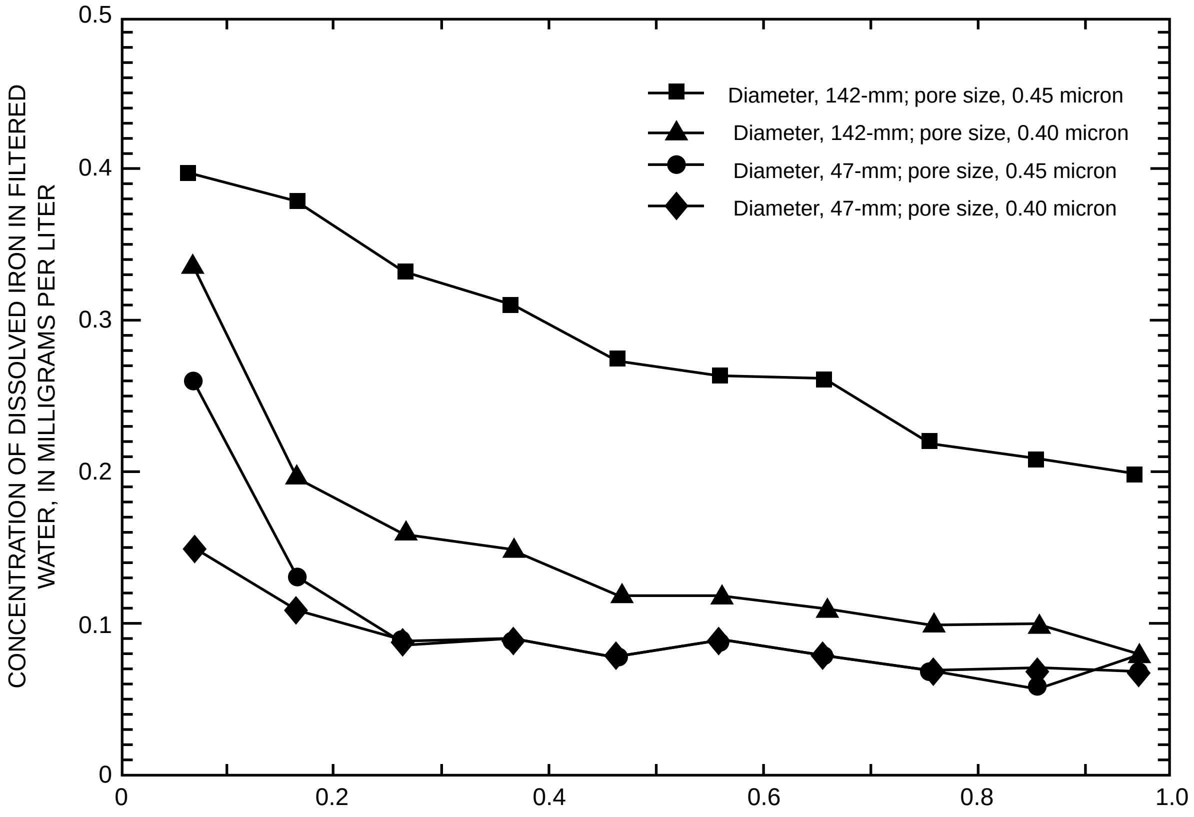

Figure 7. The effect of filter diameter, pore size, and total volume of water processed, on measured concentrations of dissolved iron (from Horowitz and others, 1992).

deionized water that was used to condition the filters could also result in a similar pattern of increasing concentrations with subsequent aliquots of the filtrate because the initial aliquots could be diluted by this deionized water (Horowitz and others, 1994).

Chemical-speciation kinetics may be a major issue affecting measured dissolved concentrations in highway runoff samples. Several physical and chemical processes affect the speciation of trace elements at different time scales, including complexation, flocculation, chemical precipitation, biological reactions, and sorption-desorption reactions (Revitt and Morrison, 1987; Davis and Kent, 1990; Sansalone, Buchberger, and Al-Abed, 1996; Sansalone and Buchberger, 1997). All these reactions are complex, variable, and interdependent, with reaction rates that are different for each trace element. Furthermore, mechanisms that control reaction rates are poorly understood and require further study (Davis and Kent, 1990; Stumm and Morgan, 1996). A few examples are examined to estimate the order of magnitude of the time scales at which these reactions may proceed. In one case, Hering and Morel (1988) measured the complexation rate of Cu and found that more than half of the free Cu had complexed within a two-hour period. In a highway-runoff study, Sansalone and Buchberger (1997) reported that dissolved concentrations of trace elements in highway runoff samples were affected by flocculation of fine particulates during the initial six to eight hours of holding time. Therefore, they did a partitioning experiment and measured substantial changes in the partitioning of trace elements that are neither predominantly dissolved nor associated with suspended solids (Cu and Ni) but did not detect substantial changes for trace elements that were either primarily associated with suspended solids (Al, Fe, and Pb) or primarily dissolved (Zn, Mn, and Cd) over 24 hours. Davies (1986) monitored the chemical precipitation of dissolved Cd in a previously filtered hard-water solution. Cd concentrations were reduced by about 20 percent within 10 hours and 40 percent within in 20 hours. This test solution reached equilibrium at about 50 hours with an overall reduction in the dissolved phase concentration of about 85 percent. Ellis and others (1987) and Morrison and others, (1990) measured increases in dissolved trace-element concentrations caused by biochemical processes in a road-side catchbasin, during a period of a few days. These examples, however, indicate only the order-of-magnitude of potential reaction rates because the actual reaction rates depend upon conditions that will differ between storms and between samples collected within each storm. More specifically, geochemical changes on the pavement, in the drainage structures (during and between flow events) and in the sample collection bottles (until the samples are processed and or preserved) will effect these reaction rates and the apparent speciation observed in the partitioned samples.

Partitioning rates between the dissolved and suspended-solids phases are of particular concern when sampling the dissolved matrix in urban- and highway-runoff studies, because logistics may preclude sample filtering during a storm, and suspended sediment concentrations can vary by orders of magnitude within and between storms. Wood and others (1995) published reaction-rate equations and rate constants for several trace elements under different conditions of suspended sediment and salinity. These equations, reformulated in terms of the proportions of dissolved and solid-phase trace elements to the total (whole water concentration) are summarized as

$$[TE_d / TE_w]_t = 1 + k_b * [TE_s / TE_w]_{t-1}$$
$$- k_f * [SSC] * [TE_d / TE_w]_{t-1} , \qquad (2)$$

where

$[TE_d / TE_w]_t$ is the ratio of the dissolved (TE_d) to total trace element (TE_w) concentration at time step t;

$[TE_s / TE_w]_{t\text{-}1}$ is the ratio of the sediment associated (TE_s) to total trace element (TE_w) concentration during the previous time step t-1;

$[TE_d / TE_w]_{t\text{-}1}$ is the ratio of the dissolved (TE_d) to total trace-element (TE_w) concentration during the previous time step *t*-1;

$[SSC]$ is the concentration of solids in the sample container;

k_b is the backward rate constant indicating the rate of desorption from solids; and

k_f is the forward rate constant indicating the rate of sorption to solids.

Using this equation, and rate constants for Cu in a fresh-water solution containing natural particles, three hypothetical examples are presented to illustrate the potential effect of solid-solution partitioning on dissolved trace-element concentrations with time in the absence of competing reactions. The median national EMC for total Cu (0.039 mg/L) and various suspended-sediment concentrations representing a range of typical highway-runoff sediment concentrations (from Driscoll and others, 1990) are used to examine potential rates of sorption to sediment as a function of the time from sample collection (assuming all the Cu in solution is initially dissolved). Figure 8 indicates that the proportion of measured dissolved Cu will be a function of the time between sample collection and filtration and of the concentration of solids in the sample container. Within the first six hours, about 15, 80, and more than 99 percent of the initial dissolved Cu concentrations are expected to be sorbed by the solid matrix when suspended-sediment concentrations are 10, 100, and 1,000 mg/L, respectively. Therefore, it is difficult to interpret the data on dissolved concentrations unless dissolved samples are processed shortly after sample collection because the relation between a measured dissolved concentration and the actual concentration of any given trace element in the runoff at the sampling point is unknown. This consideration is important in runoff studies, especially in terms of the collection and use of composite samples for analysis of a single EMC value for each storm, because the median of national storm-event durations reported by Driscoll and others, (1990) is about 5 hours and the median of national storm-event durations reported by the USEPA (1992a) is about 9 hours. Furthermore, Sansalone and Buchberger (1997) noted that, in many runoff-monitoring programs, samples may not be retrieved and subsequently filtered within 24 hours. Also, many programs do not collect samples from pavement sheet flow (where geochemical conditions are expected to favor the dissolved phase), but rather from drainage systems in which considerable residence times and mixing can favor partitioning to the solid phase (Sansalone and Buchberger, 1997). It is for these

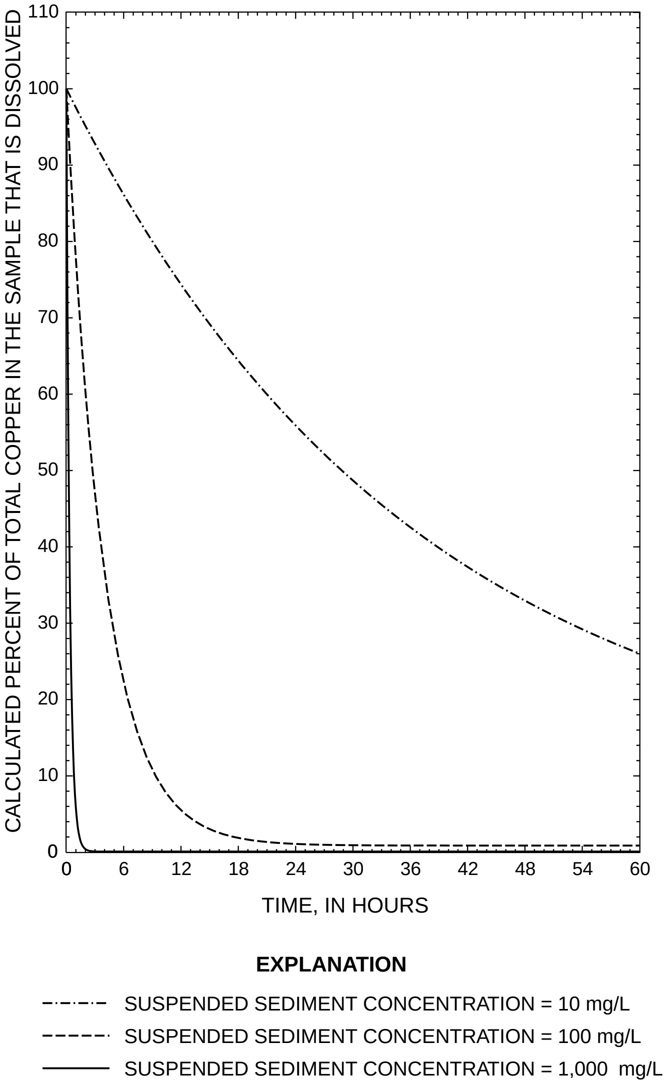

Figure 8. The percent of total copper that is dissolved in a hypothetical two-phase (water and sediment) highway-runoff sample with the median national event mean copper concentration (0.039 mg/L) and various suspended-sediment concentrations (representing a range of typical highway runoff sediment concentrations; Driscoll and others, 1990) as a function of the time from sample collection using published rate equations and rate constants for natural particles in fresh water (Wood and others, 1995) assuming that all of the copper is initially in the dissolved state.

reasons that contemporary trace-element sampling protocols require immediate filtration of samples upon collection (Horowitz and others, 1994; Radtke and others, 1998).

The existence of dissolved-matrix sampling artifacts raises serious questions about the generation of accurate, precise, and comparable dissolved trace-element data and casts doubt on the utility of substantial amounts of historical data, especially in the context of a regional or national-runoff monitoring program. It is unlikely that correction factors can be developed and applied to filtered-water data to eliminate the effects of processing artifacts, because differences in background geochemical conditions and suspended-sediment concentrations vary widely at regional and national scales. Three methods, however, are proposed to minimize filtration artifacts and enhance the comparability of dissolved (filtered) trace element data for national monitoring programs:

- use of large-surface area filters and collection of the initial aliquots for analysis (Windom and others,1991; Horowitz and others, 1994; USEPA, 1996);
- precentrifugation to remove sediment and colloids followed by filtration through a 0.45-micrometer membrane filter (Horowitz and others, 1996); and
- exhaustive filtration with more complex filtering assemblies that are designed to remove all colloids and to measure only the trace elements that are chemically dissolved (Martin and Meybeck, 1979; Hoffman and others, 1981; Taylor and Shiller, 1995).

The effects of filtration artifacts may be limited by employing one of these three methods but data from analysis of samples processed with different methods may not be comparable. Detailed documentation of all sampling and processing procedures is necessary to assess dissolved trace-element data in terms of the potential for filtration artifacts (Horowitz and others, 1996).

For regional or national runoff-monitoring programs, the dissolved matrix may provide valuable information about the chemistry of runoff speciation, but use of this matrix alone may lead to an underestimation of the effects of highway runoff on receiving waters. For example, Yousef and others (1985a; 1985b) measured both dissolved and whole-water concentrations in highway runoff and the retention basin receiving that runoff. Analysis of samples collected from the retention basin indicated that reductions in concentrations of dissolved Cd, Cr, Cu, Ni, Pb, and Zn, were on the order of 30-, 30-, 56-, 44-, 63-, and 88-percent, respectively compared to dissolved concentrations measured in the highway runoff. Analysis of whole-water samples collected from the retention basin, however, indicated that reductions in concentrations of Cd, Cr, Cu, Ni, Pb, and Zn, were on the order of

47-, 66-, 73-, 92-, 97-, and 98-percent, respectively, compared to whole-water concentrations measured in the highway runoff. The reductions in trace element concentrations for whole-water samples were generally 1.5 to 2 times greater than for the dissolved trace element samples because the difference in dissolved concentrations did not account for the relatively large effect of the removal of sediment and associated trace elements by settling in the pond (Yousef and others, 1985a; 1985b).

Suspended Sediment

Suspended sediment, also referred to as suspended solids and suspended particulate matter, is operationally defined as the material that is collected with the water phase in the water column that does not pass through a 0.45-micrometer or a 0.40-micrometer filter. Methods used to separate the suspended solids from the water matrix prior to chemical analysis include filtration, gravity dewatering, and centrifugation. Each of these methods has been used extensively in water-quality and geochemical studies. Samples are filtered by in-line filtration using membrane filters or by tangential filtration using a stack of membrane filters (Horowitz, Elrick and Hooper, 1989a). The gravity-dewatering method is accomplished by allowing the entrained suspended sediment to settle out over time in a sealed bottle at room temperature (Jenne and others, 1980; Horowitz, 1986). In the centrifugation method, centripetal force is used to accelerate the separation of the solid from the liquid phase (Horowitz, Elrick and Hooper, 1989a). Typically, the separated solids are then chemically processed to extract trace elements for chemical analysis. The two types of sediment-digestion techniques, operationally defined as "total recoverable" and "total" (Fishman and Friedman, 1989), were discussed previously in the section on whole-water analysis. A number of sequential extraction methods can be used to evaluate the potential bioavailability and environmental behavior of trace elements present in sediment by measuring the ease of release of trace elements into solution (Tessier and others 1979; Hamilton and others 1984; Fiedler and others, 1994; Kane, 1995).

Properties of suspended-sediment particles, including specific surface area, number and type of surface groups, and surface charge, as well as geochemical characteristics of the solution will influence how trace elements partition between the dissolved and suspended-sediment matrixes (Sigg, 1998). Partitioning is also a function of the chemical characteristics of each trace element. In natural waters, the relative affinity of trace elements for the solid matrix generally decreases in the order Pb>Zn>Cd≈Cu (see table 3). This order, however, is not absolute. For example, in waters in which iron oxides predominate, the order is Pb>Cu>Cd≈Zn (Sigg, 1998); but high concentrations of dissolved organic matter (DOM) may cause a redistribution of trace elements such that the order would be Pb>Cd>Zn>Cu because Cu and Zn are complexed by DOM (Breault and others, 1996; Radovanovic, and Koelmans, 1998). Also, anthropogenic and natural organic material (such as tire particles, vegetation, and biota) commonly are separated with and analyzed as a component of the suspended sediment. These organic materials can have high trace-element affinities. For example, algae can become enriched with trace elements and can be measured as part of a suspended-sediment load (Sigg, 1998).

Benefits

Monitoring the suspended-sediment matrix in highway and urban runoff may provide information for trace-element studies that have various objectives. Historically, chemical analysis of suspended sediment has provided information for the study of geochemical cycling, contaminant transport, trace-element loads, temporal variability and trend analysis, as well as the study of biological effects of sediment-associated trace elements (Horowitz, 1995; Buckler and Granato, 1999). Although analysis of this matrix provides data suitable for meeting these objectives, chemical analysis of suspended sediment is particularly suited for studying short-term spatial and temporal variability in trace-element concentrations. Use of this matrix, therefore, may provide useful information as a component of storm-runoff monitoring studies.

Fewer data sets are available for trace metals in the suspended-sediment matrix than for whole- or filtered-water samples because (with the exception of Canada; Persaud and others, 1993) currently there are few Federal, State, or local water-quality criteria or regulatory limits based on sediment-associated trace-element concentrations. The lack of sediment-associated water-quality criteria is due in part to substantial disagreements over how to estimate the bioavailability of sediment-associated trace elements

(Forstner and Wittmann, 1981; Salomons and Forstner, 1984; Horowitz, 1991). Similarly, use of the suspended sediment-sampling matrix for chemical analysis of trace elements is not as prevalent in the highway runoff literature as either whole- or filtered-water matrix sampling. Historically, however, many highway- and urban-runoff studies have noted correlations between suspended solid and trace element concentrations from the analysis of whole-water samples (Gupta and others 1981; Harrison and Wilson, 1985a; Driscoll and others, 1990; Sansalone, J.J., Buchberger, S.G., and Koechling, M.T., 1995).

When chemical analysis of suspended sediment has been included in runoff studies, use of this matrix has yielded information about trace-element speciation, the distribution among different grain sizes, and the source, fate, and transport of trace elements. Highway- and urban-runoff studies in which sequential extraction schemes are used to differentiate the suspended-sediment-associated trace elements among chemical fractions (including: ion exchangeable; acid soluble; reducible—associated with Fe- and Mn-oxides; reducible—associated with an organic fraction; and residual—associated with the mineral matrix) commonly provide valuable information about the physical and chemical mechanisms within and between storms that influence the quality of runoff and the potential effect on receiving waters (Wilber and Hunter, 1979; Harrison and others, 1981; Ellis and Revitt, 1982; Hamilton and others, 1984; Harrison and Wilson, 1985b; Yousef and others, 1990; Flores-Rodriguez and others, 1994). For example, Harrison and Wilson (1985b) utilized sequential extraction of suspended solids separated from highway runoff by centrifugation to show that the sediment had chemical characteristics similar to those of road-surface dusts. Flores-Rodriguez and others (1994) demonstrated that structural changes in the solids and chemical changes in the associations between trace elements and solids reduced the chemical availability of some trace elements as stormwater runoff moved through an urban drainage system. Also, several studies have shown that differences in the intensity, duration, and type of storm affect the grain-size distribution of suspended sediment, which in turn affects the total load and partitioning of trace elements between the dissolved and suspended matrixes (Harrison and Wilson, 1985c; Sansalone and others 1995; Sansalone and Buchberger, 1996; Sansalone and others, 1998). Further study of the suspended sediment-sampling matrix may provide the basis for quantification of transport processes, which may explain some of the wide variability that is characteristic of measured highway- and urban-runoff concentration data sets. Marsalek and others (1997) showed that trace-element concentrations in the fine (less than 45 μm) size fraction of suspended sediment in bridge runoff were greater than in corresponding bulk suspended-sediment samples. This enrichment, however, was considered insignificant in terms of the bulk sediment load because the fine fraction represented less than one percent of the total mass of solids at that site. Although the concentrations of trace elements in the bulk suspended sediment were only 43-, 44-, 76-, and 61-percent of the fine-fraction concentrations of Cu, Ni, Pb, and Zn, respectively, bulk suspended-sediment trace-element concentrations exceeded Canadian aquatic sediment-quality guidelines. If these discharges are uncontrolled they could substantially reduce receiving water quality (Marsalek and others, 1997).

Information gained from analysis of the grain-size distribution of sediment-associated trace elements as a function of geology, climate, land use, and environmental practices could aid in the development, design, implementation, and evaluation of BMPs. For example, Harrison and Wilson (1985b) measured higher concentrations of trace elements in suspended-sediment samples than in street-dust samples. They determined that the apparent enrichment per unit mass was caused by selective removal of the larger grain sizes in the roadside catchbasins, which shifted the grain-size distribution in suspended-sediment samples toward the trace-element-rich fine fractions. More recently, while investigating the trace-element composition and speciation in street sediment, Stone and Marsalek (1996) found that silt and clay (less than 63 microns), fine sands (63 to less than 250 microns), medium sand (250 to less than 500 microns) and coarse sand (500 to less than 2000 microns) accounted for about 4, 27, 30, and 39 percent of the total trace-element load, respectively. The fine fractions tend to stay in suspension in retention facilities and are hard to remove by street cleaning operations. They concluded that the measurement of bulk sediment-associated trace-element concentrations is adequate for determining total loads, but the measurement of concentrations as a function of grain size is necessary to assess remedial options.

In receiving waters, the role of suspended sediment in the biological and geochemical cycling of trace elements in fluvial systems is well established (Forstner and Wittmann, 1981; Salomons and Forstner, 1984). Even in natural-waters with suspended-sediment concentrations as low as 10 mg/L, the sediment may be a substantial source for many trace elements. For example, Horowitz (1991, 1995) demonstrates the potential effect of different sediment concentration on the solid phase contribution to whole-water trace-element concentrations (table 4). As suspended-sediment concentrations approach 100 mg/L, the solid phase may be the dominant source of trace elements in natural waters Horowitz (1991, 1995). The percentiles of different suspended-sediment concentrations reported by the USGS NASQAN program from 1974 to 1981 indicate their frequency of occurrence: 18 mg/L (25th percentile), 67 mg/L (50th percentile), and 193 mg/L (75th percentile; Smith and others, 1987). In comparison, the range of suspended-solids concentrations in highway runoff was reported as 4.0 to 1,160 mg/L (Smith and Lord, 1990), while the range of suspended-solid concentrations for urban runoff was reported as 1.0 to 36,200 mg/L (Makepeace and others, 1995). Suspended sediment from runoff discharges may also settle to the bottom sediment in receiving waters and may interact with natural sediment in the deposition and resuspension cycles of natural streams. For example, Harrison and Wilson (1985c) noted the resuspension of previously deposited runoff-derived sediment near an outfall when they measured upstream suspended-sediment concentrations that were less than 2.0 mg/L, highway-runoff outfall concentrations of about 100 mg/L, and downstream suspended-sediment concentrations that were about 230 mg/L.

Technical Concerns

Although chemical analysis of the suspended-sediment matrix may provide information about the physical and chemical processes that influence the quality and potential effects of runoff on the aquatic environment, the potential for improper sampling and processing are of concern when using this matrix in trace-element-monitoring programs. The highly heterogeneous lateral and vertical distribution of suspended sediment in the water column (caused by differences in grain size, density, and the distribution of kinetic energy in the flowing water) makes it difficult to collect a representative sediment sample. This difficulty may be the largest potential source of bias in measurements of sediment-associated trace-element concentrations (Webb and others, 1999). Methods for the physical collection of representative samples of suspended sediment from fluvial systems and from runoff drainage structures are described by Edwards and Glysson (1999) and Bent and others (2001), respectively. Although the "contamination problem" is perceived to be relatively minor for sampling the suspended-sediment matrix, the potential for sampling artifacts from extensive contact with pumps, tubing, filters, and other equipment used in the separation process must be recognized and addressed with QA/QC measures.

When monitoring highway and urban drainages, rapid changes in flow and concentrations of sediment and trace elements in runoff may complicate efforts to obtain sufficient sediment mass in individual aliquots to represent in-storm processes using standard automatic sampling techniques. If suspended-sediment concentrations are low (less than about 100 mg/L), physical and chemical limitations of the separation and analysis process may affect the quality and reproducibility of measured trace-element concentrations because replicate analyses of small aliquots of suspended-sediment can display marked variability (Horowitz, 1995). Although a sediment mass as small as 50 mg may be sufficient for trace element analysis, a single grain of unusual composition in a 50 mg sample may generate a non-reproducible analytical result (Horowitz, 1995). In comparison, Standard Reference Materials (SRMs) produced by the National Institute of Science and Technology (NIST), which have been exhaustively processed and tested for chemical content and homogeneity prior to distribution, are distributed with a "Certificate of Analysis" that indicates a minimum sample size for aqueous sediment (commonly 250 to 500 mg) that is typically five to ten times the minimum possible sample size (NIST, 1998; 2000).

Table 4. Solid-phase contributions to whole-water trace-element concentrations of rivers in the conterminous United States and Canada for various suspended-sediment concentrations

[Modified from Horowitz, 1991. **Dissolved concentration:** Dissolved trace-element concentration values are averages from such sources as Shiller and Boyle (1987); Taylor and Shiller (1995); Windom and others (1991); Krabbenhoft (unpublished data). **Bed sediment trace-element concentration:** Fine-graned (<63 µm) bed sediment chemical data from unimpacted areas (Horowitz, 1991). **SSATEC:** Suspended sediment-associated trace-element concentration (µg/L) = [Bed sediment trace-element concentration ((µg/g) x Suspended-sediment concentration (g/L)]. **Total concentration:** Total concentration (µg/L) = [SSATEC (µg/L)] + [Dissolved concentration (µg/L)]. **Percent of total:** Percent of total trace-element concentration that is associated with suspended sediment. g/L, gram per liter; mg/L, milligrams per liter; µg/g, microgram per gram; µg/L, microgram per liter; µm, micrometer]

Element	Dissolved concentration (µg/L)	Bed sediment trace-element concentration (µg/g)	Suspended-sediment concentration (10 mg/L)			Suspended-sediment concentration (100 mg/L)		
			SSATEC (µg/L)	Total concentration (µg/L)	Percent of total	SSATEC (µg/L)	Total concentration (µg/L)	Percent of total
Antimony	0.05	0.6	0.006	0.056	11	0.06	0.11	55
Arsenic	.5	7	.07	.57	12	.7	1.2	58
Cadmium	.01	.6	.006	.016	38	.06	.07	86
Chromium	.07	20	.2	.27	74	2.0	2.07	97
Cobalt	.05	18	.18	.23	78	1.8	1.85	97
Copper	.2	25	.25	.45	56	2.5	2.7	93
Lead	.05	50	.5	.55	91	5.0	5.05	99
Mercury	.006	.05	.0005	.0065	8	.005	.011	46
Nickel	.3	25	.25	.55	46	2.5	2.8	89
Selenium	.08	.4	.004	.084	5	.04	.12	33
Zinc	.2	90	.9	1.1	82	9.0	9.2	98

Element	Dissolved concentration (µg/L)	Bed sediment trace-element concentration (µg/g)	Suspended-sediment concentration (500 mg/L)			Suspended-sediment concentration (1,000 mg/L)		
			SSATEC (µg/L)	Total concentration (µg/L)	Percent of total	SSATEC (µg/L)	Total concentration (µg/L)	Percent of total
Antimony	0.05	0.6	0.3	0.35	86	0.6	0.65	92
Arsenic	.5	7	3.5	4.0	88	7.0	7.5	93
Cadmium	.01	.6	.3	.31	97	.6	.61	>99
Chromium	.07	20	10	10.07	>99	20	20.07	>99
Cobalt	.05	18	9.0	9.05	>99	18	18.05	>99
Copper	.2	25	12.5	12.7	98	25	25.2	>99
Lead	.05	50	25	25.05	>99	50	50.05	>99
Mercury	.006	.05	.025	.031	81	.05	.056	89
Nickel	.3	25	12.5	12.8	98	25	25.3	>99
Selenium	.08	.4	.2	.28	71	.4	.48	83
Zinc	.2	90	45	45.2	>99	90	90.2	>99

Also, the NIST typically supplies a sample volume (usually about 50 grams) that is about 1,000 times the minimum sample volume needed for analysis to provide for replicate analysis to address potential problems in the digestion process and(or) for repeat quality assurance and quality control measurements. Also, when suspended-sediment concentrations are low, the filter pad may contain a substantial proportion of the material that is digested and analyzed. In this case, the sediment should be removed from the filter pad prior to actual chemical analysis (Tramontano and Church, 1984). If discrete samples are combined for analysis of a composite sample, however, limitations caused by low sediment concentrations can be surmounted by collecting a large sample volume and concentrating the sediment to achieve the necessary sample volumes for analysis of the recovered sediments (Horowitz, 1995).

Although there are several ways to collect and process sufficient amounts of suspended sediment to compensate for sample inhomogeneity and detection limit problems, these procedures are difficult in terms of the logistics (Carpenter and others, 1975; Etchebar and Jouanneau, 1980; Ongley and Blachford, 1982; Horowitz, 1986; Horowitz, Elrick, and Hooper, 1989a; 1989b). Composite samples can also be collected in order to surmount potential problems caused by inhomogeneities among aliquots. The production and use of composite samples, however, leads to certain limitations and tradeoffs, such as a substantial loss of temporal resolution. The importance of such a tradeoff must be evaluated in the context of the particular problem being addressed to determine if the loss in temporal resolution is scientifically acceptable.

The time between collection and processing of trace elements in the suspended-sediment matrix can substantially affect the total concentration of trace elements that may be attributed to the solid phase. For example, figure 8 indicates that a substantial proportion of a trace element (Cu) that is initially in the dissolved phase may partition toward the solid phase in as little as one hour after a sample is collected. Furthermore, the total time between collection and the completion of the separation process may affect the redistribution of trace elements among grain-size fractions and may affect the chemical speciation in the solid matrix. If grain-size specific determination of trace element concentrations or chemical partitioning (for example, partial chemical extractions) are of interest, then this redistribution can be important.

As with whole-water samples, many of the sediment-associated trace-element concentrations reported as "total" are actually "total recoverable," and the proportion digested by a specific technique is in part dependent upon the geochemistry of local sediment. Therefore, it is important to document the digestion method, especially in the context of a regional or national monitoring program. Potential differences in performance among nominally equivalent digestion methods may be a substantial source of uncertainty in available data on concentrations of sediment-associated trace elements. For example, Siaka and others (1998) used four different digestion mixtures including HNO3-HCl (3:1 and 1:3), HNO3-H2O2 (1:1), and HNO3-H2SO4 (1:1) and found that measured trace element concentrations were different among the acid mixtures used, and varied among the different trace elements. Combined results for three trials for each of the four mixtures are summarized in figure 9, which indicates the population statistics of the combined trials with respect to certified total recoverable and total digestion concentrations for the standard reference materials used in the experiment. A comparison of the medians indicate that these four mixtures can produce large differences in analytical results and that are largely trace-element specific. Siaka and others (1998) also found substantial variation in measured concentrations that were caused by differences in the type of heating used in their experiments (hotplate versus microwave digestion), the power setting of the microwave (from 40- to 100-percent of the maximum power), digestion time (from 5 to 75 minutes in different trials), and other factors. These results demonstrate that the details of the digestion procedure need to be specified, documented, and verified by a QA/QC program to produce accurate and comparable results.

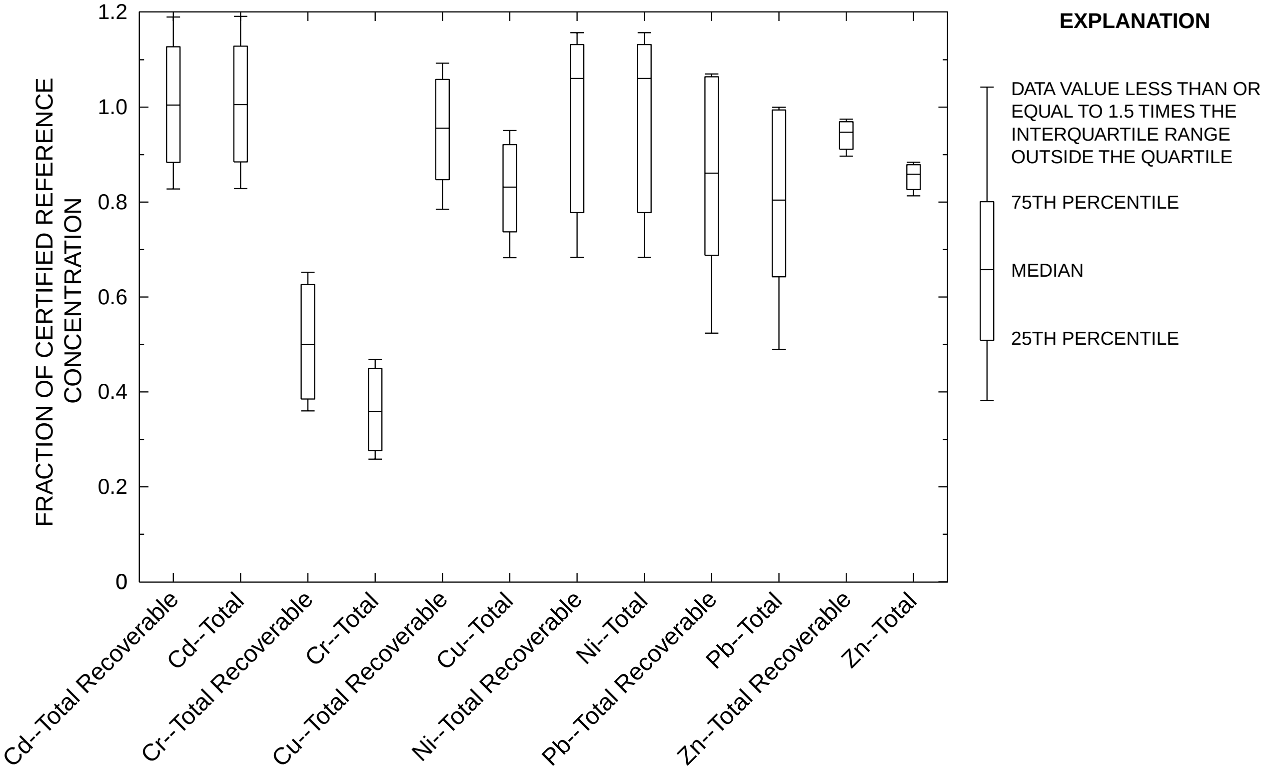

Figure 9. The distribution of variability in median trace-element concentrations measured when different mixtures of digestive agents are used in a standard reference sediment matrix as compared to certified total recoverable and total digestion values (data from Siaka and others, 1998).

Digestion procedure-specific factors are compounded when using sequential extraction to evaluate the potential bioavailability and environmental behavior of sediment-associated trace elements, because several chemical digestion procedures are used in series to determine trace-element concentrations in the different chemical fractions. Lack of uniform protocols for each step of the extraction is a potential source of variability, which precludes direct comparability among results from laboratories that use even slightly different methods and(or) reagents (Fiedler and others, 1994; Quevauviller, 1998). Moreover, variability in results from use of sequential extraction is compounded by the extraction procedures, because each result in the sequence is dependent upon the residual from the previous extraction step.

Potential differences in performance among laboratories are an issue with both suspended and bottom sediment because of sample inhomogeneities and differences in laboratory techniques. The results of an interlaboratory comparison (fig.10) of analyses of a well-mixed sediment sample by more than 25 professional water-quality laboratories indicates that laboratory performance can be highly variable. The bulk of data ranges from 42 percent to 190 percent of the MPV, and a number of outliers differ by orders of magnitude from the MPV (Long and Farrar, 1995). The large variability in the results of analysis are noteworthy in light of the fact that all of the MPVs are well above current USEPA detection limits for analysis of sediment samples (Dowling, 1999), and that these laboratories, by participating in an interlaboratory comparison, have some components of a QA/QC system (Jones, 1999) in place. Therefore, laboratory performance must be properly documented through a QA/QC program to ensure comparability of data from sample to sample within a study and among data collected from different studies.

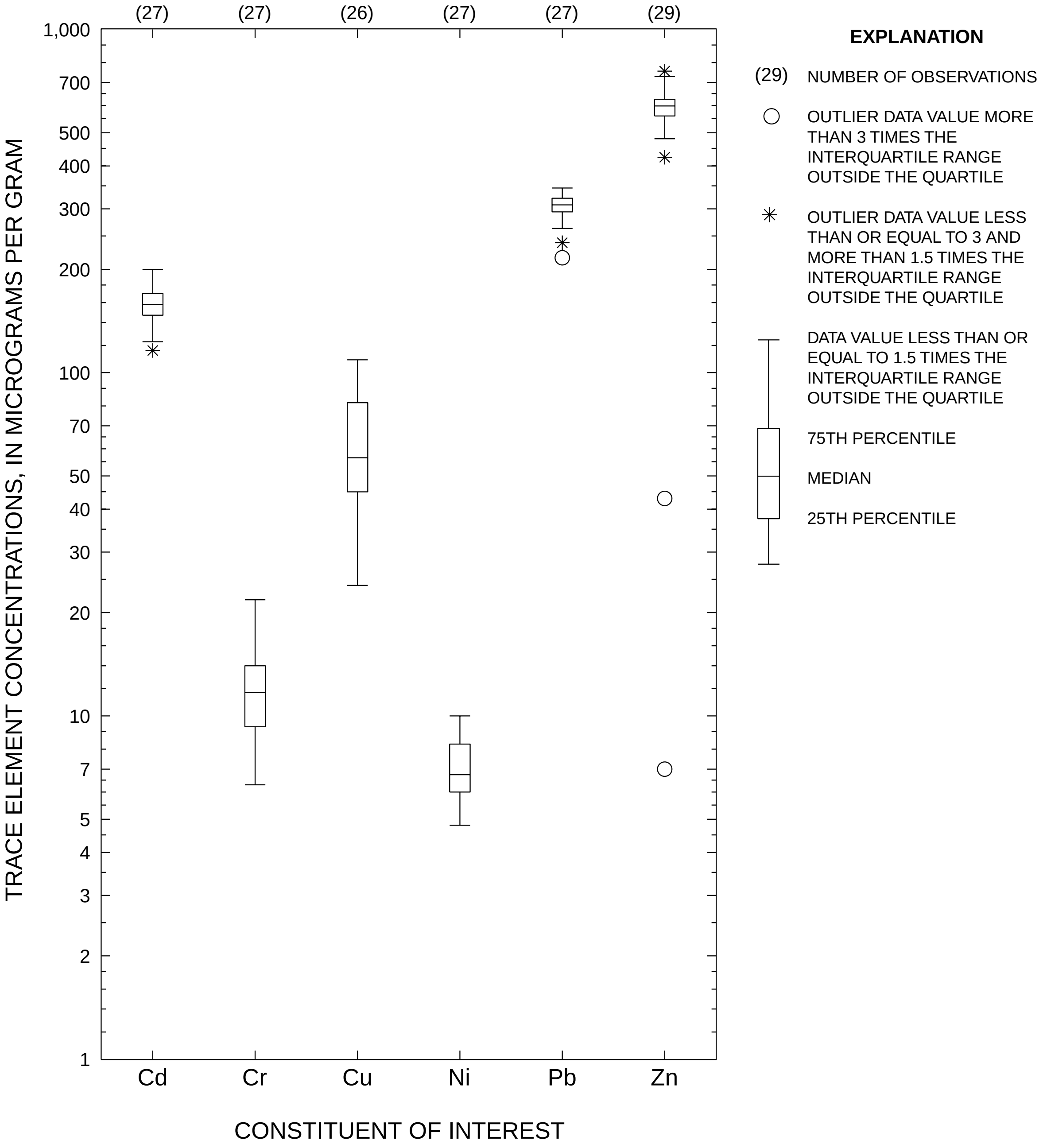

Figure 10. The distribution of total-recoverable trace-element concentrations measured in a standard reference sample of bed material (excluding a far outlier of 0.6 micrograms per kilogram for Cr) by laboratories participating in the USGS interlaboratory evaluation program. Data from Long and Farrar (1995).

Bottom Sediment

Bottom sediment is also referred to as bed sediment, bottom or bed material, bottom or bed solids, mud, muck, or simply just sediment. Bottom sediment consists of the geological, anthropogenic, and biological material that has been deposited and retained within a sampling site at the time of collection. Unlike the dissolved or the suspended-sediment matrixes, the bottom sediment matrix is not operationally defined by a particle-size separation technique. Although not operationally defined on a physical basis, measured trace element concentrations are defined by the chemical separation of a digestion or extraction process. As for whole water and suspended sediment, results of chemical analysis of bottom sediment are dependent upon chemical processing (such as total-recoverable digestions, total digestions, and sequential extraction techniques) to extract trace elements for chemical analysis (Tessier and others 1979; Hamilton and others, 1984; Fishman and Friedman, 1989; Fiedler and others, 1994; Kane, 1995). Also, for bottom sediment, the USEPA Toxicity Characteristics Leaching Procedure (TCLP) is sometimes used as a digestion/extraction procedure to assess the capacity for trace elements to leach from bottom sediment (USEPA, 1992b) and the results of this process may vary from other analytical techniques.

The distribution of trace elements within the bottom sediment of drainage structures, structural BMPs, and receiving waters depends partly upon the chemical and physical processes that control sediment-particle transport. Sediment-bound trace elements can dissolve into the water column, enter the food chain, and have other environmental effects when geochemical conditions (for example, pH, redox, dissolved oxygen, bacterial action) change. Trace elements from bottom sediment can be dispersed over a wide geographical area when hydraulic conditions change. For example, during high flows, water velocities may be sufficient to mobilize the sediment and associated trace elements and move them downstream, where they are redeposited in low-energy depositional zones (Horowitz, 1991; Breault and others, 2000). Therefore, bottom sediment also may be regarded as a major source of suspended-sediment associated trace elements.

In depositional zones affected by highway and(or) urban runoff, bottom sediment is commonly characterized as having: a high water content; a distinctive grey to black color; a high organic-matter content —commonly measured as total organic carbon (TOC); a density lower than that of local natural geologic material; and a relatively fine grain-size distribution (Mudre and Ney, 1986; Breault and others, 2000). In contrast, relatively coarse-grained sediment with lower concentrations of TOC and trace elements, which are more characteristic of local natural geologic material, are found in non-depositional environments and in erosional areas (Breault and others, 1998; Breault and Harris, 1997). Consequently, the hydraulic characteristics of the depositional environment define the physical and chemical characteristics of the bottom-sediment profile. Therefore, the focus of individual studies tend to be grouped into investigations of bulk surficial-sediment quality (usually defined as the top 3-20 centimeters of the sediment profile); bulk core-sediment quality (which generally includes surficial sediment and sediment at depth —below 20 centimeters in the profile); and discrete vertical-profile studies (which are usually used to define the distribution of constituents at depth within the profile).

Benefits

Monitoring the bottom-sediment matrix may provide information for trace-element studies with various objectives. Historically, chemical analysis of bottom sediment has provided information for the study of geochemical cycling, temporal variability, and trend analysis (on the order of months to years), as well as the study of biological effects of sediment-associated trace elements (Horowitz, 1995; Buckler and Granato, 1999). Surficial sampling of the sediment column is used primarily in studies of the spatial distribution of trace elements. Sediment samples at depth may be used to establish local trace-element baseline levels, to delineate historical changes in sediment-associated trace-element concentrations, or to determine average sediment and sediment-associated trace-element loading and(or) deposition rates. Bottom-sediment sampling can provide regional geochemical reconnaissance data for use in identifying environmental effects of point and nonpoint sources of contamination (Webb, 1978; Fauth and others, 1985).

The use of bottom-sediment samples offers several logistical advantages over sampling water and(or) suspended sediment as a trace-element-monitoring matrix. When compared to suspended-sediment monitoring, it is easier to collect the requisite mass of bottom sediment required for an analysis, especially when suspended-sediment concentrations are less than 100 mg/L in the water column. Because bottom-sediment samples may represent a time-integrated history of local deposition, a single core may represent water-quality conditions on a time scale from weeks to years. A single water or suspended sediment sample, on the other hand, may represent water-quality conditions only on a time scale from minutes to hours. For example, Callender and Van Metre (1997), analyzed sediment cores from a number of lakes and reservoirs across the midwest and southeast United States. They measured Pb concentrations in vertical sediment-core-profiles that recorded the history of the use and subsequent ban of leaded gasoline between the early 1900s and the mid-1990s. Furthermore, concentrations and accumulation rates of Pb in cores collected at different sites showed the effects of surrounding land use. Pb accumulation rates in cores from urban sites were about 20, 10, and 5 times the Pb accumulation rates measured in cores from rural, agricultural, and suburban sites, respectively. Use of bed sediment, therefore, may provide useful information as a reconnaissance tool to identify potential sites for more intensive stormwater monitoring efforts, and as a time-integrating component of storm-runoff monitoring studies to put results from short-term runoff monitoring programs into historical perspective.

The merits of monitoring trace elements by sampling bottom-sediment are apparent from information available in the highway- and urban-runoff literature. The effectiveness of BMPs commonly can be inferred from examination of bottom-sediment quality within the drainage systems and receiving waters. For example, Yousef and others (1984) found that bottom sediment under a bridge with scuppers that drain directly to a lake had concentrations of Cr, Cu, Ni, Pb, and Zn that were about 2 to 4 times the concentrations in bottom sediment under a second bridge, which had drains diverting runoff to the local land surface. These two bridges were along the same and highway over the same lake. Dupuis and others (1985) also detected enriched metal concentrations in bottom sediment near highway outfalls. Schiffer (1989) determined that bottom-sediment samples collected in wetlands near highways with structural BMPs, such as holding ponds, showed lower concentrations of trace elements than samples collected in wetlands near highways without structural BMPs. Legret and others (1995) measured trace elements in runoff and in surficial- and core-sediment samples from a detention pond. They found that concentrations of Cd, Cr, Cu, Ni, Pb, and Zn were 2-10 times higher in runoff than in surficial sediment, which in turn had concentrations 2-5 times higher than deeper sediment. These results indicate that this detention pond was only partially effective. Guo, (1997) measured the depth and sediment chemistry of an 18-year-old detention basin to determine the efficiency of the basin for removing trace elements and sediment. He found that the basin was effective in removing sediment, but not as effective in removing trace elements in comparison to predicted removal efficiencies for these constituents in the detention basin (Guo, 1997).

Use of the bottom-sediment matrix also can provide information about the effects of trace elements in highway runoff on the watershed scale. Mudre and Ney (1986) studied sediment deposition in six small watersheds in Virginia crossed by a relatively low-traffic-volume highway (6,000 to 15,000 vehicles per day). They found that concentrations of trace elements in bottom sediment downstream of the highway outfall were controlled by explanatory factors including overland-flow distance from the pavement to the stream, stream velocity, and organic content of the sediment. Also, they found that high flows during a wet year washed away local contaminated deposits, and concluded that trace-element concentrations vary with precipitation totals from year to year. Callender and Rice (2000) examined correlations between population density, traffic density, and concentrations of Pb and Zn in bottom-sediment samples from the Chattahoochee River Basin that has an urban-to-suburban-to-rural-land use gradient. They found that traffic density can be used as a predictor of sediment-associated Pb and Zn concentrations. This is particularly interesting given the fact that the effects of local traffic density were apparent in downstream sediment concentrations measured in this large watershed (52,840 square kilometers) that stretches from the Atlanta Georgia Metropolitan Area to the Gulf of Mexico. Tuit and others (2000) found that concentrations of platinum-group elements (PGEs) in Boston Harbor sediment were five times greater than background PGE concentrations in sediment and concluded that this enrichment was caused by uncontrolled runoff from roads and highways that carry residuals from automotive catalytic converters.

In a review of available studies on the effects of runoff on aquatic biota, Buckler and Granato (1999) determined that sediment deposits from highway outfalls correlated with measured concentrations of trace elements in biological tissue and with effects on biodiversity in receiving waters. For example, van Hassel and others (1980) found direct correlations among traffic density, trace-element concentrations in stream sediment, and trace-element concentrations in benthic insects and fish. Breault and others (2000), using Canadian sediment-quality guidelines (Ecosystem Conservation Directorate Evaluation and Interpretation

Branch, 1995), found that concentrations of trace elements were in the "probable range" for adverse effects on benthic organisms at 77 percent of 135 surficial-sediment-sampling sites in the Lower Charles River Basin, Massachusetts, where the source of sediment is largely urban and highway runoff. Among the trace elements studied by Breault and others (2000) at 135 sites, Pb, with 123 sites (91 percent); Cd, with 113 sites (84 percent); Zn, with 112 sites (83 percent); Cu, with 99 sites (73 percent); Ni, with 85 sites (63 percent); and Cr, with 72 sites (53 percent) exceeded the highest tier "probable range" concentrations as defined by the Canadian sediment-quality guidelines.

Technical Concerns

Although chemical analysis of the bottom-sediment matrix has many benefits, large spatial and temporal variability at the sampling site and improper sampling and processing also are of concern when this matrix is used in trace-element-monitoring programs. Differences in the physical and chemical characteristics of bottom sediment from place to place and at different depths are expected, because a variety of hydrologic and chemical processes can affect deposition, resuspension, and chemical partitioning of trace elements (Baudo, 1990; Forstner, 1990; Allen, 1995; Stumm and Morgan, 1996). Measuring trace-element concentrations that are representative of a sampling site, therefore, requires a number of sediment samples from different points within a site. The choice of a statistical procedure for characterizing the site with a finite data set depends on the degree of confidence required to meet particular program goals (Keith and others, 1983; Hakanson, 1984; Baudo, 1990). The confidence limit is affected by the number of samples to be collected in a particular study area, how the data are to be used, and the level of chemical detail required. Regardless of the requisite degree of confidence, it is better to collect a group of subsamples to generate a final composite sample than to collect a single arbitrary sample as being representative of a sampling site. Methods for the physical collection of representative bottom-sediment samples with the associated trace elements are described by USEPA (1982), Baudo (1990), Mudroch and MacKnight (1991), Shelton and Capel (1994), and Radtke (1997).

Once representative sediment samples are collected, appropriate laboratory techniques must be applied to ensure that measured trace-element concentrations are unbiased, representative of the sample, and comparable. As for whole-water and suspended-sediment samples, there are a number of digestion techniques, including total and total recoverable, that may cause systematic differences in measured concentrations of trace elements in the same sample. Also, as for suspended-sediment samples, there are a number of accepted (but unstandardized) sequential-extraction techniques that may cause systematic differences in measured concentrations of trace elements in the same sample. Even when comparable digestion-extraction methods are used, the artifacts cause by interlaboratory variability (fig. 10) may be expected to introduce additional uncertainty when different data sets are combined for regional or national synthesis. Also, there are a number of technical issues that may confound the interpretation of trace-element data from the bottom-sediment matrix, even when appropriate protocols and QA/QC systems are used.

Sediment-associated trace-element concentrations commonly are a function of the grain-size distribution in sediment samples (Forstner and Wittmann, 1981; Salomons and Forstner, 1984; Horowitz and Elrick, 1987, 1988; Horowitz, 1991). The effect of grain size on sediment trace-element chemistry is so substantial that, if grain-size variations amongst samples are not taken into account, a study may produce misrepresentative spatial distributions (Horowitz and Elrick; 1987; Horowitz, 1991). There is a long-standing controversy over what represents the most appropriate grain-size range for mapping trace-element distributions in bottom sediments in various depositional environments (Banat and others, 1972; Copeland, 1972; Renzoni and others, 1973; Cameron, 1974; Chester and Stoner, 1975; Webb, 1978; Jenne and others, 1980; deGroot and others, 1982; Ackermann and others, 1983; Beeson, 1984; Horowitz and Elrick, 1987, 1988). The two size ranges most commonly used for trace-element analysis are less than 180-µm (typical for geochemical exploration surveys) and less than 63-µm (typical for water-quality studies). For example, the USGS NAWQA program analyzed the less than 63-µm fraction in bottom-sediment samples collected from 20 different study units across the conterminous United States in order to increase the comparability among trace-element analyses of sediment samples from rivers with widely varying grain-size distributions (Gilliom and others, 1995; Rice, 1999).

For highway- and urban-runoff studies, however, analysis of unsieved bulk samples and(or) a variety of different size fractions (including the large grain size fractions) may provide information necessary for evaluating the potential effectiveness of structural BMPs and the effect of highway runoff on receiving waters. Information about the mass distribution of different grain sizes (and associated trace-element concentrations) provides information about the potential for removal of sediment and associated trace elements by BMPs that utilized physical sedimentation for water-quality treatment (Harrison, and Wilson, 1985b; 1985c; Legret and others, 1995; Stone and Marsalek, 1996; Marsalek and others, 1997; Roger and others 1998). Unsieved bulk samples may be appropriate for reconnaissance studies because the full spectrum of the grain-size distribution commonly is transported in highway and urban runoff, and because high concentrations of trace elements are typically measured throughout the grain-size spectrum in suspended and bottom sediments (Legret and others, 1995; Sansalone, Buchberger, and Al-Abed 1996; Sansalone, Buchberger, Koran, and Smithson, 1996; Roger and others, 1998). For example, Kobriger and Geinopolos (1984) used manual street sweeping and subsequent wet vacuuming (to obtain ultrafine sediment samples) a number of times at sites on four different highways to collect road dust as part of an investigation of the sources and migration of highway-runoff constituents. They found that concentrations of Cd, Cr, Cu, Ni, Pb, and Zn were relatively consistent among different grain-size fractions (with the exception of the fraction that was larger than 3,350 μm). Therefore, bulk trace-element concentrations may be considered representative and comparable for runoff studies (fig. 11) and the use of bulk-sediment samples for analysis of trace elements could reduce potential artifacts introduced by a sieving process. If properly done, sieving samples to obtain grain-size specific trace-element concentrations provides more quantitative information at each site. In reconnaissance studies, however, use of bulk samples may allow for more spatial definition at and between sites because of the reduced processing and analysis cost for each sample collected.

Undisturbed bottom sediment can contain a historical record of sediment quality if a sufficiently large and stable depositional zone can be found, sampled, and chemically analyzed (Forstner and Wittmann, 1981; Horowitz, 1991). Typically, the ages of different strata (sediment layers) within a core are estimated using techniques such as radiometric age dating (Horowitz, 1991). Physical and chemical factors such as resuspension, bioturbation, diagenesis, and sediment focusing, however, if unaccounted for, can bias the interpretation of trace-element profiles. High flow velocities during the period thought to be represented by the core potentially can resuspend and thereby remove and(or) mix a number of strata (Lick, 1994). Resuspension, therefore, can confound meaningful interpretation of trace-element-concentration data from core samples. Bioturbation or the mixing of strata by organisms living in and on the sediment also can affect the distribution of sediment-associated trace elements (Baudo, 1990). Chemical and biological reactions that alter sediment after deposition (diagenesis) can affect the distribution of trace elements. For example, Callender (2000) measured sediment accumulation rates and Fe concentrations in interstitial waters from the upper 9 cm of two sediment cores collected from the Cheyenne River in South Dakota. One core was collected during a year of relatively high sediment deposition (more than one centimeter per year) and the other during a year of lower sediment deposition. Fe concentrations in the interstitial water were found to be higher from the core collected during the period of lower sediment deposition than they were in the rapid deposition sample (fig. 12). Higher concentrations of Fe in the interstitial waters indicate increased reduction of ferromanganese oxyhydroxides by microbiologically mediated reactions that take place in the absence of oxygen. Trace elements commonly are associated with ferromanganese oxyhydroxides in bottom sediment and can be released upon their reduction. Low sediment-accumulation rates, which allow sufficient time for oxygen depletion, reduction of ferromanganese oxyhydroxides, and subsequent redistribution of trace elements, therefore, must be considered for interpretation of trace-element-concentration data from core samples. In urban and highway runoff BMPs, which

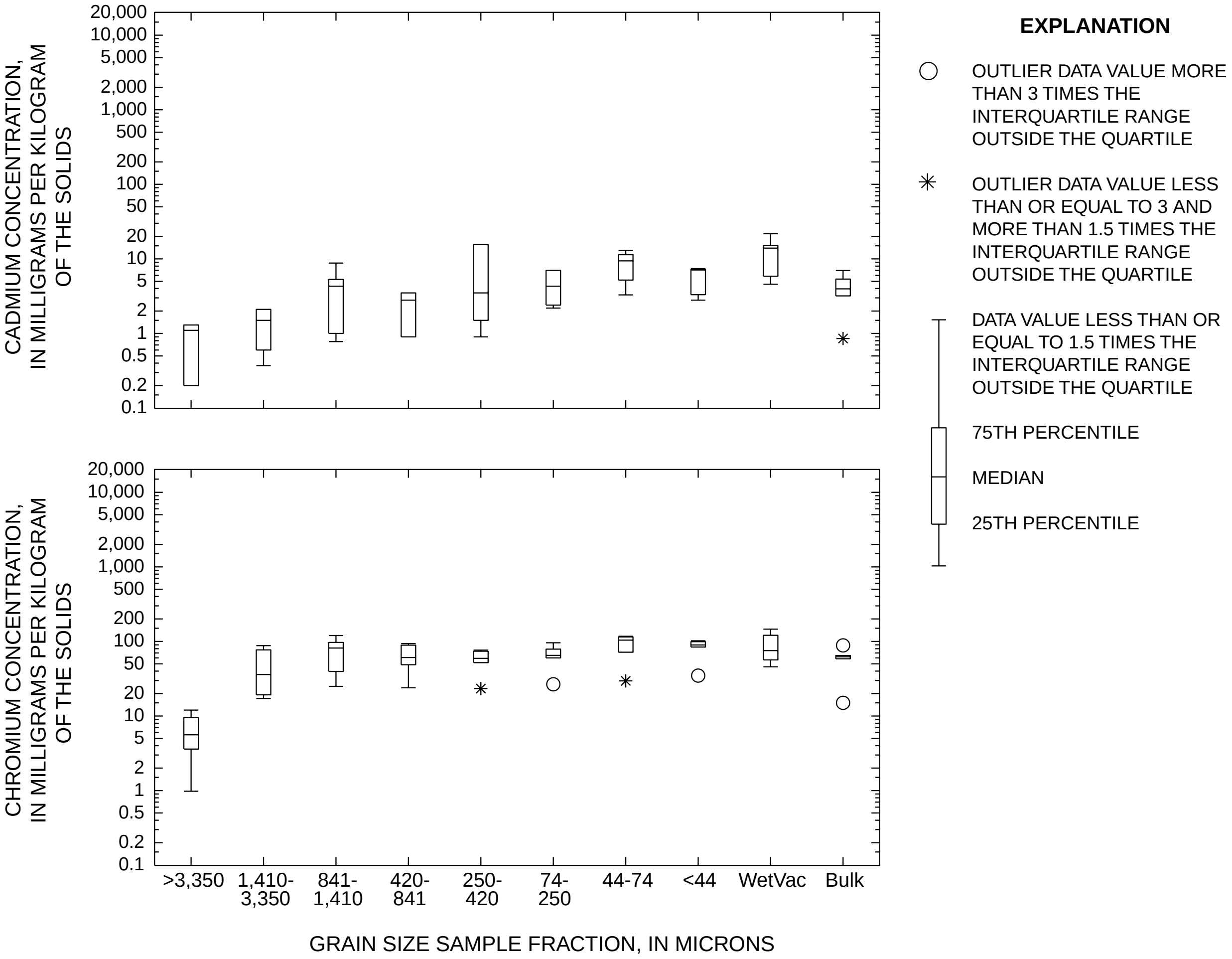

Figure 11. The distribution of total recoverable trace-element concentrations measured in road-dust samples collected by manual street sweeping and subsequent wet vacuuming (to obtain ultrafine sediment samples) at four highways in the conterminous United States by the FHWA. Data from Kobriger and Geinopolos (1984).

are designed to treat stormwater by sedimentation, the potential for the redistribution of trace elements in the sediment column may be minimized by high-sediment deposition rates. Trace-element data from core samples collected from sedimentation structures and receiving waters may not be comparable because sedimentation rates may be very different. Differences in effective sediment-deposition rates within a water body also may be a potential source of error in the interpretation of profile data for trace-element concentrations. For example, sediment focusing is the process by which fine-grain sediment and associated chemical constituents are resuspended and redistributed spatially from shallow to deeper zones by currents and episodic storms. Researchers typically use the ratio of the measured 137Cs and(or) 210Pb isotope(s) in the sediment to concentrations expected from atmospheric deposition as a measure of the sediment focusing factor to correct for this phenomenon (Wong and others, 1995; Callender and Van Metre, 1997). Finally, to compare the historical trace-element profile to background trace-element concentrations (with respect to potential anthropogenic inputs in the area of interest), it is necessary to obtain trace-element concentrations in soils that are representative of the watershed of interest (Callender and Rice, 2000).

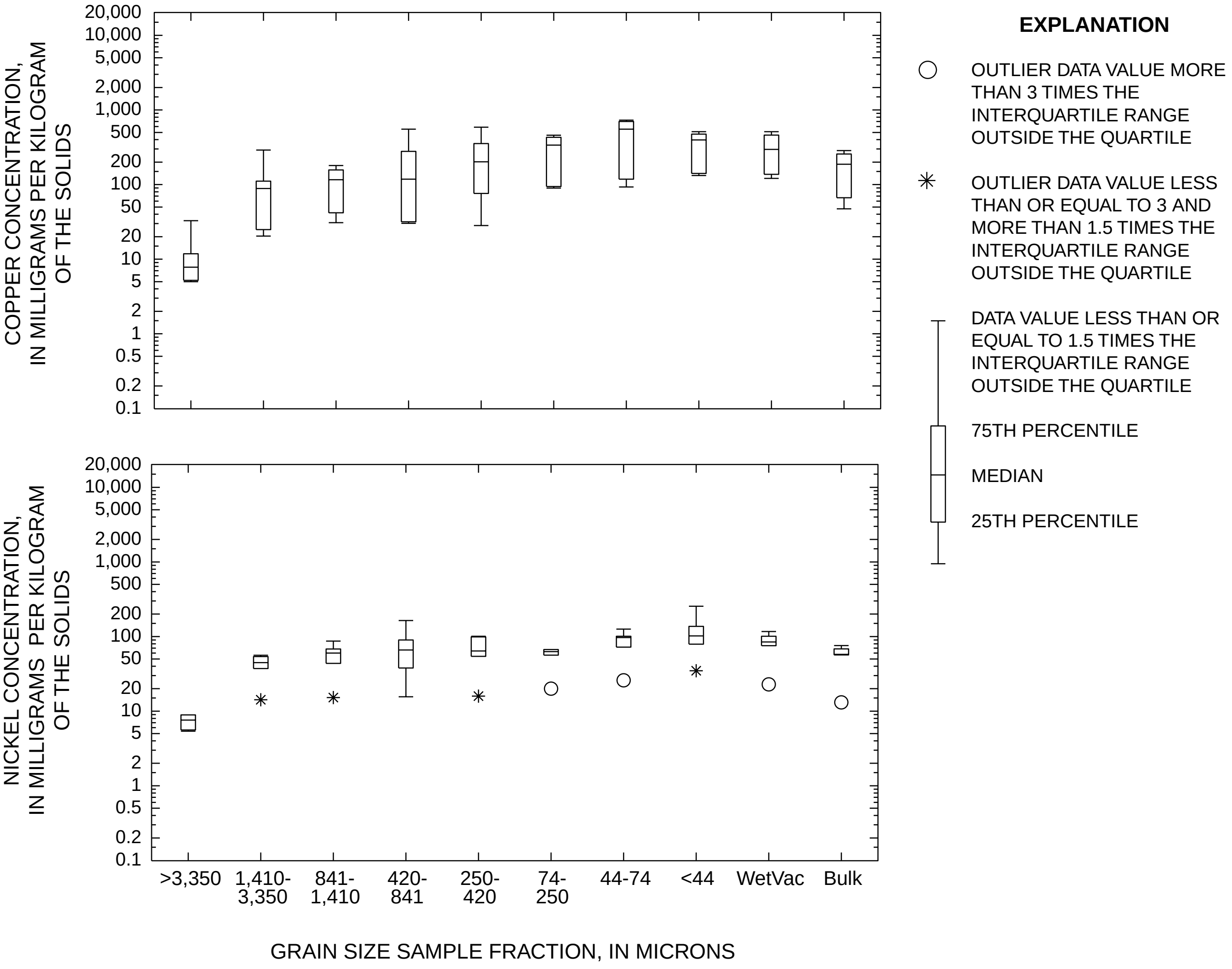

Figure 11. The distribution of total recoverable trace-element concentrations measured in road-dust samples collected by manual street sweeping and subsequent wet vacuuming (to obtain ultrafine sediment samples) at four highways in the conterminous United States by the FHWA. Data from Kobriger and Geinopolos (1984)—*Continued*.

Biological Tissue

Collection and chemical analysis of biological tissues may represent one of the most direct measures of trace-element bioavailability in an aquatic ecosystem (Crawford and Luoma, 1993; Meador and Gurtz, 1994; Buckler and Granato, 1999). Trace-element concentrations in tissue are dependent upon concentrations of trace elements in sediment and the water column as well as on the local geochemistry (Luoma and Fisher, 1997; Bricker, 1999), habitat (Meador and Gurtz, 1994), and many other physical and biological factors (Crawford and Luoma, 1993; Meador, Hupp, and others, 1993; Luoma and Fisher, 1997). Chemical analysis of tissues has been used in local, regional, and national water-quality studies in conjunction with the analysis of water and sediment quality to examine the relations between trace constituents in the environment and bioaccumulation in aquatic organisms (Crawford and Luoma, 1993; Gurtz and Muir, 1994; Meador and Gurtz, 1994). When chemical data from the analysis of tissues, water, and sediment are used in conjunction with other biological indicators (such as community assessments), effects on individuals and populations of aquatic biota also can be examined.

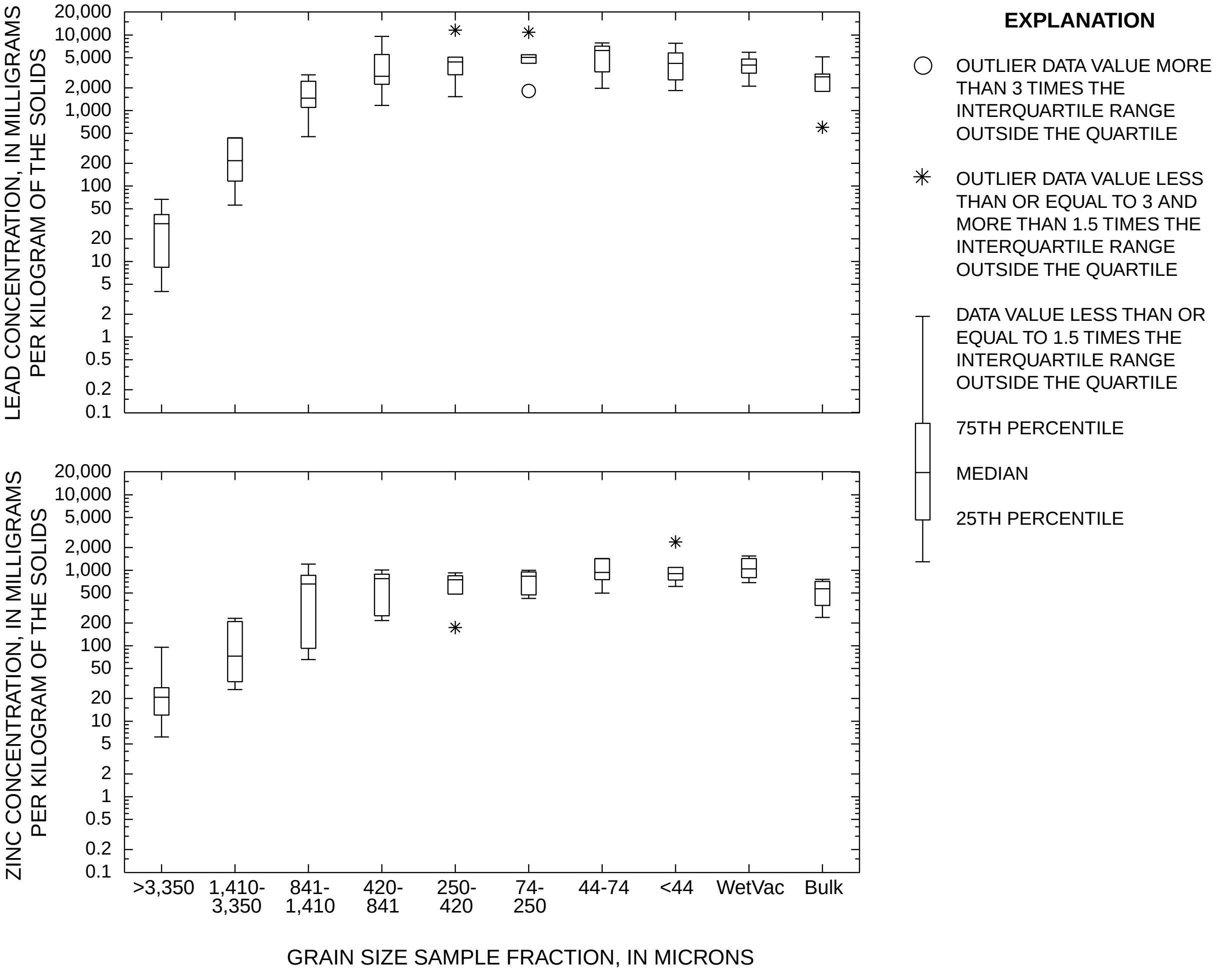

Figure 11. The distribution of total recoverable trace-element concentrations measured in road-dust samples collected by manual street sweeping and subsequent wet vacuuming (to obtain ultrafine sediment samples) at four highways in the conterminous United States by the FHWA. Data from Kobriger and Geinopolos (1984)—*Continued*.

Benefits

Studies that utilize the chemical analysis of tissue samples from different organisms provide information about cause-and-effect relations because each taxon responds differently to changes in local geochemistry, habitat, food, mobility, physiology, and life history (Gurtz, 1994). The size, weight, and life stage of available organisms vary seasonally and from year to year with natural conditions. For example, comparison of the characteristics of algae, aquatic invertebrates (including aquatic insects, mollusks, crustaceans, and worms), and fish indicates the different types of information that can be obtained from different biological tissue matrixes. Algae have a short life span (days to weeks), they readily exchange constituents with the water column and sediment, and being sedentary, reflect local water and sediment quality in the short term (Porter and others, 1993, Gilliom and others, 1995). In comparison, aquatic invertebrates have longer life spans (months to years) than algae, are abundant at many sites, accumulate trace elements proportionally to environmental concentrations, live in close association with bottom sediment, and are not highly mobile from area to area. Therefore, aquatic invertebrates also are good indicators of local water and sediment quality (Crawford and Luoma, 1993; Cuffney and others, 1993a, 1993b; Gilliom and others, 1995). Fish have relatively long life spans (years to decades), can be highly mobile, and therefore, may be indicative of long-term watershed health (Meador, Cuffney, and Gurtz, 1993, Gilliom and others, 1995).

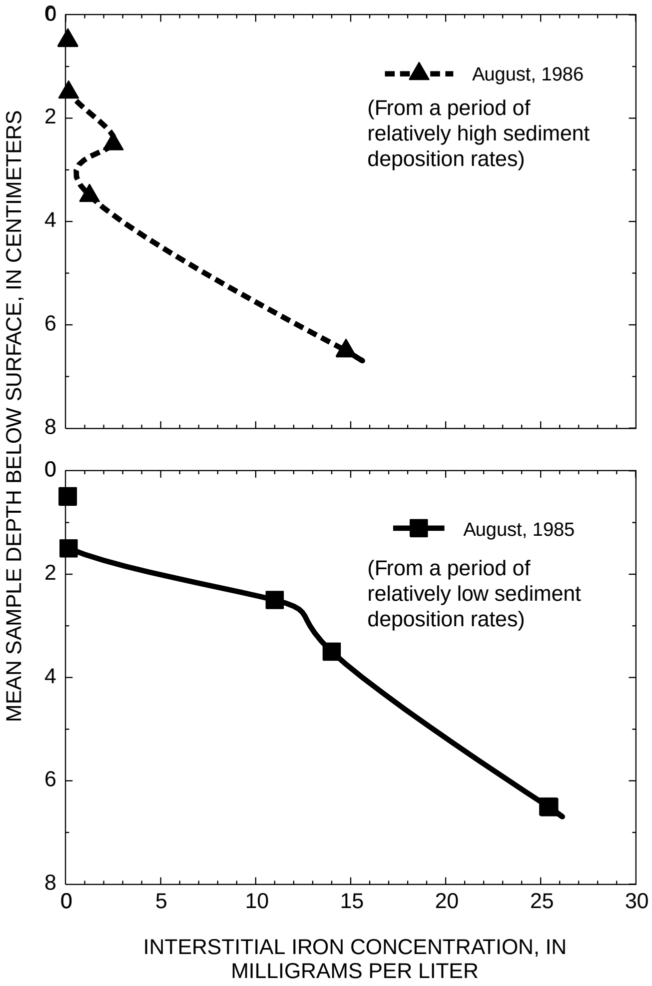

Figure 12. The vertical profiles of interstitial iron concentrations for two annual sampling dates at a site in the Cheyenne River Embayment of Lake Ohae, South Dakota, indicating the effect of sediment deposition rates on phase transformation and subsequent redistribution (modified from Callender, 2000).

Therefore, it is important to consider the characteristics of different organisms when evaluating biological tissue matrix-data.

Tissue analysis has been used successfully as a component of highway- and urban-runoff-quality monitoring to assess the effects of highway runoff on aquatic biota (Buckler and Granato, 1999). In many studies, increased trace-element concentrations were detected in the tissues of animals and plants exposed to soils and sediment in highway environments, even from sites near highways with low traffic volumes (Gish and Christensen, 1973; Dupuis and others, 1985; Birdsall and others, 1986; Davis and George, 1987; Baekken, 1994, Cooper and others, 1996; Dupuis and others, 1999). Trace-element concentrations in tissue samples collected from aquatic communities near highway outfalls were elevated above background concentrations in the same species, but elevated concentrations commonly represented local "hot spots" near discharges rather than widespread downstream contamination (van Hassel and others, 1980; Dupuis and others; 1985, Baekken, 1994; Maltby and others, 1995; Cooper and others, 1996). For example, Yousef and others (1984) studied the effects of runoff from two bridges for a busy highway (with an average daily traffic volume of 50,000 vehicles per day) across a lake in Florida. In this study, trace-element concentrations in tissues of Spirogyra (an alga) and Hydrilla (an aquatic plant) were about 150 to 320 percent greater under the bridge that drained directly to the lake than under the bridge that drained to the local land surface (fig. 13).

Review of available highway-runoff-quality literature (Buckler and Granato, 1999) indicates that highway studies can successfully utilize trace analysis of tissues from many of the same organisms used in other national, regional, and local water-quality studies, including algae (Dupuis, others, 1985; McHardy and George, 1985), aquatic invertebrates (van Hassel and others, 1980; Dupuis and others, 1985; Mudre, 1985; Madigosky and others, 1991), and fish (van Hassel and others, 1980; Ney and van Hassel, 1983; Dupuis and others, 1985; Mudre, 1985). Although tissue analysis does not explicitly define the toxicity of trace constituents to the organisms sampled in these runoff studies, several studies noted the potential for bioaccumulation of trace elements higher in the food chain (Gish and Christensen, 1973; Birdsall and others, 1986, Cooper and others, 1996). Although the tissue matrix would seem to provide a simple answer to the question of bioavailability, many chemical and biological factors complicate representative monitoring of this matrix.

Technical Concerns

As for other matrixes used for analysis of trace elements, appropriate sample collection and processing methods are necessary to ensure that the data collected are representative and comparable. Organisms must be collected using appropriate biosampling methods, and the tissues collected from these organisms must be handled using suitable trace-element-sampling methods. To ensure the quality of data collected, it is important to ensure that sampling crews are properly trained in

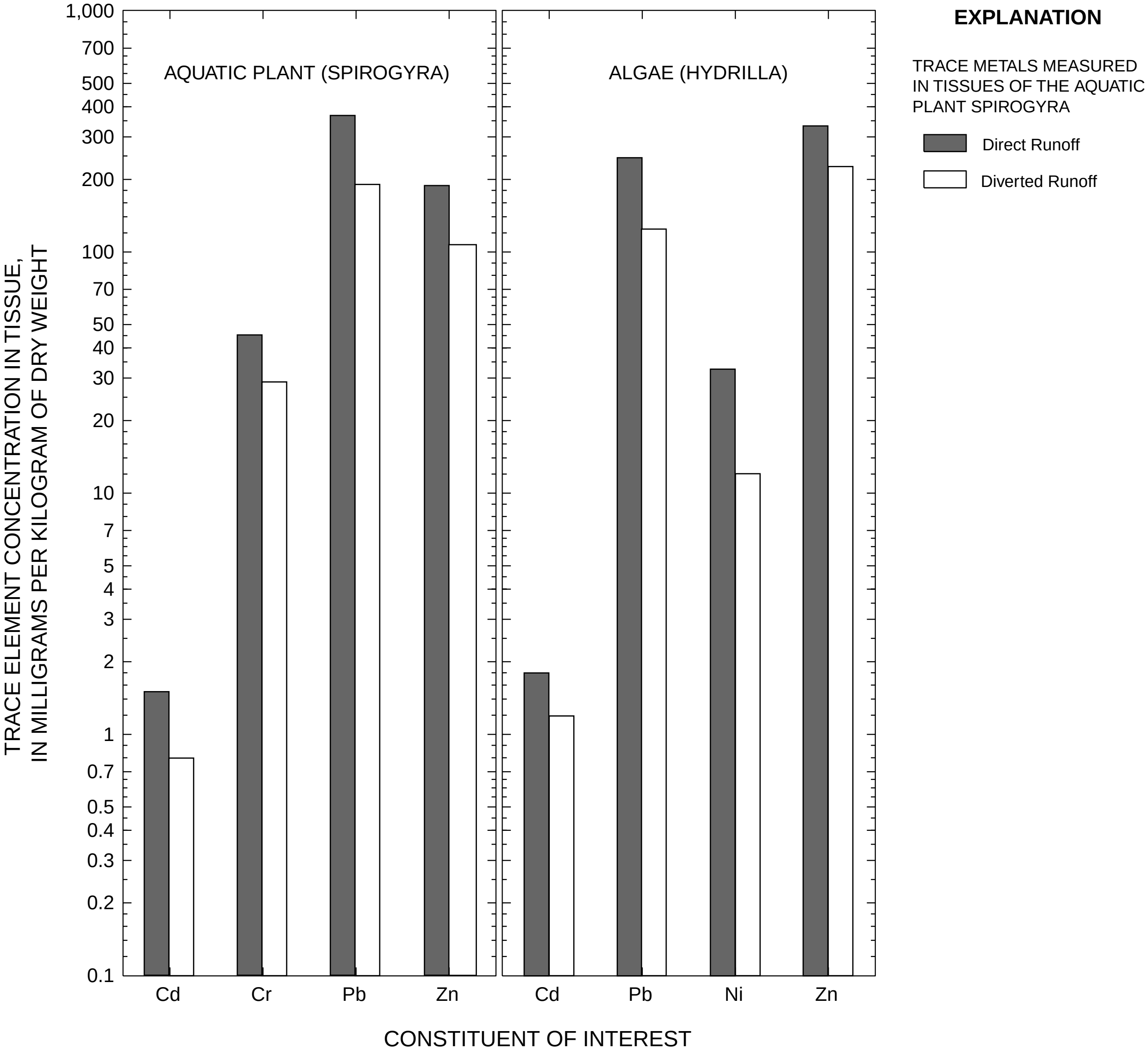

Figure 13. The concentrations of trace elements measured in tissue samples collected from a lake in Florida at two bridge sites: one with scuppers—which drain to the lake (direct runoff)—and one with a drainage system that discharges runoff to the local land surface (diverted runoff). Data from Yousef and others (1984).

biological sample-collection-methods; that samples are processed using clean methods; and that equipment, storage containers, and preservation methods and materials do not affect trace-element concentrations in biological tissues (Katz, 1984; Crawford and Luoma, 1993; Hoffman, 1996). The potential for trace-element contamination during collection, processing, shipment, sample preparation, and storage may be considerable for biological tissues (Crawford and Luoma, 1993). Also, it is important to use appropriate and consistent laboratory methods for matrix digestion and analysis of tissues, and to be aware that different digestion or extraction methods are available (Hoffman, 1996).

Biological factors to consider when evaluating the possible use of tissue analysis of one or more organisms include:

- measurable tissue concentrations that vary with environmental concentrations and exposure,
- uptake of constituents that is relatively rapid in comparison to release,

- tissue concentrations with low variability among individuals collected in order to be representative of site conditions at a given time period,
- availability of organisms that are hardy enough to withstand contaminant concentrations of interest,
- organisms that do not commonly travel beyond the immediate area,
- organisms that are abundant and widespread in the study area, so that they can be repeatedly harvested for analyses,
- organisms that can be collected, and that are large enough to meet sample-size requirements;
- organisms that are easy to find and hardy enough to withstand captivity during controlled laboratory studies, and
- a species for which biological and toxicological information is available for comparison (Crawford and Luoma, 1993).

Biological characteristics of the different organisms selected for use in a monitoring program determine the suitability of the tissues collected to determine food-chain concentrations and accumulation rates. Also, contaminant concentrations in tissues only are comparable within the same species, and for organisms at the same life stage, reproductive condition, size, weight, and sex. For example, to address comparability problems among available test species, the USGS NAWQA program developed a National Target Taxa List (NATT) to define the organisms that local teams could target for biological monitoring efforts, and a decision tree to prioritize choices among available organisms within the context of regional and national sampling objectives (Crawford and Luoma, 1993).

Different tissues within each organism accumulate different constituents selectively, so the type of tissue used for analysis is a major factor for consideration in the interpretation of tissue matrix data and is as important as variations among organisms. For example, Ney and van Hassel (1983) noted that the amount of trace-element uptake by organisms in streams affected by highway runoff depended upon the various site characteristics controlling the availability of trace elements in the local environment, on the species (because fish species associated with sediment had higher trace-element body-burdens than species associated with the water column), and on the specific affinities of the different tissues within a fish. To establish that tissue concentrations are in fact affected by a runoff source, it also is important to establish background tissue concentrations with a local control and to compare both concentrations with natural baseline concentrations in tissues of similar organisms from streams with minimal anthropogenic influences (Buckler and Granato, 1999).

Variation in habitats and the diversity of biological communities adds uncertainties to comparisons of tissue concentrations from site to site, especially at regional and(or) national scales (Meador, Hupp, and others, 1993, Crawford and Luoma, 1993). The complexity of the nation's freshwater environments; variations in flow, temperature, and water quality from season to season; and differences in surrounding land use, physical and hydrologic features, complicate the use of tissue analysis in a consistent manner on a national or regional scale (USEPA, 1986b). Therefore, extensive field records, including information such as sampling location, the date, the organism, physical characteristics (such as age, size, tissue type, and sex) are necessary to identify the many explanatory variables that can affect the concentrations of trace elements in tissue samples (Crawford and Luoma, 1993). As with other trace-element-monitoring matrixes, it is important to employ a comprehensive program of QA/QC (USEPA, 1986b; Buckler and Granato, 1999).

Sources

Source-matrix monitoring is the practice of collection, processing, and chemical analysis of materials that may contribute constituents to highway and urban runoff. If a comprehensive analysis of constituents in stormwater and potential source materials is available, the concentrations of certain indicator constituents may indicate the relative magnitude of different sources. Qualitatively, source matrixes for highway and urban runoff include atmospheric deposition, soil, highway-construction materials, vehicle contributions, highway-maintenance materials, natural (from animals and plants) debris, and anthropogenic litter. These sources commonly are integrated on paved surfaces as dust and dirt accumulations that provide a primary source of trace elements in runoff. Source-matrix monitoring is a valuable method for identifying contaminants of concern, fingerprinting different potential sources, identifying the relative magnitude of potential sources, and estimating loads of constituents from these sources. The value of source-matrix-monitoring information is indicated by the fact that many of the original studies that examined sources of runoff constituents (Sartor and others, 1972; Shaheen and Boyd, 1975; Christensen and Guinn, 1979) still are cited widely more than 20 years after publication (Brinkmann, 1985; Barrett and others, 1993; Armstrong, 1994; Young and others, 1996; Callender and Rice, 2000).

It is important to note that the physical and chemical properties of source matrixes commonly change with time. Since the early 1970s, many source matrixes have changed, and implementation of environmental legislation has resulted in the improvement of air quality, the quality of atmospheric deposition, and the quality of receiving waters (USEPA, 1997,1999). During the past 30 years, changes also have been made in highway construction materials, highway-maintenance materials (pesticides, herbicides, and deicers), and maintenance practices that affect the environmental availability of these materials (Barrett and others, 1993; Armstrong, 1994; Young and others, 1996). Materials used in fuels, lubricants, automotive parts, and exhaust systems also have been changing to improve performance, meet changing safety criteria, and reduce emissions of priority pollutants (USEPA, 1999). A number of studies have detected trace elements that are not commonly studied in water-resource investigations. For example, Ti and tungsten (W) from studded tires (Bourcier and others, 1980); trace elements from automotive catalysts—including Pl, Pt, rhodium (Rh), cerium (Ce), lanthanum (La), neodymium (Nd), and zirconium (Zr)—(Helmers, 1996; Zereini and others, 1997; Tuit and others, 2000); and Cu, Sb and tin (Sn) from asbestos-free brake linings (Armstrong, 1994; Reifenhauser and others, 1995) have been detected in runoff, receiving waters, and biota. Concentrations and potential loads of trace elements from various sources differ among studies, but similar source matrixes commonly are identified as primary contributors of trace elements in highway and urban runoff. If comprehensive and timely analysis of trace elements from various potential sources is available, this information can be used to identify emerging contaminants; to identify likely sources of trace elements detected in water, sediment, and biota; and to estimate relative contributions from different sources.

It is especially important to apply good sampling and analytical design as well as an extensive QA/QC program to the analysis and interpretation of the results of source-monitoring programs. Small errors in the measurement of contaminant sources can be magnified by many times when estimates of annual and(or) areal loads are calculated. Confidence in the results of source-matrix monitoring depends on many of the same factors that are necessary for quantification of trace elements in other matrixes. It is necessary to collect samples representative of the source; to collect, process, and analyze the samples in a way that will not introduce sampling artifacts; and to collect and publish information on a substantial QA/QC program (Jones, 1999). If reliable source-matrix-monitoring data are available within the context of a national or regional highway-runoff database, quantification of potential sources may be useful in explaining some of the large variations in concentrations and the loads of highway-runoff constituents from site to site and season to season and year to year.

Vehicular Sources

Fuel and vehicle exhaust contain a number of trace elements that may be entrained in runoff and transported to receiving waters. The most obvious example is the dramatic increase and decrease of aquatic Pb concentrations, which correspond to the use and subsequent elimination of leaded fuels (Callender and Van Metre, 1997). Similarly, in a recent highway-runoff study, Marsalek and others (1997) found that Pb concentrations in bridge runoff were about 10 percent of the average Pb EMCs recorded in earlier runoff studies, whereas the EMCs for Cd, Ni, and Zn were comparable to historical values. Marsalek and others (1997) reported, however, that EMCs for Cu were about twice the historical values. Source-matrix studies (Hildemann and others, 1991; Hee, 1994) reveal that fuels and exhaust contain a number of elements in measurable concentrations (including Al, Br, calcium (Ca), cobalt (Co), Fe, potassium (K), lithium (Li), Mg, Mn, Na, Pt, Sb, strontium (Sr), Ti, and V), in addition to the commonly studied trace elements (Cd, Cr, Cu, Ni, Pb, and Zn). Knowledge of the chemical constituents in fuel and exhaust also can indicate the potential speciation of trace elements in precipitation and runoff. For example, Laxen and Harrison (1977) noted that auto exhaust contains inorganic complexes as well as metal chlorides, bromides, oxides, sulfides, and ammonium halides, most of which have relatively high water solubility.

Lubricants, including motor oil and grease, are also a potential source of trace elements in runoff. Hunter and others (1982) measured trace elements in used crankcase oil and found relatively high concentrations of Cr (11–16 mg/kg), Cu (32–190 mg/kg) , Ni (9–12 mg/kg), Pb (10,500–16,600 mg/kg), and Zn (860–6,280 mg/kg). Concentrations of Zn are expected to be relatively high in lubricants because Zn commonly is used as a stabilizing additive (Yousef and others, 1985b). Concentrations of Cd in motor and lubricating oils are expected to be about 0.2 and 0.1 mg/kg, respectively (Lagerwerff and Specht, 1970; Falahi-Ardakani, 1984). In a review of semivolatile and volatile organic compounds in highway and urban runoff, Lopes and Dionne (1998) reported that oil and grease concentrations in urban stormwater ranged from about 1 to 480 mg/L, and concentrations of oil and grease associated with suspended sediment, bottom sediment, and urban soils ranged from about 8 to 507,000 mg/kg. Therefore, the use of organic tracers may be useful in assessing the predominance of lubricants as a potentially substantial source of trace elements in runoff. Technical concerns for monitoring organic chemicals in runoff are discussed by Lopes and Dionne (1998).

The contributions of trace elements from automotive brake materials depend upon the brake design, the road geometry and traffic intensity. The composition of automotive brakes has been changing throughout the period of record for highway-runoff studies because of regulatory changes (Armstrong, 1994). Hildemann and others (1991) reported measurable concentrations of a number of elements in brake-dust samples (including Al, Br, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Ni, Pb, Pt, Sb, Sr, Ti, V, and Zn). Helmers (1996) reported measurable concentrations of Sb and Sn in the roadside environment and attributed the presence of these trace elements to the increased use of asbestos-free brake linings. Legret and Pagotto (1999) reported Cd, Cu, Pb, and Zn concentrations in European brakes of about 2.7; 142,000; 3,900; and 21,800 mg/kg, respectively. In comparison, Armstrong (1994) analyzed 20 different brake pads from vehicles in the United States and found concentration ranges of about 200–205,000; 100–119,000; and 100–188,000 mg/kg for Cu, Pb, and Zn, respectively. Although these concentrations are high, and may represent a substantial source of trace elements in urban runoff, the geometry of limited-access highways should minimize brake use between exits unless traffic volumes are high. For example, Legret and Pagotto (1999) calculated loads from different sources and noted that concentrations of brake-associated trace elements were lower than expected (on the basis of brake-life data for different vehicle types) because of the relatively low braking frequency on the section of limited-access highway that they studied. This case indicates the influence of highway characteristics on potential brake-associated trace-element loads and the potential for variability in measured trace-element concentrations with the proximity of a given highway site to an exit.

Tire-wear particulates are a noted constituent of road dust and of suspended sediment in runoff; these particulates contribute trace elements to runoff and receiving waters. As with brakes, Hildemann and others (1991) reported concentrations of a number of elements in tire-wear particulates including Al, Br, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Pt, Sb, Sr, Ti, V, and Zn. Legret and Pagotto (1999) reported Cd, Cu, Pb, and Zn concentrations in tire material of about 2.6, 1.8, 6.3, and 10,250 mg/kg, respectively. In comparison, Falahi-Ardakani (1984) reported much higher concentrations of Cd (about 20–90 mg/kg) in tire material. To put these concentrations in context, Christensen and Guinn (1979) calculated tread wear to estimate Zn loads from tires. They estimated that a typical tire (of diameter 65 cm and width 15 cm) would produce about 3,200 grams of tire particulates and (using a concentration of 7,300 mg/kg of Zn in tire rubber) about 23,360 mg of Zn over a 32,000-kilometer tread life. They calculated that each vehicle, therefore, would be expected to produce about 400 mg of tire particulates, including 3 mg of Zn, per kilometer. As with brakes, tire loads also are expected to vary with road geometry and traffic intensity.

Sources in the Highway Environment

Pavement, bridges, safety structures, and other materials may be a potential source of trace elements in highway runoff (Hopke and others, 1980; Gupta and others 1981; Kobriger and Geinopolos, 1984; Legret and Pagotto, 1999). For example, Faure and others (2000) used the organic chemical signature of asphalt to determine that pavement materials constitute a substantial proportion of bottom sediment in depositional areas affected by highway and road runoff. Dupuis and others (1999) reported that blasting abrasives and chips of leaded paint generated by bridge maintenance activities may have adverse effects on receiving waters. Legret and Pagotto (1999) estimate the annual Zn load from galvanized road barriers to be 950 g/km/y from a one-year-long experiment in which a piece of barrier was mounted on a roof and rain running off the barrier was collected for analysis. Data describing the chemical composition of most road-construction materials may be available from manufacturers and suppliers, but this information has not been systematically catalogued in an accessible publication. The availability of such information would be a boon for interpretation of runoff data by transportation agencies. Estimating the contribution of highway-construction materials to runoff, however, raises many technical concerns that must be addressed on a case-by-case basis.

Road dust contains a number of materials that may contribute trace elements (table 1). Hopke and others (1980) identified soil, pavement particulates, vehicle-exhaust emissions, rust from vehicles and highway structures, tire-wear particulates, and salt as primary components of road dust. Gupta and others (1981) noted that local soils constitute a considerable proportion of highway-runoff solids. Kobriger and Geinopolos (1984) noted that soil, cement, vehicle exhaust, rust, tire wear, and deicing agents are the primary sources of particulates. Furthermore, they estimated that among vehicle-derived particulates, tire wear (37 percent), direct pavement wear (37 percent), engine and brake wear (18 percent), and settleable exhaust particulates (7 percent) were primary sources. Beckwith and others (1986) studied trace-element and magnetic relationships for urban-source sediment and identified exhaust particles, wheel-hub particulates, and corroded bodywork as source matrixes. Hildemann and others (1991) measured a number of source materials, including exhaust from vehicles with and without catalytic converters, brake dust, tire dust and road dust. In this study, Al concentrations in road dust were between one and two orders of magnitude higher than in the direct vehicular sources, and were similar to geologic materials (as described in table 1), thus indicating that local soil may constitute a significant proportion of road dust. Rogge and others (1993) used analyses of organic chemicals characteristic of each potential source to estimate that fine road dust consists of vehicular exhaust particulates (7 percent), vehicular aerosol emissions (5 percent), tire particles (5 percent), and vegetative detritus (2 percent). They also concluded that atmospheric aerosols in the urban environment are, chemically, similar to road dust. More recently, Sansalone, Buchberger, Koran, and Smithson (1996) also indicated that deposition and accumulation of solids on road surfaces is caused by traffic, vehicular-component wear, pavement degradation, roadway maintenance, littering, and atmospheric deposition.

Local soils represent a substantial proportion of the road dust that may be entrained by stormwater runoff (Gupta and others,1981; Kobriger and Geinopolos, 1984). Shacklette and Boerngen (1984) measured concentrations of soil-associated trace elements in runoff at more than 1,300 sampling points across the conterminous United States (fig. 14). They found that natural concentrations of many trace elements varied by one or more orders of magnitude. Therefore, the trace-element contribution of natural soils may introduce a potentially large source of variability from site to site in trace-element concentrations measured in runoff samples. This variability may not be explained without soil-matrix-monitoring data. Also, in some mineral-rich areas of the United States, small concentrations of natural soils in runoff may substantially increase trace-element loads in highway runoff, urban runoff, and receiving waters. Measurements of soil-associated trace-element concentrations also can be used to establish baseline (or background) concentrations for the assessment of anthropogenic inputs (Shacklette and Boerngen, 1984). For example, Ames (1994) compared concentrations of trace elements in soils and bottom sediment in several watersheds in Washington state and found that concentrations of the elements Al, Ba, Cr, Fe, Ni were similar in soils and sediment, but concentrations of Cu, Hg, Mn, Pb and Zn in streambed sediment were two or more times the watershed soil concentrations. Callender and Rice (2000) used soil samples and natural streambed-sediment samples to establish baseline-background trace-element concentrations as an indication of the natural and anthropogenic trace-element inputs along a rural-to-urban land-use gradient in the Apalachicola–Chattahoochee-Flint River Basin in the southeastern United States. In a study of watershed soils and streambed sediment, Prych and others (1995) found that concentrations of trace elements and organic carbon were higher in bottom sediment than in local soils. One soil sample from a highway right of way was enriched in Cu, Hg, Mn, Pb, Sb, Zn and other trace elements. Enriched trace elements in soils near highways are

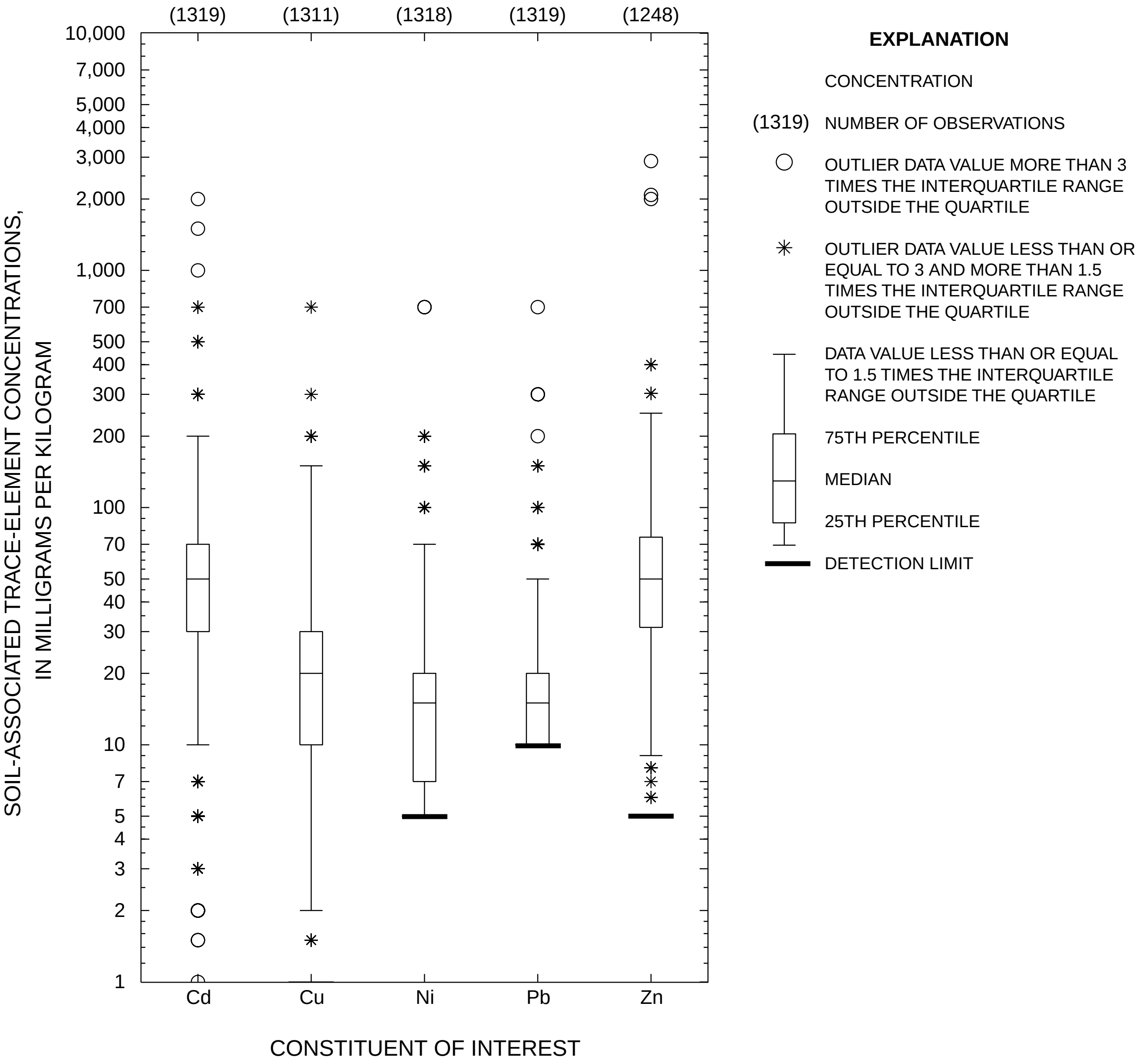

Figure 14. The distribution of natural soil-associated trace-element concentrations from sampling sites near highways across the conterminous United States. Data from Shacklette and Boerngen (1984).

typical, commonly with exponential decays in surface-soil concentrations with increasing distance from the highway (Kobriger and Geinopolus, 1984; Speiran, 1998). Flores-Rodriguez and others (1994) compared trace-element concentrations from natural soils and from highway and urban sediment. They found that trace-element concentrations were enriched by factors of 26, 2, 79, and 11, for Cd, Fe, Pb, and Zn, respectively, in highway sediment, and 1-24, 1-2, 2-106, and 1-18, for Cd, Fe, Pb, and Zn, respectively, in urban sediment when compared to concentrations in natural soil.

Technical concerns related to soil sampling are similar to those for sampling bottom sediment. Areal variability is an important concern, and the chemistry of surface soils is more variable than that of soils at depth because the upper soils are affected by anthropogenic inputs (Ames and Prych, 1995; Prych and others, 1995). To obtain soil samples representative of the natural geology, it is advisable to collect and composite three or more samples from a depth that represents material deposited and(or) formed in the selected plot before widespread industrial influences (Ames and Prych, 1995; Prych and others, 1995). A QA program is important to assess field variability, repeatability of the laboratory measurements, and differences among digestions-recovery methods. Results of soil analysis also are affected by the digestion or sequential extraction methods used. Ames and Prych, (1995) noted that for Washington-State soils, total-recoverable trace-element concentrations were about 7 to 56 percent of concentrations from the total digestion method, and concentrations derived from partial-extraction procedures were about 1 percent of concentrations from the total digestion method.

The potential effect of atmospheric deposition on the pavement and on local soils (which may be entrained in stormwater) has long been a concern for highway and urban runoff studies (Gupta and others, 1981; Brinkmann, 1985; J.A. Colman, K.C. Rice, and T.C. Willoughby, USGS, written commun., 2000). Warren and Birch (1987) noted that trace-element concentrations in road dust and local soils increase with increasing local airborne metal concentrations. Local sources of trace elements potentially can confound site comparisons in the context of a regional or national synthesis. For example, Driscoll and others (1990) noted the effect of one site on population statistics. This site had a median EMC for Zn that was more than 10 times the median of that for the other 20 sites used in the synthesis. Driscoll and others (1990) noted that Zn concentrations characteristic of runoff from the relatively low-volume highway at this site, which is affected by a local zinc-smelting operation, would indicate an inverse relation between Zn concentrations and average daily traffic if they were included in the synthesis. When data from this site are omitted from the national data set, however, there is a significant (r-squared=0.7) relation between increasing average daily traffic and increasing Zn concentrations among the remaining sites used in the analysis (Driscoll and others, 1990).

Although local sources can have important effects on measured runoff quality, studies indicate that the highway is commonly a local net contributor to atmospheric deposition because measured trace-element concentrations commonly decrease with distance from the road surface (Kobriger and Geinopolos, 1984; Falahi-Ardakani, 1984, Harrison and Johnston, 1985; Speiran,1998; Legret and Pagotto, 1999). Hildemann and others (1991) sampled and analyzed sources such as domestic heating appliances; exhaust from catalyst- and non-catalyst-equipped vehicles; diesel trucks; and fine particulates (less than 2 micrometers) of paved road dust, brake dust, and tire dust. These and other values were then used to estimate local air-pollution loads in Los Angeles by source type on the basis of estimates of the relative use of each source. The estimates made by Hildemann and others (1991) indicated that vehicular sources (including paved road dust, brake dust, tire dust, exhaust from diesel trucks, and exhaust from vehicles) would contribute between 38- and 44-percent of the contaminants found in urban air. In another example, Ondov and others (1982) measured concentrations of trace metals in urban air and the Baltimore Harbor Tunnel (presumably affected by vehicle exhaust) and found that the air in the tunnel was enriched in trace-element concentrations—Br and Pb (about 20 times); Cu and Mg (5–10 times); Al, Cd, Cr, Fe, Sb, and Zn (2-5 times); and Mn and Ni (1–2 times)—as compared to urban air. Measured concentrations and loading rates of trace elements at most highway sites reflect variations in dustfall, average daily traffic and, land use in the area, as well as many other contributing parameters (Yousef and others, 1985b). Also, monitoring atmospheric deposition as a source for constituents in highway runoff is difficult and involves many technical concerns that are addressed by J.A. Colman, K.C. Rice, and T.C. Willoughby, USGS, written commun., (2000). Therefore, the assumption that constituent concentrations in atmospheric deposition samples collected on the highway right-of-way may be subtracted from constituent concentrations in runoff is questionable.

Deicing chemicals also have been studied as potential sources of trace elements in runoff (Kobriger and Geinopolos, 1984; Brinkmann, 1985; Granato, 1996; Legret and Pagotto, 1999). In these studies, many elements have been measured as components of deicing chemicals (including boron (B), Br, Ca, Cl, Cr, Cu, Fe, K, Mg, sodium (Na), Ni, Pb, Sr, V, and Zn). Deicing chemicals are a source of major ions that can affect the geochemistry of runoff and receiving waters. Deicing chemicals, however, are not a major source of trace elements in highway runoff, but they are not a trivial source either, especially because they are widely applied to many impervious surfaces (roads, driveways, walkways and parking lots) on the watershed scale, particularly in urban catchments (Granato, 1996). Deicing chemicals are different from other sources because they are applied purposefully to maintain safe travel conditions at prescribed application rates, which depend on climate, pavement area, and environmental concerns. The variation in annual deicing-chemical loads at a single site can be substantial. During a 5-year road-salt study in southeastern Massachusetts, total annual deicing-chemical loads (and therefore the associated trace-element loads) varied by a factor of four from year to year depending on the severity of winter weather (Granato, 1996). It is expected that this variability would be even greater among different sites with different climates, and that differences in the use of deicing chemicals may contribute to differences in measured trace-element concentrations.

DATA-QUALITY ISSUES FOR REGIONAL OR NATIONAL SYNTHESIS

The quality of available data is a primary concern for evaluation of trace-element-monitoring data, especially in terms of a regional or national synthesis, because results of water-quality studies may be used as the basis for the formulation of agency policies and may, therefore, have substantial economic and environmental implications. To assess the potential precision, accuracy, representativeness, completeness, and comparability of trace-element data, it is necessary to evaluate the availability, suitability and completeness of documentation necessary to establish that data-quality objectives necessary for a regional or national synthesis are fulfilled. The necessary documentation includes information about monitoring protocols, QA/QC efforts, and ancillary data.

The Intergovernmental Task Force on Monitoring Water Quality (ITFM, 1995a,b) noted that among existing environmental-monitoring programs, the lack of consistent water-quality-monitoring protocols is "one of the biggest barriers to sharing water monitoring data," especially within the context of a regional or national synthesis. The ITFM has not established a single monitoring protocol; however, use of performance-based methods systems (PBMS) for field and laboratory work is recommended. PBMS accommodate the use of different collection, processing, and analysis protocols as long as the accepted methods produce a sample population of results that are within levels of confidence defined by data-quality objectives. To assess different field methods, side-by-side sampling is done (using identical laboratory methods). To assess different laboratory methods, field duplicates, and analytical reference materials are used. Efforts to establish a set of protocols within a PBMS, however, are not trivial, so it is advisable to use established protocols that are suitable for the collection of trace-element data (ITFM, 1995a,b).

Even when using proven monitoring protocols, a well-designed QA/QC program is a critical component of the documentation necessary to establish the validity, scientific defensibility, and utility of trace-element data. Jones (1999) describes principles and practices for QA/QC in terms of a regional and(or) national runoff-quality-monitoring data set. Briefly, use of standard protocols are necessary to ensure that the quality of data collected and information gained from the use of various blank samples, replicate samples, split samples, spiked samples, synthetic samples, and standard reference samples are used to document the quality of data collected. These activities must be carried out within a system of data validation, data-quality assessment, and independent quality audits (Jones, 1999). QA/QC programs are especially important for trace-element monitoring because trace elements are ubiquitous in the environment, they are present in low concentrations in environmental samples, and the partitioning of trace elements between sampling matrixes and sample collection and processing equipment can be considerable.

Ancillary information also is needed to evaluate available data for a national synthesis because this information may provide explanatory variables that can be used to standardize data to a common basis for comparison, or to account for some of the otherwise unexplainable variability in the data. Many of the site characteristics that have been used in the FHWA's evaluations of highway-runoff quality, including information about the highway, local land use, geology, and climate (Granato and others, 1998), are especially relevant to interpretation of trace-element data on a national or regional scale. Currently, however, there are no established national formats for documentation and exchange of ancillary information and data from highway-runoff research studies (Transportation Research Board, 1997).

Documentation of monitoring protocols, QA/QC efforts, and ancillary data is especially important for the evaluation of historical trace-element monitoring data because monitoring and analysis methods have changed considerably over the past 30 years. Quantitative use of historical data collected during different time periods from different sites may be difficult, because changes in methods and long-term trends in diffuse trace-element contamination from anthropogenic sources would tend to obscure relations between explanatory variables and measured trace-element concentrations. Within this context, historical changes in detection limits are a particularly vexing problem for the interpretation of trace-element-monitoring data sets. For example, in compiling the master data file for evaluation of contaminant loadings and environmental effects from highway stormwater runoff, Driscoll and others (1990) noted, "it was virtually impossible to unequivocably determine the actual detection limit associated with each contaminant concentration." They could not determine the detection limits because this information was not explicitly documented in available ancillary data and because the data were produced by a number of different analytical laboratories over an extended period of time.

Detection limit artifacts affect the accuracy and precision of individual values as well as the statistical characteristics of entire data sets. Uncertainty in the accuracy and precision of individual values tends to increase as concentrations approach the lower analytical detection limit. For example, in an assessment of interlaboratory evaluation data, Granato and others (1998) noted that uncertainties (expressed as relative percent error) in measured trace-element concentrations in standard reference solutions (SRS) increased exponentially with decreasing concentrations. The most probable value (MPV) of trace-element concentrations in SRS samples that are near detection limits have uncertainties of about plus or minus 100 percent for the "best" (the top 5 percent) laboratories, and uncertainties of about plus or minus 400 percent for "most" (the top 95 percent) laboratories. In comparison, when the MPV concentrations of reference solutions are about two orders of magnitude above detection limits, uncertainties in the populations of MPV concentrations from interlaboratory studies are generally reduced to within plus or minus 10 percent (Granato and others, 1998). Even when nominal laboratory detection limits are available, effective detection limits for individual data sets may vary because of operational differences in analytical techniques, which are necessitated by variations in the chemical characteristics of individual samples. For example, Granato (1996) found that in a study to examine deicing chemicals as a source of trace constituents in highway runoff, Ba, Co, Li, Mn and Zn were detected in the more dilute (0.001 percent) solutions but not in the more concentrated (0.5 percent) solutions. This detection-limit artifact was caused by laboratory procedures that necessitated dilution of the more concentrated samples because of the high salinity. Therefore, although both samples were analyzed by the same method (with the same nominal detection limit), the dilution produced a much higher effective detection limit for the more concentrated sample. The statistical characteristics of entire data sets can be affected when a significant number of values are below one or more detection limits. Driscoll and others (1990) noted that, depending upon the method of statistical analysis, an overestimation of measures of central tendency and an underestimation of measures of spread are caused by a significant number of values below the detection limit that are omitted or set equal to the detection value. Different methods for dealing with the effects of one or more detection limits within a data set are available, but utilization of the various methods requires knowledge of the different detection limits within the data (Helsel, 1990; Helsel and Hirsch, 1992). Therefore, it is necessary to document detection limits and use caution when interpreting trace-element data that are at or near the detection limit, especially when different data sets are combined for regional or national synthesis.

SUMMARY

Trace elements have been a primary focus of most highway- and urban-runoff studies because stormwater runoff may be a source of trace elements that are regulated for aquatic-life protection. There are many technical issues of concern for monitoring trace elements in highway and urban runoff. Trace elements, by definition, are difficult to quantify, especially in stormwater-runoff studies. Trace elements in highway runoff accumulate on the road surface as a result of local and regional atmospheric deposition and regular highway operation and maintenance activities. The FHWA and State Transportation Agencies are concerned about the potential effects of highway runoff on the watershed scale and for the management and protection of watersheds. Information that is documented as valid, current, and scientifically defensible is needed by transportation agencies to support necessary planning and management decisions. Currently, because of many technical concerns, most trace-element monitoring data are considered to be suspect, and the responsibility to provide published data-quality information to support the validity of reported results rests with the data-collection agency.

Paved surfaces are fundamentally different physically, chemically and hydraulically from the natural freshwater systems that have been the focus of most trace-element-monitoring studies. Therefore, existing scientific conceptions of the behavior of trace elements in the environment are based largely upon research on natural systems, not on systems typical of pavement runoff. Paved surfaces are characterized by extreme conditions of temperature, kinetic energy, chemistry, and hydraulics. Furthermore, the logistics of sampling runoff in the highway and urban environment are different than the logistics of sampling many natural freshwater systems. Therefore, trace-element-monitoring programs may benefit if conducted within the framework of automated monitoring and sampling programs that standardize the process and provide a record of the variations in flow and water-quality characteristics.

Trace elements have both natural and anthropogenic sources, including the sample collection, processing, and handling materials used in many trace-element-monitoring studies. Trace elements also react with these materials within the time scales typical for collection, processing, and analysis of runoff samples. The relative effect of potential contamination and(or) attenuation of trace elements in runoff samples is a function of the concentration of major and trace elements, organic chemicals, and sediment in solution. Sampling artifacts are especially important when measured concentrations are at or near analytical detection limits. Historically, anthropogenic sources in developed areas were thought to produce trace-element concentrations high enough to obscure the effects of contamination from sample collection and processing procedures, but studies show that even trace-element data from urban-runoff studies may be affected by sampling artifacts. Without sufficient supporting documentation, however, it is impossible to determine how sampling artifacts affect monitoring data sets. Therefore, great care is required to collect and process samples in a manner that will minimize potential sample contamination and variability in the sampling process. Standardization of sampling protocols designed to minimize these sampling artifacts for each matrix of interest will maximize the comparability and technical defensibility of data used in a regional or national synthesis.

A wide spectrum of geochemical conditions commonly precludes the definitive physical and chemical characterization of aqueous systems. To study the characteristics and potential effects of trace elements in highway and urban runoff, six matrixes are typically sampled—whole water, dissolved (filtered water), suspended sediment, bottom sediment, biological tissue, and sources (from vehicles and the highway environment). These matrixes are operationally defined in an effort to maximize comparability of data sets. Each matrix, however, is associated with a number of technical concerns that must be understood and addressed through use of proper sampling protocols designed to minimize inherent problems and maximize the accuracy, precision, comparability, and representativeness of data collected. The whole-water matrix appears to be the most appropriate for monitoring runoff quality at a given site because of the unique nature of the monitoring environment, the range of trace-element concentrations expected in runoff samples, and the logistics of sampling stormwater. If it is possible to separate filtered water and suspended sediment immediately at the time of sample collection, information about the chemical partitioning of trace elements in runoff and receiving waters may be gained. The bottom-sediment matrix appears to be an appropriate reconnaissance tool for identifying past and present trace-element contamination in drainage systems and receiving waters. The biological-tissue matrix appears to be appropriate for measuring the potential effect of trace element contamination when used in conjunction with community assessments and trace-element concentrations derived from the analysis of bottom sediment and(or) whole water-samples from runoff. The source-monitoring matrix appears to be appropriate for identification of emerging contaminants and estimation of relative loads from different potential sources.

Results of water-quality studies are used as the basis for the formulation of agency policies and can have substantial economic and environmental implications. Therefore, the data quality is a primary concern for evaluation of trace-element monitoring data, especially in terms of a regional or national synthesis. Documentation necessary to establish data quality includes information about monitoring protocols, quality assurance and quality control efforts, and ancillary data. This documentation is especially important for the evaluation of historical trace-element-monitoring data because trace-element monitoring and analysis methods have been in constant flux over the past 30 years.

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Chapter 7. A Review of Semivolatile and Volatile Organic Compounds in Highway Runoff and Urban Stormwater

By THOMAS J. LOPES and SHANNON G. DIONNE

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A Review of Semivolatile and Volatile Organic Compounds in Highway Runoff and Urban Stormwater

By Thomas J. Lopes *and* Shannon G. Dionne

Abstract

Many studies have been conducted since 1970 to characterize concentrations of semivolatile organic compounds (SVOCs) in highway runoff and urban stormwater. To a lesser extent, studies also have characterized concentrations of volatile organic compounds (VOCs), estimated loads of SVOCs, and assessed potential impacts of these contaminants on receiving streams. This review evaluates the quality of existing data on SVOCs and VOCs in highway runoff and urban stormwater and summarizes significant findings. Studies related to highways are emphasized when possible. The review included 44 articles and reports that focused primarily on SVOCs and VOCs. Only 17 of these publications are related to highways, and 5 of these 17 are themselves review papers. SVOCs in urban stormwater and sediments during the late 1970's to mid-1980's were the subject of most studies.

Criteria used to evaluate data quality included documentation of sampling protocols, analytical methods, minimum reporting limit (MRL) or method detection limit (MDL), quality-assurance protocols, and quality-control samples. The largest deficiency in documenting data quality was that only 10 percent of the studies described where water samples were collected in the stream cross section. About 80 percent of SVOCs in runoff are in the suspended solids. Because suspended solids can vary significantly even in narrow channels, concentrations from discrete point samples and contaminant loads estimated from those samples are questionable without information on sample location or how well streamflow was mixed. Thirty percent or fewer of the studies documented the MRL, MDL, cleaning of samplers, or use of field quality-control samples. Comparing results of different studies and evaluating the quality of environmental data, especially for samples with low concentrations, is difficult without this information.

The most significant factor affecting SVOC concentrations in water is suspended solids concentration. In sediment, the most significant factors affecting SVOC concentrations are organic carbon content and distance from sources such as highways and power plants. Petroleum hydrocarbons, oil and grease, and polycyclic aromatic hydrocarbons (PAHs) in crankcase oil and vehicle emissions are the major SVOCs detected in highway runoff and urban stormwater.

The few loading factors and regression equations that were developed in the 1970's and 1980's have limited use in estimating current (1998) loads of SVOCs on a national scale. These factors and equations are based on few data and use inconsistent units, and some are independent of rainfall. Also, more cars on the road today have catalytic converters, and fuels that were used in 1998 are cleaner than when loading factors and regression equations were developed.

Comparisons to water-quality and sediment-quality criteria and guidelines indicate that PAHs, phenolic compounds, and phthalates in runoff and sediment exceeded U.S. Environmental Protection Agency drinking-water and aquatic-life standards and guidelines. PAHs in stream sediments adjacent to highways have the highest potential for adverse effects on receiving streams.

Few data exist on VOCs in highway runoff. VOCs were detected in precipitation adjacent to a highway in England, and chloromethane, toluene, xylenes, 1,2,4-trimethylbenzene, and 1,2,3-trichloropropane were detected in runoff from a highway in Texas. In urban stormwater, gasoline-related compounds were detected in as many as 23 percent of the samples. Land use could be the most significant factor affecting the occurrence of VOCs, with highest concentrations of VOCs found in industrial areas. Temperature is another factor affecting the occurrence and concentrations of VOCs. Urban land surfaces are the primary non-point source of VOCs in stormwater. However, the atmosphere is a potential source of hydrophilic VOCs in stormwater, especially during cold seasons when partitioning of VOCs from air into water is greatest. Tetrachloroethene, dichloromethane, and benzene were the only VOCs detected in storm-water that exceeded U.S. Environmental Protection Agency drinking-water standards.

INTRODUCTION

Runoff from highways and urban areas has long been recognized as a source of contaminants that could affect the Nation's water resources. Federal, State, and local agencies and universities have conducted or sponsored research since about 1970 to characterize runoff quality, estimate contaminant loads, and assess impacts on receiving streams. Sampling protocols, analytical methods and detection limits, and quality-assurance/quality-control (QA/QC) protocols have improved during this time. In addition, new contaminants are being released into the environment, more is known about their toxic effects, and water-quality criteria for contaminants have been established or changed. In light of these changes, highway-runoff and urban-stormwater studies need to be periodically reviewed for quality of data and whether the results address current water-quality issues.

Semivolatile organic compounds (SVOCs) and volatile organic compounds (VOCs) are two groups of contaminants that have been measured in runoff from highways and urban areas. SVOCs are operationally defined as solvent-extractable organic compounds that can be determined by gas chromatography/mass spectrometry (GC/MS) (Furlong and others, 1996). Examples of SVOCs include phthalates, phenols, and polycyclic aromatic hydrocarbons (PAHs). Smith and others (1988) reviewed the sources of several types of SVOCs and processes affecting their fate and distribution in surface water. SVOCs are present in many products, including plastics, dyes, and disinfectants, and PAHs are produced by burning gasoline, oil, wood, and other fuels. SVOCs typically are hydrophobic and by definition have a moderate tendency to volatilize (Karickhoff and others, 1979; Lucius and others, 1989). These properties control how SVOCs are distributed among air, water, and soil when released into the environment. Because they are hydrophobic and moderately volatile, SVOCs preferentially distribute into organic phases, such as tissue and sediments containing organic carbon (Witkowski and others, 1987; Smith and others, 1988).

SVOCs are an environmentally significant group of contaminants because they may accumulate to concentrations that will adversely affect aquatic organisms. Benthic organisms that live in contaminated sediment are most affected because sediments have the largest fraction of SVOCs; however, organisms that feed on benthic species also may be affected. Adverse effects could include mortality, reduced fecundity, and inhibited or abnormal growth. Recently, scientists have become aware of compounds that disrupt the endocrine system and reproduction of fish, reptiles, and mammals (Colborn and others, 1993). Endocrine disruption occurs when a compound either mimics natural hormones or blocks their function. Certain phthalates and PAHs are among the organic compounds that cause endocrine disruption, although their effect is weaker than the effect of some pesticides. In a national survey, concentrations of phenols in bottom sediment were found to correlate with concentrations of 11-ketotestosterone in male carp at an alpha-level of 0.05, suggesting these SVOCs also could cause endocrine disruption (Goodbred and others, 1997).

VOCs are operationally defined as organic compounds that can be extracted from water by purging with an inert gas, then trapped and determined by GC/MS (Connor and others, 1998). VOCs are present in many products including fuels, solvents, refrigerants, paints, adhesives, and deodorants. VOCs also are present in vehicle exhaust and chlorinated water. In contrast to SVOCs, VOCs can be either hydrophobic or hydrophilic, have a high tendency to volatilize, and distribute preferentially into air because of their volatility.

VOCs have low aquatic toxicity (Rowe and others, 1997). Except for spills, concentrations found in highway runoff and urban stormwater are too low to cause a toxic response in aquatic species. However, VOCs in highway runoff and urban stormwater could enter drinking-water supplies and have chronic effects on the consumers. For example, ground water in Tucson, Arizona, was contaminated with low concentrations of VOCs in urban stormwater (Pritt and others, 1996).

Objectives and Scope

The objectives of this review are to evaluate the quality of existing data on SVOCs and VOCs and to summarize significant findings. This is not an exhaustive review of all studies that contain information on SVOCs and VOCs, but a review of studies that focused primarily on SVOCs and VOCs in highway runoff, urban stormwater, precipitation, and sediments. Studies related to highway runoff are emphasized when possible. Measures of extractable organic compounds, such as petroleum hydrocarbons and oil and grease, are included in the discussion of SVOCs, but pesticides and polychlorinated biphenyls are not within the scope of this report.

A total of 44 articles and reports published between 1976 to 1998 were reviewed. Only 17 of these publications were related to highways, and 5 of these 17 are themselves review papers. SVOCs in urban stormwater and sediments were the subjects of most studies.

Criteria for Data Quality

Studies done since 1970 are useful if they were documented such that the quality, interpretations, and limits of the data can be qualified. Documentation should be able to answer several important questions, such as: Where, when, and how were samples collected? What analytical methods were used to identify and quantify contaminants, and what was the minimum reporting limit (MRL) or method detection limit (MDL)? What QA/QC steps were taken to assure data are representative, accurate, and precise? These questions comprise the criteria for evaluating the quality of existing data.

MONITORING TRACE ORGANIC CHEMICALS

Because of their physical and chemical properties, different samplers and sampling procedures are needed for SVOCs and VOCs. SVOCs can be sampled using a variety of samplers because analyte loss during sampling is not a significant issue. The choice and use of a sampler depends on sampling objectives and logistical considerations. For example, discrete point samplers are adequate for obtaining occurrence data, but do not obtain accurate concentrations of SVOCs unless the stream is well mixed and suspended solids are evenly distributed in the stream cross section. The best techniques to obtain accurate data are equal-width-increment (EWI) and equal-discharge-increment (EDI) sampling using samplers that collect depth-integrated samples (Wells and others, 1990). However, these sampling techniques are difficult in flashy runoff from urban areas and highways, which is why automatic samplers commonly are used in stormwater studies. Regardless of the sampler type, the sampler should be made of noncontaminating materials. Generally, metal and glass are the best materials for sampling trace concentrations of organic compounds. Teflon is the preferred material when metal and glass cannot be used, such as for sampling lines for automatic samplers.

In contrast, analyte loss during sampling is a significant issue for VOCs because of their volatility. Three types of samplers and sampling techniques are used to collect VOC samples, all three of which collect discrete point samples. If point sources are not nearby, point sampling for VOCs is not as significant an issue as for SVOCs because VOCs are mostly in the dissolved phase and not sorbed to sediments (Rathbun, 1998). The two most common sampling techniques are to manually dip a 40-mL (milliliter) glass vial directly into the stream or to obtain a sample with another container and then transfer the water to a vial. Vials are then quickly sealed with a Teflon-lined septum cap. Dipping a vial directly into the stream eliminates potential contamination from sampling equipment. However, this technique is limited to the length of the sampler's arm and can be hazardous during high-flow conditions. A stainless steel and copper sampler (Shelton, 1997) is more versatile and safer than dip sampling because it collects samples at greater depths and can be suspended from bridges. Sample water is collected directly into sample vials, which are sealed when the sampler is retrieved from the stream.

Laboratory and field testing has shown that this sampler collects accurate data (Gregory Delzer, USGS, written commun., 1997). VOCs should not be collected using automatic samplers with peristaltic pumps that do not quickly seal vials because the negative pressure created by the pumps and volatilization from open vials can bias sample results. Recently, ISCO Inc. developed the model 6100 automatic sampler for sampling VOCs in streams. This sampler uses a positive-displacement pump and quickly seals vials. Laboratory testing of this sampler indicates it produces accurate data with less than 2 µg/L (micrograms per liter) of carryover between samples (Gregory Delzer, written commun., 1997).

Preservation of water samples for analysis of SVOCs and VOCs depends on laboratory requirements. SVOC samples usually are chilled at 4˚C. VOC samples usually are chilled and may be acidified to a pH of less than 2 using hydrochloric acid. Some laboratories require addition of ascorbic acid to VOC samples if free chlorine is present.

GC/MS is the most accurate method of identifying and quantifying most SVOCs and VOCs. Even if laboratories use the same analytical method, they may report varying MRLs and MDLs that can create difficulties in data interpretation (Cole and others, 1984). MRLs and MDLs can vary because of the sample matrix, study objectives require different values, and analytical methods improve with time. For example, MRLs and MDLs that meet current regulatory requirements may be satisfactory for compliance monitoring. However, organic compounds in stormwater commonly occur at concentrations below water-quality criteria (Makepeace and others, 1995), so regulatory requirements may be inadequate to determine if compounds are present, to estimate loads, to identify causal factors and emerging problems, and to use data in the future if water-quality criteria are lowered. The National Water-Quality Laboratory of the U.S. Geological Survey (USGS) reports SVOCs in water as low as 5 µg/L (Fishman, 1993), SVOCs in sediment as low as 50 µg/kg (micrograms per kilogram) (Furlong and others, 1996), and VOCs in water as low as 0.05 µg/L (Connor and others, 1998). Extraction and recovery efficiencies are lower for SVOCs than for VOCs, which is why SVOCs have higher MRLs and MDLs. Extraction and recovery efficiencies less than 90 percent are common for compounds that sorb to sediments (Furlong and others, 1996), whereas extraction and recoveries for most VOCs are 95 percent or greater (Connor and others, 1998).

Results of water-quality studies can form the basis of or alter agency policies and have significant economic and social implications. Studies should be supported by a QA/QC plan to ensure that these results are based on quality data. QA is the precautionary actions used to prevent systematic bias. Examples of QA are using noncontaminating materials and sample containers, cleaning equipment, preserving samples soon after collection, and shipping samples overnight. QC includes the steps used to check that QA is effective and to evaluate variability due to random error. Examples of QC are equipment blank samples to ensure that equipment is clean, replicates to assess sample variance and analytical precision, and samples spiked with analytes to evaluate analyte degradation and recovery. QC samples generally comprise 10 to 15 percent of all samples. The QA/QC plan usually is an unpublished document, but should be briefly described with study results. For large studies, the QA/QC plan often is a published document, such as that by Mueller and others (1997).

Sample Collection

Documentation of sample collection should include where, when, and how highway runoff and urban stormwater samples were collected. Documenting sample location is important so sampling can be repeated to evaluate apparent anomalies and to define changes with time. All studies answered the question of where samples were collected (table 1, at end of chapter), although the level of detail varied. Some studies provided maps showing precise sample locations; however, most studies included generalized maps or described sample locations. An extreme case of generalizing was Line and others (1997), who only stated that samples were collected in North Carolina. Studies included in this review were conducted in the United States (fig. 1) and in Canada, Germany, Japan, Norway, Spain, Switzerland, and the United Kingdom. Most studies in the United States were conducted along the northeast coast and in southern states where population densities are greatest. Few studies have been conducted in the Great Lakes region and the central and western states.

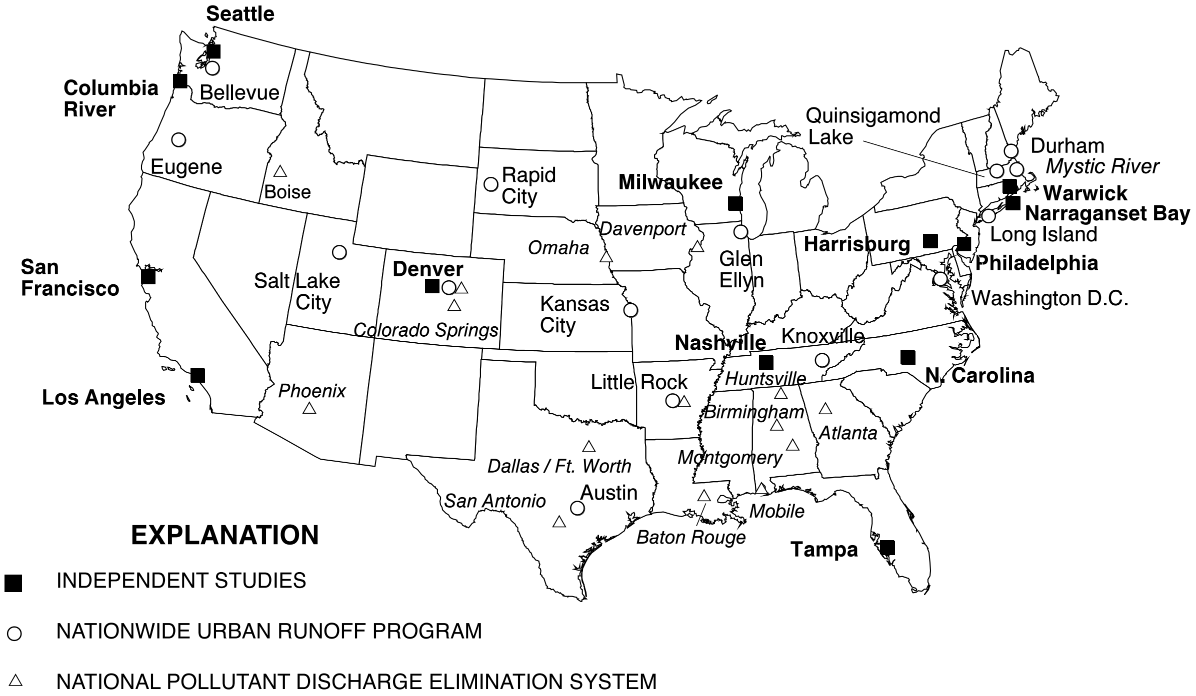

Figure 1. Cities in the United States where semivolatile and volatile organic compounds have been studied in highway runoff and urban stormwater.

Seventeen studies were related to SVOCs and VOCs in highway runoff or in rain, snow, and sediment near highways. Ten of the 17 studies related to highways were in the United States (Wiland and Malina, 1976; Zawlocki and others, 1980; Gupta, 1981; Hoffman and others, 1983, 1984, 1985; Hoffman and Quinn, 1987; Latimer and others, 1990; Barrett and others, 1993; Baldys and others, 1997); four were in England (Butler and others, 1984; Johnston and Harrison, 1984; Harrison and Johnston, 1985; Hewitt and Rashed, 1990); and one was in each of Canada (Boom and Marsalek, 1988), Norway (Gjessing and others, 1984), and Germany (Stotz, 1987). PAHs were the topic of most highway-related studies.

The priority pollutant monitoring project of the Nationwide Urban Runoff Program (NURP) had the widest geographic distribution and is the most frequently cited study of organic contaminants in urban stormwater. The U.S. Environmental Protection Agency's (USEPA) priority pollutants, including SVOCs and VOCs, were monitored in 15 cities in 14 states (Cole and others, 1984). Concentrations of the priority pollutants were measured in 86 stormwater samples collected from drainage basins with residential, commercial, or industrial land use.

Marsalek and Schroeter (1988) conducted a study similar to NURP in 12 Canadian cities in the Great Lakes region. Up to 125 stormwater and sediment samples from 81 sites with residential, commercial, industrial, or transportation land use were analyzed for 50 priority pollutants, including PAHs and chlorinated benzenes.

A set of independent urban stormwater studies conducted by the USGS comprise another type of study with a wide geographic distribution. In 1991, USEPA required cities with a population of 100,000 or more to monitor stormwater quality and obtain municipal National Pollutant Discharge Elimination System (NPDES) permits. The USGS monitored stormwater from drainage basins with residential, commercial, or industrial land use in 16 of these cities in 11 states (Delzer and others, 1996). Most of these cities are in southern and central states (fig. 1). A total of 642 stormwater samples were analyzed for up to 210 properties and constituents, including the priority pollutants. VOC data were compiled to characterize the occurrence of VOCs in stormwater (Delzer and others, 1996) and identify nonpoint sources (Lopes and

Bender, 1998). Data on SVOCs and other contaminants that were measured in stormwater samples were not compiled.

Documenting when samples were collected is necessary to know if unusual weather occurred during the respective studies and to determine if state-of-the-art sampling and analytical methods were used. The question of when samples were collected was answered in about 84 percent of the studies. The majority of data were collected during the late 1970's to mid-1980's, including data related to highway runoff. Only 20 percent of studies, most of which were NPDES studies, collected data after 1990. Typically, the time between data collection and publication was about 2 to 4 years, although Latimer and others (1990) was published 10 years after data were collected. Studies that did not report when data were collected were published between 1982–91; therefore, data probably were collected prior to the mid-1980's.

The validity and comparability of data depend on several criteria, including documented sampling protocols. Description of the sampling protocol should include information on the type and material of the sampler; where in the stream cross section samples were collected; if discrete or composite samples were analyzed; and if whole water, suspended solids, or filtrates were analyzed. Most studies provided some, but none provided all information on the sampling protocol.

About 80 percent of studies reported the type of sampler. Water samples were collected with buckets, bottles, trays, cans, storage tanks, drums, and automatic samplers. Snow and sediment were sampled with corers, trowels, ponar samplers, jars, and lysimeters. Atmospheric deposition and rain were sampled with funnels. Line and others (1997) collected samples for VOCs with automatic samplers that were not designed for these contaminants; therefore, volatilization from sample water probably biased results.

About 60 percent of studies reported the sampler material. Most samplers were made of metal or glass, which are good materials to use for sampling organic contaminants. Studies that used flow splitters and samplers made of fiberglass and plastics included Zawlocki and others (1980), Gjessing and others (1984), Johnston and Harrison (1984), and Harrison and Johnston (1985). Sorption to these materials may have biased the SVOC and VOC data of these studies. Hewitt and Rashed (1990) conducted a study in the same area as Johnston and Harrison (1984) and Harrison and Johnston (1985) and may have used the same equipment, but there is insufficient information to determine this from the article. Seven studies used automatic-pumping samplers. Three NPDES studies (Lopes and others, 1995; von Guerard and Weiss, 1995; and Baldys and others, 1998) noted that sampling lines were made of Teflon. The other studies did not document the sampler-line material.

The largest deficiency in documenting data quality was that only 10 percent of studies described where water samples were collected in the stream cross section, if streamflow was well mixed, or if equal-width-increment or depth-integrated techniques were used. The representativeness of discrete point samples and interpretations based on those data, especially load estimates, are questionable without this information. Sample location could have affected results because SVOC concentrations depend on suspended solids concentrations (Hunter and others, 1979; Hoffman and Quinn, 1987; and Barrett and others, 1993). Suspended solids concentrations can have significant horizontal and vertical variations (Horowitz and others, 1989) even in channels less than 5 ft wide (Edwards and Glysson, 1986). Samplers do not need to be sophisticated devices like electronically activated point samplers to obtain representative samples. However, the water samplers used in these studies and lack of information on flow conditions suggest most studies sampled surficial streamflow along the streambank. Stream velocity and suspended sediment concentrations typically are lowest along the banks, so point samples collected along the streambanks may result in biased (low) contaminant concentrations and load estimates. This may not be a significant issue in stormwater drainages where streamflow usually is fast and shallow.

About 90 percent of studies described whether samples were discrete or composite samples. About 70 percent of studies that described sampling methods manually collected discrete water samples. Eight studies composited stormwater samples, but two of these studies did not document whether these were time-weighted or flow-weighted composites. Composite samples were obtained using cone or churn splitters (Lopes and others, 1995; von Guerard and Weiss, 1995) and a flow splitter (Zawlocki and others, 1980). Other studies did not describe how samples were composited. About 90 percent of studies described whether bottom-sediment samples were point samples or composites and the depth interval of bottom sediment that was sampled. Most samples were point samples collected from the upper 10 centimeters of bottom sediment. Ellis and others (1985) and Brown and others (1985) composited surficial bottom-sediment samples from several sites. Gavens and others (1982) and Butler and others (1984) sieved bottom sediment and Hoffman and others (1984) sieved suspended solids for a consistent grain size among samples. Comparing bottom-sediment concentrations is difficult because most studies did not analyze for organic carbon, which is the most common way of normalizing organic contaminant concentrations in sediments.

About 90 percent of studies described whether whole-water samples were analyzed or if suspended solids and filtrates were analyzed separately. Unless stated otherwise, it was assumed that whole-water samples were analyzed. About 30 percent of studies separated suspended solids and analyzed the filtrate, solids, or both. Separation was done by filtration with glass fiber filters or by centrifugation.

Analytical Methods and Minimum Reporting and Detection Limits

Documenting the analytical methods, MRLs, and MDLs is important to use data from different studies for a common objective. About 90 percent of studies described the analytical method for contaminant identification and quantitation. Gas chromatograph/flame-ionization detection (GC/FID) was the most commonly used analytical method. GC/MS was used to identify analytes or confirm GC/FID results in about 30 percent of the studies. About 30 percent of studies documented analytical precisions and recoveries. Generally, precision was less than 25 percent and recoveries were greater than 80 percent.

About 30 percent of studies, most of which were conducted in the 1990’s, documented the MRL or MDL. The MRL is the lowest concentration that can accurately be quantified. The MDL is the lowest concentration that the method can detect. For studies done in the 1980’s, Brown and others (1985) reported an MRL of 1 µg/L for petroleum hydrocarbons, Schondorf and Herrmann (1987) reported MDLs ranging from 0.03 to 0.15 ng/L (nanograms per liter) for PAHs, Zawlocki and others (1980) reported an MRL of 100 µg/L for a variety of SVOCs, and Boom and Marsalek (1988) and Marsalek and Schroeter (1988) reported an MRL of 0.05 µg/L for PAHs. Except for Zawlocki and others (1980), these limits compare well with current (1998) limits of the USGS. The high MRLs ranging from 5 to 100 µg/L used by Line and others (1997) could explain why few SVOCs and VOCs were detected in stormwater from industrial sites.

Quality Assurance and Quality Control

The validity and use of data depend on documenting the procedures used to ensure that high - quality data were collected. Most studies described some precautionary action to ensure sample integrity, but few studies described thorough QA/QC procedures. Only Cole and others (1984) described a QA/QC plan, although they were unable to evaluate the effectiveness of the plan for NURP.

As previously noted, about 60 percent of studies used noncontaminating materials such as glass and metal. However, only 30 percent of studies documented that equipment was cleaned before sampling or that samples were preserved. Chilling samples at 4˚C was the most commonly used method for preserving samples. Infrequently described precautionary steps included use of Teflon-lined or metal lids, covering jars with aluminum foil, homogenizing samples before splitting into equal portions, slowly melting snow samples to minimize volatilization, sampling in well-mixed parts of a storm drain, shipping samples overnight, and using nitrogen to filter samples for SVOCs. Studies that retrieved samples up to 2 weeks after collection without chilling were Johnston and Harrison (1984) and Harrison and Johnston (1985). Latimer and others (1990) left samples at room temperature for up to 2 days before analysis. Line and others (1997) used automatic samplers for VOCs and retrieved and chilled samples sometimes hours after they were collected.

Both laboratory and field QC samples are needed to evaluate sample and analytical quality. About 30 percent of studies reported analyzing laboratory QC samples and 15 percent analyzed field QC samples. Laboratory QC samples included blanks, lab-split duplicates, surrogate recoveries, and performance-evaluation samples. Four studies reported using laboratory blanks and surrogate recoveries to correct environmental concentrations. The use of field QC samples became prevalent after most of the studies in this review were conducted. Except for NURP, the only studies that reported analyzing field QC samples were conducted in the 1990's. Field QC samples included equipment blanks, trip blanks, replicates, and spikes. Evaluating the quality of environmental data, especially low concentrations, is difficult because few studies collected QC data and documented that samplers were cleaned.

SUMMARY OF STUDY RESULTS

Most highway-runoff and urban-stormwater studies were conducted to address regional or local issues. However, results from all studies could provide useful qualitative information to answer some general questions of national importance. For example, do certain SVOCs and VOCs occur more frequently and at higher concentrations in particular regions of the country? If so, do factors such as climate affect occurrence and concentrations of these compounds? What are the sources of SVOCs and VOCs? Can loads of SVOCs be estimated on a national scale? Could SVOCs and VOCs have an adverse effect on water resources? These questions are the focus of this summary.

Semivolatile Organic Compounds

SVOCs were the subjects of most highway runoff and urban stormwater studies. Much has been learned about these compounds, especially the extractable organic compounds and polycyclic aromatic hydrocarbons (PAHs).

Occurrence

Characterizing the occurrence of SVOCs in highway runoff and urban stormwater for the entire United States is not possible because few studies reported detection frequencies or were conducted in the Great Lakes region and the central and western states. Studies that reported detection frequencies are Cole and others (1984), Boom and Marsalek (1988), Marsalek and Schroeter (1988), Lopes and others (1995), von Guerard and Weiss (1995), and Baldys and others (1998). SVOC concentrations vary by several orders of magnitude, which is typical of stormwater quality (table 7, at end of chapter). Table 7 was compiled assuming that unknown sample types and samples described as sediment samples, but reported in milligrams per liter or nanograms per liter, were whole-water samples. Thirty SVOCs were measured but not detected in stormwater (table 2, at end of chapter).

Total oil and grease and hydrocarbon concentrations in runoff ranged from less than 1 to 480 milligrams per liter (mg/L) (table 7). In suspended sediment, bottom sediment, and soils, oil and grease and hydrocarbon concentrations ranged from 8 to 507,000 micrograms per gram (μg/g). The highest concentrations in water and solid phases were associated with highways and industrial land use.

Studies that analyzed petroleum hydrocarbons and oil and grease for the classes of organic compounds that comprise these measurements were Zawlocki and others (1980), Eganhouse and Kaplan (1981b), Brown and others (1985), Fam and others (1987), Hoffman and Quinn (1987), Marsalek and Schroeter (1988), and Barrett and others (1993). Comparing results is difficult because fractions were separated using non-standard procedures (Hoffman and Quinn, 1987). Most extractable organic compounds in stormwater are aliphatic compounds and, except for polar compounds, about 80 percent or more are in the solid phase. The high solubilities of polar compounds, such as phenols, ketones, and alcohols, explain the large percentages measured in filtrates. Generally, aromatic compounds, phenolic compounds, PAHs, alcohols, and ketones comprise less than 1 percent to about 15 percent of the extractable organic compounds.

Concentrations of individual PAHs in runoff ranged from less than 1 to 120 μg/L. Highest concentrations were associated with industrial land use; few data exist for individual PAHs in highway runoff. In solid phases, concentrations of individual PAHs ranged from less than 1 to 200 μg/g. Of the few studies that reported total PAH concentrations, the maximum concentrations were 18,210 μg/L in whole water and 1,100 μg/g in solid phases. The maximum detection frequency of PAHs in both urban stormwater and snow was 90 percent. Most PAHs were detected in less than 25 percent of samples (Cole and others, 1984; Boom and Marselak, 1988; Marsalek and Schroeter, 1988; Lopes and others, 1995; von Guerard and Weiss, 1995; and Baldys and others, 1998).

Johnston and Harrison (1984) tentatively identified 2-chlorophenol and 2,4-dichlorophenol in bulk deposition adjacent to a highway. Baldys and others (1997) detected phenolic compounds at concentrations between 1 and 16 μg/L in 90 percent of highway runoff samples. Phenolic compounds were detected in 15 percent or less of urban stormwater samples from NURP (Cole and others, 1984), 55 percent for urban stormwater samples from Phoenix (Lopes and others, 1995), and were not detected in urban stormwater samples from Colorado Springs (von Guerard and Weiss, 1995) and Dallas-Fort Worth (Baldys and others, 1998). When detected, concentrations of phenolic compounds in urban stormwater generally were less than 20 µg/L.

Related Factors

Of the factors that affect SVOC concentrations in water, the most significant is suspended solids concentration. About 80 percent or more of SVOCs in stormwater are associated with the solid phase due to the hydrophobic character of these contaminants (Hunter and others, 1979; Zawlocki and others, 1980; Eganhouse and Kaplan, 1981a; Brown and others, 1985; Hoffman and Quinn, 1987; and Barrett and others, 1993).

Organic carbon content is the most significant factor affecting SVOCs in the solid phase (Butler and others, 1984; Ellis and others, 1985; and Witkowski and others, 1987). Mineral particles are less effective at sorbing nonionic SVOCs (Witkowski and others, 1987), thus grain size does not appear to be a significant factor affecting SVOC concentrations in sediments unless small grains have an organic coating (Witkowski and others, 1987; Gavens and others, 1982). In contrast, trace-element concentrations in sediments are strongly correlated with grain size because ionic elements adsorb to small particles that have charged surfaces (Horowitz and Elrick, 1987).

Sorption of SVOCs to solids is reflected in the high concentration of SVOCs in the initial runoff from a storm and correlation between concentrations of solids and SVOCs throughout a storm (Hunter and others, 1979; Stenstrom and others, 1984; Brown and others, 1985; Hoffman and others, 1984, 1985; and Hoffman and Quinn, 1987). The initial runoff, commonly called first flush, can have concentrations of suspended solids and sorbed SVOCs that are several factors higher than concentrations in composite samples. Suspended solids concentrations typically decrease during a storm due to flushing of particles that accumulated on the land surface (Novotny, 1995).

Land use also affects SVOC concentrations. Most studies found higher SVOC concentrations in runoff, snow, and bottom sediment from highways or industrial areas compared to residential and commercial areas (Hoffman and others, 1983, 1984; Hoffman and Quinn, 1987; Evans and others, 1990; Latimer and others, 1990; Bomboi and Hernandez, 1991; and Baldys and others, 1998). For example, PAH concentrations in snow near highways and a steel plant were similar, and PAHs were more frequently detected and concentrations were higher than NURP stormwater data (Boom and Marsalek, 1988). Gjessing and others (1984) found PAHs in snow up to 50 meters from a highway, the furthest of all contaminants they measured, and that PAHs were fractionated during atmospheric transport. Johnston and Harrison (1984) found PAHs in rain up to 70 meters from a highway and that concentrations decreased with distance. Butler and others (1984) found that PAH concentrations in bottom sediment decreased with distance from highways.

Storm characteristics, such as rainfall intensity and volume of runoff, are important factors affecting SVOC concentrations and loads in stormwater and sediments. As rainfall intensity increases, stream velocity and sediment-carrying capacity increase, resulting in increased SVOC concentrations in stormwater (Hoffman and Quinn, 1987; Barrett and others, 1993). In bottom sediment, Evans and others (1990) found that PAH concentrations weakly correlated with monthly rainfall and that concentrations increased about 4 to 30 days after a storm. Gupta (1981) observed higher concentrations of oil and grease in highway runoff and Prahl and others (1984) observed higher PAH concentrations in atmospheric particulates during winter compared to summer months. Schondorf and Herrmann (1987) found that freezing can concentrate organic compounds in water. During thaws, soluble organic compounds elute in the first and last parts of the melt and that about 90 percent of PAHs elute with the particulates during the last 20 percent of the melt. These observations indicate that concentrations and loads of SVOCs could vary seasonally.

Not all studies found a relation between storm characteristics and SVOC concentrations and loads. Stenstrom and others (1984) found no correlation between oil and grease concentrations and streamflow rates, total rainfall, time since beginning of storm, rainfall intensity, or antecedent dry days. Hunter and others (1979), Herrmann (1981), and Hoffman and others (1984) found that SVOC concentrations did not correlate with antecedent conditions. Zawlocki and others (1980) found no correlation between SVOC loads and rainfall, traffic volume, or runoff volume, although they noted that traffic volume during the storm had a greater effect than rainfall.

Conclusions have been mixed whether highway surface type significantly affects SVOC concentrations (Barrett and others, 1993). Gupta (1981) measured oil and grease concentrations from paved surfaces that were 20 times greater than from grass-covered surfaces, but concluded that land use was the most important factor. Strenstrom and others (1984) measured oil and grease concentrations 25 times greater from parking lots compared to residential areas. Wakeham and others (1980) concluded that PAHs in street dust were from asphalt. Zawlocki and others (1980) noted that higher suspended solids concentrations occurred in highway runoff at a site with a median barrier and side railings compared to another site without these features. Other variables, such as traffic volume and drainage, may be more important factors affecting SVOC concentrations than surface type (Stotz, 1987; Barrett and others, 1993).

Sources

Crankcase oil and vehicle emissions were consistently identified as the primary source of SVOCs in stormwater (Hunter and others, 1979; Zawlocki and others, 1980; Stenstrom and others, 1984; Brown and others, 1985; Hoffman and Quinn, 1987; Fam and others, 1987; Yamane and others, 1990; Latimer and others, 1990; and Bomboi and Hernandez, 1991). The significance of PAHs in automobile emissions is indicated by concentrations in sediment, snow, and rain that decrease with distance from highways (Butler and others, 1984; Johnston and Harrison, 1984; Gjessing and others, 1984; Harrison and Johnston, 1985; and Hewitt and Rashed, 1990).

Emission of most PAHs from automobiles is directly related to their concentration in gasoline (Westerhold and others, 1988). Naphthalene and its alkylated homologues comprise about 0.5 percent by weight of gasoline (Canadian Petroleum Institute, 1994); 13 other PAHs occur in gasoline at less than 0.01 to 54 mg/L (Westerhold and others, 1988). About 95 percent of PAHs in gasoline are decomposed during gasoline combustion. However, in gasoline with low PAH content, a large percentage of the PAHs emitted are formed during combustion, including 70 to 80 percent of cyclopenta[*cd*]pyrene and benzo[*b*&*k*]fluoranthene. Gasoline exhaust contains about 1 to 2 parts per million of phenol and o-cresol (Lucius and others, 1989) and is a possible source of phenolic compounds in stormwater.

Load Estimates

Estimates of SVOC loads and mass balances have been made on different scales to evaluate the relative importance of different sources and transport mechanisms. For example, Edwards (1983) estimated that forest and agricultural fires comprise 75 percent of the annual global release of PAHs. Hoffman and Quinn (1987) estimated 470,000 tons per year of petroleum hydrocarbons are released to waters of the United States and that up to 50 percent of this amount could be discharged in urban stormwater. Bjorseth and Ramdahl (1985) estimated that automobile emissions comprise one-third of the 6,000 tons of PAHs emitted each year in the United States. In contrast, Edwards (1983) estimated that automobiles, buses, and trucks comprise only 1.6 percent of benzo(a)pyrene emissions in the United States. The difference could be because Bjorseth and Ramdahl (1985) did not correct for catalytic converters, which were in about 50 percent of cars.

At a regional scale, Hoffman and others (1983, 1984) estimated hydrocarbon and PAH loads to Narraganset Bay, and Marsalek and Schroeter (1988) estimated SVOC loads to the Great Lakes. Estimates by Hewitt and Rashed (1990) and Stotz (1987) indicated that 30 percent or less of the PAHs emitted along highways is transported in runoff and the remainder is dispersed. Other estimates have been made at a local scale (Butler and others, 1984; Gjessing and others, 1984; Johnston and Harrison, 1984; Harrison and Johnston, 1985; Boom and Marsalek, 1988; and Hewitt and Rashed, 1990).

Few regression equations or loading factors have been developed for SVOCs compared to other constituents such as suspended solids and nutrients. Most equations and factors were based on few data and have little statistical power and large uncertainties, especially for regional and national application. Also, studies reported loading factors with inconsistent units so comparisons are difficult or with units that limit their application (table 3, at end of chapter). For example, Hoffman and Quinn (1987), Stotz (1987), and Barrett and others (1993) report loading factors that are independent of rainfall and, therefore, apply only to areas with climates similar to their study areas. Gupta (1981) estimated loads from highways using regression equations for runoff, pollutant build-up and wash-off, and loads of suspended solids. Correlations between other contaminants and suspended solids were used to convert loads of suspended solids into loads of the other contaminants. However, conversion equations were developed for individual sites and have only site-specific application. Marsalek and Schroeter (1988) used a procedure similar to Gupta (1981) to estimate loads to the Great Lakes.

Using study results to develop equations and factors of SVOC loads and concentrations at a national level, particularly from highways, is not possible because ancillary information was not documented, raw data were rarely reported, laboratory reporting levels varied, and few studies were related to SVOCs from highways. In addition, vehicles emit fewer SVOCs and VOCs today than when most studies were conducted (U.S. Environment Protection Agency, 1996a). The lower emissions are probably due to catalytic converters and to the use of cleaner-burning fuels. Gasoline-powered cars without catalytic converters emit 25 times more total aerosol PAHs in comparison to cars with catalytic converters, and diesel trucks emit 7 times more PAHs than cars with catalytic converters (Rogge and others, 1993). Therefore, the few loading factors that are available in the literature probably have limited application for estimating current loads of SVOCs and VOCs.

Comparison to Water-Quality and Sediment-Quality Standards and Guidelines

The potential for SVOCs to adversely affect water resources can be made by comparing SVOC concentrations in urban stormwater, snowmelt, and sediment to water-quality and sediment-quality standards and guidelines. Makepeace and others (1995) and Boom and Marsalek (1988) concluded that certain PAHs, phenol, *m*- and *p*-cresols, pentachlorophenol, and phthalates in stormwater were a concern for drinking water and aquatic life. Of the PAHs, total PAH, acenaphthene, fluoranthene, and benzo(a)pyrene in urban stormwater exceeded drinking-water standards of the United States, Canada, and World Health Organization (WHO). Concentrations of fluoranthene in stormwater exceeded acute and chronic aquatic regulation values of the United States.

For this report, SVOC concentrations in sediments were compared to recently developed sediment-quality guidelines (USEPA, 1996b) as another assessment of their potential adverse effects. No single set of sediment-quality guidelines is universally accepted in the United States. Therefore, the method of USEPA (1996b) was used to determine an upper threshold concentration for selected SVOCs above which there is a high probability of adverse effects on aquatic life. However, guidelines do not exist for all SVOCs detected in urban stormwater and upper threshold concentrations may be over- or under-protective depending on site-specific conditions.

Briefly, USEPA (1996b) used several sets of sediment-quality guidelines that were developed using different methods and have considerable inconsistencies among them. Rather than select one set of guidelines over another, USEPA (1996b) used all available sediment guidelines for a contaminant to classify sites into one of three tiers based on the probability of adverse effects on aquatic life. Tier 1 sites have a high probability of adverse effects on aquatic life, Tier 2 sites have an intermediate probability of adverse effects on aquatic life, and Tier 3 sites have no indication of adverse effects on aquatic life. USEPA (1996b) used lower threshold guidelines, above which adverse effects occasionally occur, to define the Tier 2/Tier 3 boundary, and upper threshold guidelines, above which effects may be frequent or severe, to define the Tier 1/Tier 2 boundary. For a site to be designated as Tier 1, the measured contaminant concentration at that site must exceed at least two of the upper threshold guidelines for that contaminant.

The guideline used in this comparison was the Tier 1/Tier 2 boundary concentration (table 4, at end of chapter). The upper threshold values used were (1) the effects range-median (Long and Morgan, 1991; Long and others, 1995); (2) the apparent effects threshold-high (Barrick and others, 1988); (3) the probable effect level used by the Florida Department of Environmental Protection (1994); (4) the probable effect level used by the Canadian Council of Ministers of the Environment (1995); (5) the USEPA sediment-quality criterion (USEPA, 1996b); and (6) the USEPA sediment-quality advisory level (USEPA, 1996b).

In the future, guidelines for PAHs are likely to change to PAH mixtures because PAHs typically co-occur in the environment. Testing and modeling is being conducted to determine the toxicity of PAH mixtures in sediment, which will form the basis for sediment-quality criteria for PAH mixtures (USEPA, 1998).

About 70 percent of surface-soil samples near a highway exceeded upper threshold concentrations of benz(a)anthracene, benzo(a)pyrene, chrysene, or pyrene, or of more than one of these PAHs, indicating adverse effects are probable (Butler and others, 1984). About 60 percent of bottom sediments from an urban stream exceeded upper threshold concentrations of fluoranthene, anthracene, pyrene, or benzo(a)pyrene, or of more than one of these PAHs (Ellis and others, 1985). Other studies had samples that exceeded upper threshold values, but the percentage of exceedence is unknown. For example, particulates in vehicle emissions and in the atmosphere exceeded upper threshold concentrations of benzo(a)pyrene (Prahl and others, 1984; Bjorseth and Ramdahl, 1985). Suspended sediments and street dust from highways and commercial areas exceeded upper threshold concentrations of fluoranthene, phenanthrene, pyrene, acenapthlyene, and benzo(a)pyrene (Hoffman and others, 1984 and 1985; Marsalek and Schroeter, 1988).

Volatile Organic Compounds

Few studies have been done on VOCs in highway runoff and urban stormwater. This summary of VOCs is mostly from the National Urban Runoff Program (NURP) and National Pollutant Discharge Elimination System (NPDES) studies.

Occurrence

Harrison and Johnston (1985) and Baldys and others (1997) were the only studies of VOCs in highway runoff. Harrison and Johnston (1985) sampled 2-week composites of atmospheric deposition at three sites near a highway in England. A total of 48 compounds were identified and quantified on a relative basis. Toluene and C_2-alkylbenzene were the major components in atmospheric deposition. No variation with distance from the highway was observed. Twenty-one highway runoff samples were collected at four sites between 1992–94 and analyzed for VOCs and other contaminants in the Dallas–Fort Worth area (Baldys and others, 1997). Chloromethane, toluene, xylenes, 1,2,4-trimethylbenzene, and 1,2,3-trichloropropane were detected in about 5 to 28 percent of samples at concentrations between 0.2 and 4.0 µg/L.

Most of the data on VOCs were collected during the NURP and NPDES studies. Together, these studies provide information on the occurrence of VOCs in most regions of the United States. For the NURP, the most frequently detected VOCs were dichloromethane, naphthalene, and chloroform, detected in 10 to 12 percent of all samples (Cole and others, 1984). In contrast, the most frequently detected VOCs for NPDES studies were toluene, xylenes, chloroform, and trimethylbenzene, detected in 12 to 23 percent of all samples (table 5, at end of chapter) (Delzer and others, 1996). A lower MRL for the NPDES studies could account for the greater frequencies of detection. Comparing VOC detections among regions of the United States may be possible using the NURP and NPDES data, but would be difficult because of the different reporting limits. Most detected concentrations of VOCs in urban stormwater for the NURP and NPDES studies were less than 10 µg/L and ranged from 0.2 to 43 µg/L.

The prevalence of gasoline-related compounds in NPDES data compared to NURP data probably is because stormwater was sampled closer to its source at NPDES monitoring sites and because the NURP did not measure xylenes, trimethylbenzenes, methyl *tert*-butyl ether (MTBE). MTBE and other ether oxygenates are added to gasoline to reduce vehicle emissions and enhance octane ratings. MTBE usage as an octane enhancer started about 1979. The use of MTBE to produce cleaner burning gasoline increased considerably during the late 1980’s. In 1996, 17.6 billion pounds of MTBE were produced, making it the VOC with the third highest production (Chemical and Engineering News, April 8, 1996). MTBE’s widespread use, high solubility, and resistance to degradation (Squillace and others, 1997) could account for its frequent occurrence in urban stormwater (Delzer and others, 1996) and in shallow urban ground water (Squillace and others, 1996).

Related Factors

Land use could be the most significant factor affecting the occurrence of VOCs. Lopes and Bender (1998) found that concentrations of gasoline-related and chlorinated VOCs were significantly higher in industrial areas as compared to commercial and residential areas and that MTBE was detected more frequently in commercial areas. Most VOCs have industrial applications (Pankow and Cherry, 1996), which probably is why concentrations were higher in industrial areas. The frequent detection of MTBE in commercial areas could be from spills at gas stations, which typically are located in commercial areas. Line and others (1997) infrequently detected VOCs in first-flush samples from industrial sites in North Carolina; sampling methods and high MRLs could account for the few detections.

Temperature is a significant factor affecting the occurrence of VOCs. A study by von Guerard and Weiss (1995) observed that more detections of VOCs occurred during snowmelt than during storm runoff. For all NPDES data, MTBE, benzene, xylenes, and 1,2,4-trimethylbenzene were detected more frequently during winter than summer (Delzer and others, 1996; Lopes and Bender, 1998). This higher detection of VOCs could be caused by the increased partitioning of VOCs from air into precipitation or slower volatilization from stormwater during cold months.

Sources

Lopes and Bender (1998) concluded that urban land surfaces are the primary nonpoint source of VOCs in stormwater. Most VOC concentrations in NPDES samples were higher than those in equilibrium with concentrations measured in urban air, indicating the atmosphere was not the source. VOCs associated with certain products, such as gasoline, frequently occurred together, and concentrations were significantly correlated and different among urban land uses. Model results indicated that VOC concentrations near the reporting limits evolved by volatilization. The primary source of VOCs probably was spills and VOCs sorbed to organic particulates and impervious surfaces, although partitioning between precipitation and VOCs in the atmosphere could be a source for MTBE.

The seasonal detection of some VOCs suggests that the atmosphere could be a nonpoint source. Measurements by Kawamura and Kaplan (1983), Pankow and others (1984), Harrison and Johnston (1985), Ligocki and others (1985), and Adachi and Kobayashi (1994) support the hypothesis that the atmosphere near highways and urban areas is a source of VOCs, although concentrations in precipitation were less than or equal to 0.2 µg/L. Concentrations of MTBE in precipitation estimated from concentrations in air range from less than 1 to about 4 µg/L (Squillace and others, 1996). These estimated concentrations of MTBE are why Squillace and others (1996) hypothesized precipitation could be a major source of MTBE detected in shallow urban ground water. Pankow and others (1997) demonstrated that MTBE and other VOCs in the atmosphere can be transported in recharge into sandy aquifers.

Comparison to Water-Quality Standards

From the NURP data, Makepeace and others (1995) concluded that tetrachloroethene, dichloromethane, and benzene could be a concern if stormwater entered drinking-water supplies. For the NPDES data, Delzer and others (1996) found that concentrations of MTBE in urban stormwater were less than the lower limit of the USEPA draft lifetime health advisory of 20 µg/L. Other VOCs detected in NPDES samples were compared to drinking-water standards (USEPA, 1996c) in table 6 (at end of chapter) because VOCs have low aquatic toxicities (Rowe and others, 1997) and primarily are a threat to drinking-water supplies. Less than 0.5 percent of NPDES samples exceeded drinking-water standards of dichloromethane and tetrachloroethene, similar to the NURP study (Makepeace and others, 1995).

INFORMATION NEEDS

This review has shown that highways can be major sources of SVOCs detected in water and sediment. However, there is insufficient information to determine if highways are sources of VOCs or to estimate loads and concentrations of SVOCs and VOCs from highways. Nationally consistent data are needed to (1) characterize the regional occurrence and concentrations of SVOCs and VOCs in highway runoff, (2) determine which are the most important factors affecting runoff quality, (3) estimate contaminant loads and concentrations on regional and national scales, and (4) identify water resources that potentially are affected.

A strategy is needed so that the distribution of information adequately represents factors affecting highway runoff in the United States. This strategy should define regions that have different values of factors that are expected to significantly correlate with water and sediment quality. For example, streams in drainage basins with residential and commercial land use are being monitored in regions with significantly different climate (Lopes and Price, 1997) because urban stormwater quality is significantly correlated with mean annual precipitation (Driver and Tasker, 1990). Other factors, such as highway-surface type, drainage, and traffic load, could be incorporated into this plan to develop a similar strategy for highways.

Information that is needed includes chemical data on SVOCs and VOCs in runoff, precipitation, and sediment to characterize their occurrence and ranges in concentrations. PAHs, oil and grease, and petroleum hydrocarbons are the primary classes of SVOCs associated with highway runoff. However, phenolic compounds and VOCs are in vehicle exhaust and could also be in highway runoff, precipitation, and sediment along highways. Parameters that could be related to chemical concentration, such as pH, dissolved oxygen, and total organic carbon, should also be measured. These data should be collected using appropriate procedures and materials and documented in a QA/QC plan.

Factors that are significantly related to water quality need to be characterized to estimate contaminant loads and concentrations from unmonitored sites and to identify potentially affected water resources. Factors that clearly affect concentrations and loads of SVOCs in highway runoff include suspended solids and organic carbon concentrations, total rainfall, rainfall intensity, traffic loads, and how runoff is drained. It is unclear if the type of surface has a significant effect, how much temperature affects concentrations and loads of SVOCs, and if surrounding land use has an effect. These and other factors may affect VOCs in highway runoff and precipitation. Relations between water quality and significant factors can be characterized by statistical analysis of ancillary data associated with monitoring sites and storms. From these relations, techniques similar to those of Driver and Tasker (1990) can be developed to estimate constituent loads and concentrations in highway runoff throughout the United States.

Geographic information on factors included in the estimation techniques can be used to obtain a national distribution of estimated contaminant loads and concentrations. These estimates and geographic information on water resources, including ground water, could then be used to determine which water resources could be adversely affected by highways. Ground water that is shallow and is used or has the potential of being used for drinking water could be affected by water-soluble compounds like MTBE.

Deterministic studies and modeling are also needed to understand the physical and chemical processes controlling highway-runoff quality, contaminant transport and fate, and impacts on biological and drinking-water resources. For example, Hewitt and Rashed (1990) and Stotz (1987) found that 70 percent of PAHs from highways are dispersed and 30 percent are transported in runoff. The majority of PAHs could be transported through the atmosphere into water-supply reservoirs. Modeling could help determine the transport and fate of dispersed PAHs and potentially affected waters.

SUMMARY

This review evaluated the quality and geographic distribution of existing data on SVOCs and VOCs, summarized significant findings, compared concentrations in highway runoff and urban stormwater with current (1998) water-quality criteria, and identified areas where additional information is needed. A total of 44 articles and reports were reviewed. Only 17 studies were related to highways, and 5 of these are review papers. Most of the data were collected during the late 1970’s to mid-1980’s. SVOCs in urban stormwater and sediments was the subjects of most studies.

Only 10 percent of studies described where in the stream cross section water samples were collected. This was the largest deficiency in documenting the sampling protocol. About 80 percent of SVOCs in runoff are in the suspended solids. Because suspended solids can vary significantly in the stream cross section even in narrow channels, the representativeness of discrete point samples and interpretations based on those data, especially load estimates, are questionable without information regarding sample location, how samplers were used, or how well the streamflow was mixed.

Only 30 percent of studies documented the MRL or MDL of the analytical method and only 15 percent of studies used field quality-control samples. The lack of MRL and MDL documentation hinders the ability to compare stormwater quality from different parts of the country. Evaluating the quality of environmental data, especially low concentrations, is difficult because few studies collected QC data and documented that samplers were cleaned.

PAHs, petroleum hydrocarbons, and oil and grease are the major SVOCs in urban stormwater and highway runoff. Suspended solids concentrations is the most significant factor affecting SVOCs in water. In sediment, the most significant factors affecting SVOC concentrations are organic carbon content and distance from sources, such as highways and power plants. Rainfall intensity, storm volume, and land use also are important factors affecting concentrations and loads of SVOCs. The highest SVOC concentrations in runoff, snow, and bottom sediment were measured from highways and industrial areas. Crankcase oil and vehicle emissions are the primary sources of SVOCs. The few loading factors and regression equations that were developed in the 1970’s and 1980’s are inadequate to estimate current (1998) loads of SVOCs because they use inconsistent units, some are independent of rainfall and have limited application, and they are based on few data. Also, more cars have catalytic converters and fuels are cleaner than when loading factors and regression equations were developed. PAHs, phenolic compounds, and phthalates in runoff exceeded drinking-water and aquatic-life standards. PAHs exceeded upper threshold concentrations in sediments near highways, indicating adverse effects on receiving streams.

VOCs were detected in precipitation adjacent to a highway in England, and chloromethane, toluene, xylenes, 1,2,4-trimethylbenzene, and 1,2,3-trichloropropane were detected in runoff from a highway in Texas. VOCs were detected in as many as 23 percent of the urban stormwater samples; gasoline-related compounds were the most frequently detected VOCs. Land use could be the most significant factor affecting the occurrence of VOCs. The highest concentrations of VOCs were found in industrial areas, suggesting urban land surfaces are the primary nonpoint source of most VOCs. Temperature is another important factor affecting the occurrence of VOCs. MTBE, benzene, xylenes, and 1,2,4-trimethylbenzene were detected more frequently during winter than summer. The seasonal detection could be due to the increased partitioning of VOCs in air into water at cold temperatures, suggesting that the atmosphere could be a nonpoint source of some VOCs. Tetrachloroethene, dichloromethane, and benzene were the only VOCs in stormwater that exceeded drinking-water standards.

Information deficiencies identified during the review included a need to determine if highways are a source of phenolic compounds and VOCs and if the occurrence and concentrations of SVOCs and VOCs vary regionally. A better understanding of the factors that affect SVOCs and VOCs is needed to estimate contaminant loads and concentrations at unmonitored sites and to identify potentially affected water resources. Deterministic studies and modeling also are needed to understand the physical and chemical processes controlling highway-runoff quality and contaminant transport and fate.

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Tables 1–7

Table 1. Documented quality criteria of data on semivolatile and volatile organic compounds in urban stormwater and highway runoff

[°C, degrees Celsius; cm, centimeters; m, meters; µg/L, micrograms per liter; mg/L, milligrams per liter; ng/L, nanograms per liter; ng/g, nanograms per gram; ppb, parts per billion; NA, not applicable; ND, not described; SS, stainless steel; O+G, oil and grease; GC/FID, gas chromatography/flame-ionization detector; GC-MS, gas chromatography-mass spectrometry; HCl, hydrochloric acid; HPLC, high performance liquid chromatography; IR, infrared spectrometry; EWI, equal-width increment; MRL, minimum reporting limit; NaCl, sodium chloride; NPDES, National Pollutant Discharge Elimination System; NURP, Nationwide Urban Runoff Program; %, percent; ~, approximate; ---, no comment]

Reference	Where	Years data were collected	Water sampling protocol					Sediment and soil sampling protocol				Comment
			Sampler type	Material	Manual or automatic	Discrete or composite	Where in stream	Sampler type	Material	Discrete or composite	Depth (cm)	
Baldys and others, 1997	Dallas–Ft. Worth, Texas	1992–94	auto-sampler + bottles	Teflon, steel, glass	both	both	ND	NA	NA	NA	NA	Flow-weighted composites; not known if splitter used. Sampled where storm drain well mixed.
Baldys and others, 1998	Dallas–Ft. Worth, Texas	1992–93	auto-sampler + bottles	Teflon, steel, glass	both	both	ND	NA	NA	NA	NA	Flow-weighted composites; not known if splitter used. Sampled where storm drain well mixed.
Barrett and others, 1993	Review paper	1976–92	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Bjorseth and Ramdahl, 1985	Review paper	1775–84	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Bomboi and others, 1990	Madrid, Spain	1985–86	tray	metal	manual	discrete	assume all flow	NA	NA	NA	NA	Simulated rain for runoff samples; extracted water, solids separately.
Bomboi and Hernandez, 1991	Madrid, Spain	ND	tray	metal	manual	discrete	assume all flow	NA	NA	NA	NA	Same data as Bomboi and others, 1990.
Boom and Marsalek, 1988	Ontario, Canada	1986–87	corer for snow	SS	manual	discrete	NA	NA	NA	NA	NA	NA
Brown and others, 1985	Tampa	1982–83	ND	ND	ND	both	ND	ponar	ND	composite	0–5	Discrete samples of first flush, composite-type unknown; whole water and suspended solids analyzed.
Butler and others, 1984	England	ND	NA	NA	NA	NA	NA	ND	ND	discrete	0–4, 4–8	Samples sieved to 18 mesh.
Cole and others, 1984	15 NURP cities	1979–82	ND	ND	ND	both	ND	NA	NA	NA	NA	Compilation of coordinated studies; low-weighted composites.
Delzer and others, 1996	16 NPDES cities	1991–95	vials	glass	manual	discrete	ND	NA	NA	NA	NA	Compilation of independent studies; sampling procedures varied.
Edwards, 1983	Review paper	1956–82	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Eganhouse and Kaplan, 1981a	Los Angeles, California	1978	ND	steel	manual	discrete	center, below surface	NA	NA	NA	NA	Whole and filtered water analyzed.
Eganhouse and Kaplan, 1981b	Los Angeles, California	1978	ND	steel	manual	discrete	center, below surface	NA	NA	NA	NA	Same data as Eganhouse and Kaplan, 1981a.
Ellis and others, 1985	London, England	ND	NA	NA	NA	NA	NA	grab sampler	SS	composite	surface	NA

Table 1. Documented quality criteria of data on semivolatile and volatile organic compounds in urban stormwater and highway runoff—*Continued*

Reference	Where	Years data were collected	Water sampling protocol					Sediment and soil sampling protocol				Comment
			Sampler type	Material	Manual or automatic	Discrete or composite	Where in stream	Sampler type	Material	Discrete or composite	Depth (cm)	
Evans and others, 1990	United Kingdom	1987–88	NA	NA	NA	NA	NA	jars	glass	discrete	0–10	Collected bottom sediment monthly for 1 year.
Fam and others, 1987	San Francisco, California	ND	bottles + buckets	glass + metal	manual	discrete	ND	NA	NA	NA	NA	Particulates and filtrate analyzed.
Gavens and others, 1982	London, England	ND	ND	ND	ND	ND	ND	corer	SS	discrete	0–10, 290–300	Whole water analyzed; sediment samples sieved into several fractions.
Gjessing and others, 1984	Norway	1981–82	cans	aluminum	manual	discrete	ND	gravity corer	acrylic	discrete	0–2	NA
Gupta, 1981	Milwaukee, Harrisburg, Nashville, Denver	1975–78	ISCO	ND	both	both	ND	NA	NA	NA	NA	Oil and grease sampled manually; whole water analyzed. Flow-weighted composites.
Harrison and Johnston, 1985	England	1981–83	funnel	plastic, glass	passive auto-sampler	composite	NA	NA	NA	NA	NA	Includes data from Johnston and Harrison, 1984.
Herrmann, 1981	Germany	1979	auto-sampler	ND	auto	discrete	ND	pan	ND	NA	surface	Sampled stream, snow, street dust, bed load, rain. Mostly whole water analyzed.
Hewitt and Rashed, 1990	England	ND	funnel, auto-samplers	ND	passive auto-sampler	discrete	NA	trowel	ND	discrete	0–10, 10–20, 20–30	Bulk deposition sampled; autosampler for SWRO.
Hoffman and others, 1983	Narraganset Bay	1979–81	bucket	metal	manual	discrete	ND	NA	NA	NA	NA	Samples collected at about 30-minute intervals; suspended solids and filtrate analyzed.
Hoffman and others, 1984	Narraganset Bay	1979–81	bucket	metal	manual	discrete	ND	NA	NA	NA	NA	Same data as Hoffman and others, 1983.
Hoffman and others, 1985	Rhode Island	1979–81	bucket	metal	manual	discrete	ND	NA	NA	NA	NA	Samples collected at about 30-minute intervals; suspended solids and filtrate analyzed.
Hoffman and Quinn, 1987	Review paper	1969–87	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Hunter and others, 1979	Philadelphia, Pennsylvania	1974	ND	ND	manual	both	ND	NA	NA	NA	NA	Flow-weighed composites; centrifuged water and particulates analyzed separately.
Johnston and Harrison, 1984	England	1982–83	funnel	plastic	passive auto-sampler	composite	NA	NA	NA	NA		Bulk deposition sampled biweekly.
Latimer and others, 1990	Warwick, Rhode Island	1979–81	bucket	metal	manual	discrete	ND	trowel	SS	discrete	ND	Suspended solids and filtrate analyzed. Soil, vegetation, street dust sampled.
Line and others, 1997	North Carolina	1993–94	auto-sampler	ND	auto-sampler	discrete	ND	NA	NA	NA	NA	Only first-flush samples. Samples iced after collection and preserved at lab.

Table 1. Documented quality criteria of data on semivolatile and volatile organic compounds in urban stormwater and highway runoff—*Continued*

Reference	Where	Years data were collected	Water sampling protocol					Sediment and soil sampling protocol				Comment
			Sampler type	Material	Manual or automatic	Discrete or composite	Where in stream	Sampler type	Material	Discrete or composite	Depth (cm)	
Lopes and Bender, 1998	16 NPDES cities	1991–95	vials	glass	manual	discrete	ND	NA	NA	NA	NA	Includes data from Delzer and others, 1996.
Lopes and others, 1995	Phoenix, Arizona	1991–93	auto-samplers	Teflon, steel, glass	both	both	ND, EWI for stream	NA	NA	NA	NA	Discrete manual samples for VOCs, phenols, O+G. Flow-weighted composites from churn splitter.
Makepeace and others, 1995	Review paper	1970–94	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Marsalek and Schroeter, 1988	Canada, Great Lakes region	1979–83	auto-samplers	metal, glass	pumping and passive auto-samplers	flow-weight composite	bank, ND	filtered water	ND	ND	ND	Filtered at 5 micron due to high solids. Also collected street sediments.
Prahl and others, 1984	Seattle, Washington and Columbia River	1979–80	pump	glass	manual	discrete	middle, 1–2 m deep	filtered water	NA	NA	NA	Only analyzed suspended sediment filtered from water using nitrogen. Also sampled air.
Schondorm and Herrmann, 1987	Germany	1986	snow lysimeter	Aluminum foil covered plywood	manual	discrete	NA	NA	NA	NA	NA	NA
Stenstrom and others, 1984	Richmond, California	1980–81	bottles	glass	manual	discrete	ND	NA	NA	NA	NA	Sampled at turbulent locations for uniform sample.
Stotz, 1987	Germany	1978–81	ND	ND	ND	composite	ND	NA	NA	NA	NA	Whole water and centrifuged samples analyzed; unknown composite type.
von Guerard and Weiss, 1995	Colorado Springs, Colorado	1992	auto-samplers	Teflon, glass	both	depth integrated manual	ND, flow turbulent, mixed	NA	NA	NA	NA	Discrete manual samples for VOCs, phenols, O+G. Flow-weighted composites from churn and cone splitter.
Wakeham and others, 1980	Switzerland, Seattle, Washington	1976–77	NA	NA	NA	NA	NA	gravity, piston corers	ND	NA	max 6.4 m	Gravity cores for shallow (<1 m) cores, piston for deep cores.
Wiland and Malina, 1976	Austin, Texas	1976	bottle	glass	manual	discrete	ND	NA	NA	NA	NA	Simulated rainfall for runoff
Yamane and others, 1990	Tokyo, Japan	ND	bottle	glass	manual	discrete	ND	ND	ND	ND	ND	Whole water analyzed; sediment, street dust and highway dust analyzed.
Zawlocki and others, 1980	Seattle, Washington	1979–80	tank, drum	poly-ethylene	automatic	composite	used flow-splitter	NA	NA	NA	NA	Samples taken from well-mixed tank, drum. Flume, flow splitter made of fiberglass, contamination assumed negligible. Filtrate, particulates analyzed.

Table 1. Documented quality criteria of data on semivolatile and volatile organic compounds in stormwater and highway runoff—*Continued*

Reference	Laboratory methods			Quality assurance				Quality control		
	Instrument	**MRL**	**Comment**	**Cleaned sampler?**	**Container**	**Preservation**	**Comment**	**Field QC**	**Lab QC**	**Comment**
Baldys and others, 1997	ND	mostly 0.2–10 mg/L	USGS analytical methods	ND	ND	ND		equipment, trip blanks, matrix spikes, replicates	ND	QC data provided
Baldys and others, 1998	ND	mostly 0.2–10 µg/L	USGS analytical methods	ND	ND	ND	---	blanks, replicates, spikes	reference	No QC results discussed
Barrett and others, 1993	NA	NA	---	NA	NA	NA	---	NA	NA	---
Bjorseth and Ramdahl, 1985	NA	NA	---	NA	NA	NA	---	NA	NA	---
Bomboi and others, 1990	GC-FID, GC-MS	ND	---	ND	ND	ND	---	ND	ND	---
Bomboi and Hernandez, 1991	GC-FID, GC-MS	ND	---	ND	ND	ND	---	ND	ND	---
Boom and Marsalek, 1988	GC-FID	0.05 µg/L	---	ND	stainless steel	ND	Slowly melted snow	ND	ND	---
Brown and others, 1985	GC-FID	ND	1 µg/L	ND	glass	chilled 4˚C	Teflon-lined lids	ND	all analyses duplicated, blanks, recovery samples	Teflon-lined lids
Butler and others, 1984	GC-fluorescence	ND	---	ND	ND	ND	---	ND	ND	---
Cole and others, 1984	ND	varied	Many labs used	ND	ND	ND	Guidelines for consistent sample collection, but details not given	blanks, replicates, spikes	performance evaluation samples, surrogates	Summarized QC evaluation
Delzer and others, 1996	GC-MS	0.2–1 µg/L	USGS analytical methods	ND	glass	ND	---	ND	ND	---
Edwards, 1983	NA	NA	---	NA	NA	NA	---	NA	NA	---
Eganhouse and Kaplan, 1981a	gravimetric	ND	---	ND	glass	ND	Samples shaken and split into 2 bottles	ND	ND	---
Eganhouse and Kaplan, 1981b	gravimetric	ND	---	ND	glass	ND	Samples shaken and split into 2 bottles	ND	ND	---
Ellis and others, 1985	GC-FID, GC-MS	ND	---	yes	ND	ND	---	ND	ND	---
Evans and others, 1990	HPLC, GS-MS	ND	Recovery 83–131%	yes	glass	chilled	Covered w/ foil, capped w/metal lid	ND	blanks, recovery samples	Blank, recovery corrections made
Fam and others, 1987	GC-FID	ND	Standard methods	ND	glass	acidify, chill	---	ND	ND	---

Table 1. Documented quality criteria of data on semivolatile and volatile organic compounds in stormwater and highway runoff—*Continued*

Reference	Laboratory methods			Quality assurance				Quality control		
	Instrument	MRL	Comment	Cleaned sampler?	Container	Preser-vation	Comment	Field QC	Lab QC	Comment
Gavens and others, 1982	GC-FID, GC-MS	ND	---	yes	ND	sediment frozen; water ND	---	ND	ND	Suggest naphthalene lost during workup
Gjessing and others, 1984	GC-ND, reference	ND	---	ND	ND	ND	---	ND	ND	---
Gupta, 1981	Standard methods	ND	---	ND	ND	chilled	Overnight shipping	ND	ND	---
Harrison and Johnston, 1985	HPLC, GC-MS	ND	---	yes	glass	ND	Plastic samplers, 2 weeks w/o chilling	ND	blanks	Blank corrections made
Herrmann, 1981	HPLC, fluorescence	ND	ND	ND	ND	ND	Snow, street dust frozen in polyethylene bags	ND	ND	---
Hewitt and Rashed, 1990	HPLC	ND	---	ND	ND	ND	---	ND	ND	---
Hoffman and others, 1983	GC-FID, GC-MS	ND	Precision ~15%	ND	glass	ND	Teflon-lined lids	ND	blanks	No blank corrections needed
Hoffman and others, 1984	GC-FID, GC-MS	ND	Precision mostly 11–25%	ND	glass	ND	Teflon-lined lids	ND	blanks	---
Hoffman and others, 1985	GC-FID, GC-MS	ND	Precision mostly 11–25%	ND	glass	ND	Teflon-lined lids	ND	blanks	---
Hoffman and Quinn, 1987	NA	NA	---	NA	NA	NA	---	NA	NA	---
Hunter and others, 1979	GC-FID	ND	85–95% recovery	ND	glass	ND	---	ND	ND	---
Johnston and Harrison, 1984	HPLC	ND		yes	glass	ND	Plastic samplers, 2 weeks w/o chilling	ND	ND	43–87% recovery, corrections made
Latimer and others, 1990	GC-FID	ND	Relative deviation <20%	yes	glass	none	---	ND	blanks	Blank data given
Line and others, 1997	Standard methods	5 to 100 µg/L	---	yes	ND	chilled	Sometimes hours before samples were retrieved, chilled; autosampler for VOCs	Automatic sampler blanks	lab-split duplicates, spikes for about 10% of samples	---

Table 1. Documented quality criteria of data on semivolatile and volatile organic compounds in stormwater and highway runoff—*Continued*

Reference	Laboratory methods			Quality assurance				Quality control		
	Instrument	MRL	Comment	Cleaned sampler?	Container	Preser-vation	Comment	Field QC	Lab QC	Comment
Lopes and Bender, 1998	GC-MS	0.2–1 µg/L	USGS analytical methods	ND	glass	ND	---	ND	ND	---
Lopes and others, 1995	ND	mostly 0.2–10 µg/L	USGS analytical methods	yes	ND	chilled	Autosampler checked with concurrent manual samples	Automatic sampler and trip blanks, matrix spikes, replicates	ND	Some compounds may degrade; blanks clean
Makepeace and others, 1995	NA	NA	---	NA	NA	NA	---	NA	NA	---
Marsalek and Schroeter, 1988	GC/FID, ECD	water MDL 0.001–0.05 ppb. sediment 5–50 ppb	Recovery 60–110%, precision 12–83%	ND	reference	reference	---	ND	ND, but done	---
Prahl and others, 1984	GC-FID air samples, HPLC sediment samples	ND	---	yes	glass	air samples refrigerated, sediment frozen	Nitrogen used for filtering	ND	ND	GC, HPLC ± 15%
Schondorm and Herrmann, 1987	HPLC, fluorescense	MDL 0.03–0.15ng/L	85-90% recovery	ND	ND	ND	---	ND	ND	---
Stenstrom and others, 1984	IR, GC-FID	ND	---	yes	glass	ND	Sampled turbulent area for well mixed sample	ND	ND	---
Stotz, 1987	reference	ND	---	ND	ND	ND	---	ND	ND	---
von Guerard and Weiss, 1995	ND	mostly 0.2–10 µg/L	USGS analytical methods	yes	ND	chilled	Manual samples from turbulent, well-mixed flow	blanks, spikes	ND	Low spike recovery, blanks clean
Wakeham and others, 1980	GC-FID	1-2 ng/g	Reproduci-bility ± 25%	ND	ND	frozen or chilled at 4˚C	Preservation for samples from 2 lakes not described	ND	blanks	Data blank and recovery corrected
Wiland and Malina, 1976	IR	ND	---	ND	glass	chilled at 4˚C	Plastic sheet under truck used for simulated rain	ND	ND	---
Yamane and others, 1990	GC-FID, HPLC	ND	---	ND	glass	NaCl, HCl pH<2.0	Preserved on site	ND	ND	---
Zawlocki and others, 1980	GC/MS, Standard Methods	100 µg/L for trace organics	Trace organics precision ± 50%, results summed into compound class	ND	glass	chilled	Samples well mixed, but don't know if they are of entire storm	ND	lab-split replicates, system blanks, recoveries	Particulate replicates ± 5%, total organic extracts within 20%

Table 2. Semivolatile and volatile organic compounds not detected in stormwater

[IUPAC, International Union of Pure and Applied Chemistry; NURP, Nationwide Urban Runoff Program; NR, not reported]

IUPAC compound name (common name)	Minimum reporting limit (range), in micrograms per liter	Location	Reference
Semivolatile organic compounds			
Benzidine	40	Maricopa County, AZ	Lopes and others, 1995
	40	Colorado Springs, CO	von Guerard and Weiss, 1995
	40	Dallas/Fort Worth, TX	Baldys and others, 1998
4-Bromophenyl phenyl ether	5	Maricopa County, AZ	Lopes and others, 1995
	5	Colorado Springs, CO	von Guerard and Weiss, 1995
	5	Dallas/Fort Worth, TX	Baldys and others, 1998
	NR	Summary–NURP	Cole and others, 1984
0-Chlorobenzene	5	Colorado Springs, CO	von Guerard and Weiss, 1995
4-Chloro-3-methylphenol	30	Dallas/Fort Worth, TX	Baldys and others, 1998
bis(2-Chloroethoxy)methane	5	Maricopa County, AZ	Lopes and others, 1995
	5	Colorado Springs, CO	von Guerard and Weiss, 1995
	5	Dallas/Fort Worth, TX	Baldys and others, 1998
	NR	Summary–NURP	Cole and others, 1984
bis(2-Chloroethyl)ether	5	Maricopa County, AZ	Lopes and others, 1995
	5	Colorado Springs, CO	von Guerard and Weiss, 1995
	5	Dallas/Fort Worth, TX	Baldys and others, 1998
	NR	Summary–NURP	Cole and others, 1984
bis(2-Chloroisopropyl)ether	5	Maricopa County, AZ	Lopes and others, 1995
	5	Colorado Springs, CO	von Guerard and Weiss, 1995
	5	Dallas/Fort Worth, TX	Baldys and others, 1998
	NR	Summary–NURP	Cole and others, 1984
4-Chlorophenyl phenyl ether	5	Maricopa County, AZ	Lopes and others, 1995
	5	Colorado Springs, CO	von Guerard and Weiss, 1995
	5	Dallas/Fort Worth, TX	Baldys and others, 1998
	NR	Summary–NURP	Cole and others, 1984
1,2,5,6-Dibenzanthracene	10	Colorado Springs, CO	von Guerard and Weiss, 1995
3, 3'-Dichlorobenzidine	20	Maricopa County, AZ	Lopes and others, 1995
	20	Colorado Springs, CO	von Guerard and Weiss, 1995
	20	Dallas/Fort Worth, TX	Baldys and others, 1998
2,4-Dichlorophenol	5	Maricopa County, AZ	Lopes and others, 1995
	5	Colorado Springs, CO	von Guerard and Weiss, 1995
	5	Dallas/Fort Worth, TX	Baldys and others, 1998
	NR	Summary–NURP	Cole and others, 1984
Dimethylphthalate	5	Maricopa County, AZ	Lopes and others, 1995
	5	Colorado Springs, CO	von Guerard and Weiss, 1995
	5	Dallas/Fort Worth, TX	Baldys and others, 1998
	NR	Summary–NURP	Cole and others, 1984
4,6-Dinitro-2-methylphenol	30	Dallas/Fort Worth, TX	Baldys and others, 1998
4,6-Dinitro-ortho-cresol	30	Colorado Springs, CO	von Guerard and Weiss, 1995
	NR	Summary–NURP	Cole and others, 1984
2,4-Dinitrophenol	20	Maricopa County, AZ	Lopes and others, 1995
	20	Colorado Springs, CO	von Guerard and Weiss, 1995
	20	Dallas/Fort Worth, TX	Baldys and others, 1998
	NR	Summary–NURP	Cole and others, 1984
2,4-Dinitrotoluene	5	Maricopa County, AZ	Lopes and others, 1995
	5	Colorado Springs, CO	von Guerard and Weiss, 1995
	5	Dallas/Fort Worth, TX	Baldys and others, 1998
2,6-Dinitrotoluene	5	Maricopa County, AZ	Lopes and others, 1995
	5	Colorado Springs, CO	von Guerard and Weiss, 1995
	5	Dallas/Fort Worth, TX	Baldys and others, 1998
1,2-Diphenyl hydrazine	5	Colorado Springs, CO	von Guerard and Weiss, 1995
	5	Dallas/Fort Worth, TX	Baldys and others, 1998

Table 2. Semivolatile and volatile organic compounds not detected in stormwater—*Continued*

IUPAC compound name (common name)	Minimum reporting limit (range), in micrograms per liter	Location	Reference
Semivolatile organic compounds—*Continued*			
Hexachlorobutadiene	5	Maricopa County, AZ	Lopes and others, 1995
	5	Colorado Springs, CO	von Guerard and Weiss, 1995
	0.2–10	Dallas/Fort Worth, TX	Baldys and others, 1998
Hexachlorocyclopentadiene	5	Maricopa County, AZ	Lopes and others, 1995
	5	Dallas/Fort Worth, TX	Baldys and others, 1998
Hexachloroethane	5	Maricopa County, AZ	Lopes and others, 1995
	5	Colorado Springs, CO	von Guerard and Weiss, 1995
	5	Dallas/Fort Worth, TX	Baldys and others, 1998
Isophorone	5	Maricopa County, AZ	Lopes and others, 1995
	5	Colorado Springs, CO	von Guerard and Weiss, 1995
	5	Dallas/Fort Worth, TX	Baldys and others, 1998
Nitrobenzene	5	Maricopa County, AZ	Lopes and others, 1995
	5	Colorado Springs, CO	von Guerard and Weiss, 1995
	5	Dallas/Fort Worth, TX	Baldys and others, 1998
2-Nitrophenol	5	Maricopa County, AZ	Lopes and others, 1995
	5	Colorado Springs, CO	von Guerard and Weiss, 1995
	5	Dallas/Fort Worth, TX	Baldys and others, 1998
	NR	Summary–NURP	Cole and others, 1984
n-nitrosodi-n-propylamine	5	Maricopa County, AZ	Lopes and others, 1995
	5	Colorado Springs, CO	von Guerard and Weiss, 1995
	5	Dallas/Fort Worth, TX	Baldys and others, 1998
n-nitrosodiphenylamine	5	Maricopa County, AZ	Lopes and others, 1995
	5	Colorado Springs, CO	von Guerard and Weiss, 1995
	5	Dallas/Fort Worth, TX	Baldys and others, 1998
n-nitrosodimethylamine	5	Maricopa County, AZ	Lopes and others, 1995
	5	Colorado Springs, CO	von Guerard and Weiss, 1995
	5	Dallas/Fort Worth, TX	Baldys and others, 1998
Parachlorometacresol	30	Colorado Springs, CO	von Guerard and Weiss, 1995
Phenol	3	Colorado Springs, CO	von Guerard and Weiss, 1995
	3	Dallas/Fort Worth, TX	Baldys and others, 1998
2,4,6-Trichlorophenol	20	Maricopa County, AZ	Lopes and others, 1995
	20	Colorado Springs, CO	von Guerard and Weiss, 1995
	20	Dallas/Fort Worth, TX	Baldys and others, 1998
	NR	Summary–NURP	Cole and others, 1984
Volatile organic compounds			
Bromobenzene	0.2	Colorado Springs, CO	von Guerard and Weiss, 1995
	0.2 - 10	Dallas/Fort Worth, TX	Baldys and others, 1998
Bromochloromethane	0.2	Maricopa County, AZ	Lopes and others, 1995
	0.2 - 10	Dallas/Fort Worth, TX	Baldys and others, 1998
Bromomethane	0.2	Maricopa County, AZ	Lopes and others, 1995
(Methyl bromide)	0.2	Colorado Springs, CO	von Guerard and Weiss, 1995
	0.2 - 10	Dallas/Fort Worth, TX	Baldys and others, 1998
Chloroethane	0.2	Maricopa County, AZ	Lopes and others, 1995
	0.2	Colorado Springs, CO	von Guerard and Weiss, 1995
	0.2 - 10	Dallas/Fort Worth, TX	Baldys and others, 1998
	NR	Summary–NURP	Cole and others, 1995
2-Chloroethyl vinyl ether	1.0	Maricopa County, AZ	Lopes and others, 1995
	1.0	Colorado Springs, CO	von Guerard and Weiss, 1995
	1.0 - 50	Dallas/Fort Worth, TX	Baldys and others, 1998
Chloromethane	0.2	Colorado Springs, CO	von Guerard and Weiss, 1995
1-Chloro-2-Methylbenzene	0.2	Maricopa County, AZ	Lopes and others, 1995
(0-Chlorotoluene)	0.2	Colorado Springs, CO	von Guerard and Weiss, 1995

Table 2. Semivolatile and volatile organic compounds not detected in stormwater—*Continued*

IUPAC compound name (common name)	Minimum reporting limit (range), in micrograms per liter	Location	Reference
Volatile organic compounds—*Continued*			
1,2-Dibromo-3-chloropropane	1.0	Maricopa County, AZ	Lopes and others, 1995
(Dibromochloropropane)	1.0	Colorado Springs, CO	von Guerard and Weiss, 1995
	1.0 - 10	Dallas/Fort Worth, TX	Baldys and others, 1998
1,2-Dibromoethane	0.2	Colorado Springs, CO	von Guerard and Weiss, 1995
	0.2 - 10	Dallas/Fort Worth, TX	Baldys and others, 1998
1,2-Dichlorobenzene	0.2	Colorado Springs, CO	von Guerard and Weiss, 1995
	0.2 - 10	Dallas/Fort Worth, TX	Baldys and others, 1998
	NR	Summary–NURP	Cole and others, 1995
1,3-Dichlorobenzene	0.2	Colorado Springs, CO	von Guerard and Weiss, 1995
	0.2 - 10	Dallas/Fort Worth, TX	Baldys and others, 1998
	NR	Summary–NURP	Cole and others, 1995
1,4-Dichlorobenzene	0.2	Colorado Springs, CO	von Guerard and Weiss, 1995
	0.2 - 10	Dallas/Fort Worth, TX	Baldys and others, 1998
	NR	Summary–NURP	Cole and others, 1995
Dichlorodifluoromethane	0.2	Maricopa County, AZ	Lopes and others, 1995
	0.2	Colorado Springs, CO	von Guerard and Weiss, 1995
	0.2 - 10	Dallas/Fort Worth, TX	Baldys and others, 1998
	NR	Summary–NURP	Cole and others, 1995
1,3-Dichloropropane	0.2	Maricopa County, AZ	Lopes and others, 1995
	0.2	Colorado Springs, CO	von Guerard and Weiss, 1995
	0.2 - 10	Dallas/Fort Worth, TX	Baldys and others, 1998
2,2-Dichloropropane	0.2	Maricopa County, AZ	Lopes and others, 1995
	0.2	Colorado Springs, CO	von Guerard and Weiss, 1995
	0.2 - 10	Dallas/Fort Worth, TX	Baldys and others, 1998
1,1-Dichloropropene	0.2	Maricopa County, AZ	Lopes and others, 1995
	0.2	Colorado Springs, CO	von Guerard and Weiss, 1995
	0.2 - 10	Dallas/Fort Worth, TX	Baldys and others, 1998
cis-1,3-Dichloropropene	0.2	Maricopa County, AZ	Lopes and others, 1995
	0.2	Colorado Springs, CO	von Guerard and Weiss, 1995
	0.2 - 10	Dallas/Fort Worth, TX	Baldys and others, 1998
trans-1,3-Dichloropropene	0.2	Maricopa County, AZ	Lopes and others, 1995
	0.2	Colorado Springs, CO	von Guerard and Weiss, 1995
	0.2 - 10	Dallas/Fort Worth, TX	Baldys and others, 1998
(1,1-Dimethylethyl)benzene	0.2	Maricopa County, AZ	Lopes and others, 1995
(tert-Butylbenzene)	0.2	Colorado Springs, CO	von Guerard and Weiss, 1995
	0.2 - 10	Dallas/Fort Worth, TX	Baldys and others, 1998
1,1,2,3,4,4-Hexachloro-1,3-butadiene	0.2	Colorado Springs, CO	von Guerard and Weiss, 1995
(hexachlorobutadiene)	0.2 - 10	Dallas/Fort Worth, TX	Baldys and others, 1998
	NR	Summary–NURP	Cole and others, 1995
(1-Methylpropyl)benzene	0.2	Maricopa County, AZ	Lopes and others, 1995
(sec-Butylbenzene)	0.2	Colorado Springs, CO	von Guerard and Weiss, 1995
	0.2 - 10	Dallas/Fort Worth, TX	Baldys and others, 1998
Parachlorotoluene	0.2	Colorado Springs, CO	von Guerard and Weiss, 1995
2-Propenal	20	Maricopa County, AZ	Lopes and others, 1995
(Acrolein)	20	Colorado Springs, CO	von Guerard and Weiss, 1995
	20 - 1000	Dallas/Fort Worth, TX	Baldys and others, 1998
2-Propenenitrile	20	Maricopa County, AZ	Lopes and others, 1995
(Acrylonitrile)	20	Colorado Springs, CO	von Guerard and Weiss, 1995
	20 - 1000	Dallas/Fort Worth, TX	Baldys and others, 1998
1,1,1,2-Tetrachloroethane	0.2	Maricopa County, AZ	Lopes and others, 1995
	0.2	Colorado Springs, CO	von Guerard and Weiss, 1995
	0.2 - 10	Dallas/Fort Worth, TX	Baldys and others, 1998

Table 2. Semivolatile and volatile organic compounds not detected in stormwater—*Continued*

IUPAC compound name (common name)	Minimum reporting limit (range), in micrograms per liter	Location	Reference
Volatile organic compounds—*Continued*			
1,2,3-Trichlorobenzene	0.2	Maricopa County, AZ	Lopes and others, 1995
	0.2	Colorado Springs, CO	von Guerard and Weiss, 1995
	0.2 - 10	Dallas/Fort Worth, TX	Baldys and others, 1998
1,2,4-Trichlorobenzene	0.2	Maricopa County, AZ	Lopes and others, 1995
	0.2	Colorado Springs, CO	von Guerard and Weiss, 1995
	0.2 - 10	Dallas/Fort Worth, TX	Baldys and others, 1998
	NR	Summary–NURP	Cole and others, 1995
1,2,3-Trichloropropane	0.2	Maricopa County, AZ	Lopes and others, 1995
	0.2	Colorado Springs, CO	von Guerard and Weiss, 1995
	0.2 - 10	Dallas/Fort Worth, TX	Baldys and others, 1998

Table 3. Loading factors for semivolatile organic compounds as a function of land use

[kg, kilogram; km^2, square kilometer; km, kilometer; yr, year; cm, centimeter; m^2, square meter; PAHs, polycyclic aromatic hydrocarbons; µg, microgram; m, meter; hwy, highway; E-5, 10 to the exponent -5; --, factors were not estimated]

Compound class	Residential	Commercial	Industrial	Highway	Bridges	Reference
Stormwater						
Petroleum hydrocarbons	180 (kg/km^2)/yr	580 (kg/km^2)/yr	14,000 (kg/km^2)/yr	7,800 (kg/km^2)/yr	--	Hoffman and Quinn, 1987
	--	--	--	2.5E-5 (kg/vehicle)/km	--	Hoffman and others, 1985
	--	--	--	126 (kg/km^2)/cm rain	--	Hoffman and others, 1985
	2,560 (kg/km^2)/yr	--	--	--	--	Hunter and others, 1979
Oil and grease	--	--	--	485-76,700 (kg/km^2)/yr	4.1 kg/yr	Barrett and others, 1993
	--	--	--	9-16 (kg/km^2)/event	--	Barrett and others, 1993
	--	--	--	27-298 (kg/km^2)/cm rain	--	Wiland and Malina, 1976
	9.8 (kg/km^2)/cm rain	239 (kg/km^2)/cm rain	--	--	--	Stenstrom and others, 1984
PAHs	[1]0.009 (kg/km^2)/yr	[1]0.100 (kg/km^2)/yr	[1]2.42 (kg/km^2)/yr	[1]1.22 (kg/km^2)/yr	--	Hoffman and Quinn, 1987
	[2]0.258 (kg/km^2)/yr	[2]0.589 (kg/km^2)/yr	[2]3.97 (kg/km^2)/yr	[2]16.9 (kg/km^2)/yr	--	Hoffman and Quinn, 1987
	--	--	--	0.5-1.8 (kg/km^2)/yr	--	Stotz, 1987
	--	--	--	5.8E-8 (kg/vehicle)/km	--	Hoffman and others, 1985
	--	--	--	0.151 (kg/km^2)/cm rain	--	Hoffman and others, 1985
Bulk deposition						
Petroleum hydrocarbons	61.4 (summer) (µg/m^2)/day	--	1,130 (winter) 4,120 (summer) (µg/m^2)/day	--	--	Latimer and others, 1990
Oil and grease	--	--	--	--	8.1 kg/yr	Barrett and others, 1993
PAHs	--	--	--	[3]15.6-48 µg/m of hwy/day	--	Hewitt and Rashed, 1990
	--	--	--	29-71 (µg/m^2)/yr	--	Harrison and Johnston, 1985

[1] Low-molecular-weight PAHs.

[2] High-molecular-weight PAHs.

[3] Within 50 meters of highway.

Table 4. Upper threshold concentrations of selected semivolatile organic compounds in sediment

[CAS, Chemical Abstracts]

Compound name	CAS number	Threshold concentration, in micrograms per kilogram of sediment
Acenaphthene	83-32-9	[1]1,300
Acenaphthylene	208-96-8	640
Anthracene	120-12-7	1100
Benz[a]anthracene	218-00-9	693
Benzo[a]pyrene	50-32-8	782
Bis(2-ethylhexyl)phthalate	117-81-7	2,650
Butylbenzylphthalate	85-68-7	11,000
Chrysene	218-00-9	862
Dibenz[a,h]anthracene	53-70-3	260
1,2-Dichlorobenzene	120-83-2	350
1,4-Dichlorobenzene	95-50-1	340
Diethylphthalate	84-66-2	630
Di-n-butylphthalate	84-74-2	11,000
Fluoranthene	206-44-0	[1]6,200
Naphthalene	91-20-3	470
Phenanthrene	85-01-8	[1]1,800
Pyrene	129-00-0	1,398
1,2,4-Trichlorobenzene	120-82-1	9,200

[1] Assumes 1 percent sediment organic carbon.

Table 5. Comparison of volatile organic compounds detected in the NURP and NPDES studies

[NURP, Nationwide Urban Runoff Program; NPDES, National Pollutant Discharge Elimination System; NA, not analyzed]

Compound	Frequency of detection, in percent, NURP[1]	Frequency of detection, in percent, NPDES[2]
Toluene	2	23
Xylenes	NA	17.5
Chloroform	12	13
Trimethylbenzene	NA	12
Tetrachloroethene	5	8
Naphthalene	11	7
methyl-*tert* butyl ether	NA	7
Dichloromethane	10	6
Bromodichloromethane	1	6
Ethylbenzene	4	5

[1] Cole and others, 1984.

[2] Delzer and others, 1996.

Table 6. Comparison of volatile organic compounds in stormwater to drinking-water standards

[µg/L, micrograms per liter; IUPAC, International Union of Pure and Applied Chemistry; CAS, Chemical Abstracts; NPDES, National Pollutant Discharge Elimination System; MCL, maximum contaminant level; HAL, health advisory level (USEPA, 1996c)]

IUPAC name	CAS number	Maximum concentration in NPDES samples	Standard, in µg/L	Type of standard
Methylbenzene	108-88-3	6.6	1,000	MCL
Dimethylbenzenes	1330-20-7	15	10,000	MCL
Trichloromethane	67-66-3	7.0	[1]100	MCL
Tetrachloroethene	127-18-4	42	5	MCL
Naphthalene	91-20-3	5.1	20	HAL
Methyl *tert*-butyl ether	1634-04-4	8.7	[2]20	HAL
Dichloromethane	75-09-2	13	5	MCL
Bromodichloromethane	75-27-4	2.8	[1]100	MCL
Ethylbenzene	100-41-4	2.0	700	MCL
Benzene	71-43-2	0.8	5	MCL

[1] Total for all trihalomethanes combined cannot exceed the 100 µg/L.

[2] Standard varies from 20 to 40 µg/L.

Table 7. Concentrations of detected semivolatile and volatile organic compounds in stormwater, suspended sediment, and bottom material, and (or) soil

[NPDES, National Pollutant Discharge Elimination System; NURP, Nationwide Urban Runoff Program; NR, not reported; ND, not detected; <, less than reporting limit; --, no data]

Compound name	Location	Land use															Reference
		Highway			Residential			Commercial			Industrial			Unspecified			
		Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	
Semivolatile organic compounds, whole water, in micrograms per liter																	
Acenaphthene	United States																
	Arizona																
	Maricopa County	--	--	--	<5	<5	NR	<5	<5	NR	<5	<5	NR	--	--	--	Lopes and others, 1995
	Colorado																
	Colorado Springs	--	--	--	<5	<5	NR	<5	<5	NR	<5	<5	NR	--	--	--	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<5	<5	NR	<5	<5	NR	<5	<5	NR	--	--	--	Baldys and others, 1998
	Canada																
	Canadian Great Lakes	--	--	--	--	--	--	--	--	--	--	--	--	NR	NR	0.97	Marsalek and Schroeter, 1988
	Sault Ste Marie	--	--	--	--	--	--	--	--	--	<0.05	0.098	NR	--	--	--	Boom and Marsalek, 1988
Acenaphthylene	United States																
	Arizona																
	Maricopa County	--	--	--	<5	<5	NR	<5	<5	NR	<5	<5	NR	--	--	NR	Lopes and others, 1995
	Colorado																
	Colorado Springs	--	--	--	<5	<5	NR	<5	<5	NR	<5	<5	NR	--	--	NR	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<5	<5	NR	<5	<5	NR	<5	<5	NR	--	--	--	Baldys and others, 1998
	Canada																
	Canadian Great Lakes	--	--	--	--	--	--	--	--	--	--	--	--	NR	NR	0.96	Marsalek and Schroeter, 1988
	Sault Ste Marie	--	--	--	--	--	--	--	--	--	<.05	.153	NR	--	--	--	Boom and Marsalek, 1988
Anthracene	United States																
	Arizona																
	Maricopa County	--	--	--	<5	<5	NR	<5	<5	NR	<5	<5	NR	--	--	--	Lopes and others, 1995
	Colorado																
	Colorado Springs	--	--	--	<5	<5	NR	<5	9	NR	<5	10	NR	--	--	NR	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<5	<5	NR	<5	<5	NR	<5	7	NR	--	--	--	Baldys and others, 1998
	Summary–NURP	--	--	--	--	--	--	--	--	--	--	--	--	1	10	--	Cole and others, 1984

Table 7. Concentrations of detected semivolatile and volatile organic compounds in stormwater, suspended sediment, and bottom material, and (or) soil—*Continued*

Compound name	Location	Land use: Highway			Residential			Commercial			Industrial			Unspecified			Reference
		Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	
Semivolatile organic compounds, whole water, in micrograms per liter—*Continued*																	
Anthracene	Summary	--	--	--	--	--	--	--	--	--	--	--	--	0.009	10	NR	Makepeace and others, 1995
	Norway																
	Oslo	ND	0.379	NR	--	--	--	--	--	--	--	--	--	--	--	--	Gjessing and others, 1984
Benz(*a*) anthracene	United States																
	Arizona																
	Maricopa County	--	--	--	<10	<10	NR	<10	<10	NR	<10	<10	NR	--	--	--	Lopes and others, 1995
	Colorado																
	Colorado Springs	--	--	--	<10	<10	NR	<10	<10	NR	<10	37	NR	--	--	--	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<10	<10	NR	<10	13	NR	<10	26	NR	--	--	--	Baldys and others, 1998
	Summary–NURP	--	--	--	--	--	--	--	--	--	--	--	--	1	10	NR	Cole and others, 1984
	Summary	--	--	--	--	--	--	--	--	--	--	--	--	0.0003	10	NR	Makepeace and others, 1995
	Japan																
	Tokyo	--	--	--	NR	NR	5	--	--	--	--	--	--	--	--	--	Yamane and others, 1990
	Norway																
	Oslo	ND	0.677	NR	--	--	--	--	--	--	--	--	--	--	--	--	Gjessing and others, 1984
	Spain																
	Madrid	--	--	--	--	--	--	--	--	--	--	--	--	NR	NR	1.1	Bomboi and Hernandez, 1991
Benzo(*b*) fluoranthene	United States																
	Arizona																
	Maricopa County	--	--	--	<10	<10	NR	<10	19	NR	<10	<10	NR	--	--	--	Lopes and others, 1995
	Colorado																
	Colorado Springs	--	--	--	<10	15	NR	<10	11	--	<10	73	NR	--	--	--	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<10	<10	NR	<10	15	NR	<10	23	NR	--	--	--	Baldys and others, 1998
	Summary–NURP	--	--	--	--	--	--	--	--	--	--	--	--	NR	2	NR	Cole and others, 1984
	Summary	--	--	--	--	--	--	--	--	--	--	--	--	0.0034	1.9	NR	Makepeace and others, 1995

Table 7. Concentrations of detected semivolatile and volatile organic compounds in stormwater, suspended sediment, and bottom material, and (or) soil—*Continued*

Compound name	Location	Land use															Reference
		Highway			Residential			Commercial			Industrial			Unspecified			
		Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	
Semivolatile organic compounds, whole water, in micrograms per liter—*Continued*																	
Benzo(*b*) fluoranthene	Canada																
	Sault Ste Marie	--	--	--	--	--	--	--	--	--	<0.1	0.647	NR	--	--	--	Boom and Marsalek, 1988
	Norway																
	Oslo	1	1.171	NR	--	--	--	--	--	--	--	--	--	--	--	--	Gjessing and others, 1984
Benzo(*k*) fluoranthene	United States																
	Arizona																
	Maricopa County	--	--	--	<10	<10	NR	<10	<10	NR	<10	<10	NR	--	--	--	Lopes and others, 1995
	Colorado																
	Colorado Springs	--	--	--	<10	14	NR	<10	<10	NR	<10	90	NR	--	--	--	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<10	28	NR	<10	13	NR	<10	22	NR	--	--	--	Baldys and others, 1998
	Summary–NURP	--	--	--	--	--	--	--	--	--	--	--	--	4	10	NR	Cole and others, 1984
	Summary	--	--	--	--	--	--	--	--	--	--	--	--	0.0012	10	NR	Makepeace and others, 1995
	Canada																
	Sault Ste Marie	--	--	--	--	--	--	--	--	--	<0.1	0.99	NR	--	--	--	Boom and Marsalek, 1988
	Japan																
	Tokyo	--	--	--	NR	NR	5	--	--	--	--	--	--	--	--	--	Yamane and others, 1990
	Norway																
	Oslo	1	1.171	NR	--	--	--	--	--	--	--	--	--	--	--	--	Gjessing and others, 1984
	Spain																
	Madrid	--	--	--	--	--	--	--	--	--	--	--	--	NR	NR	0.6	Bomboi and Hernandez, 1991
Benzo(*b*) fluorene	Spain																
	Madrid	--	--	--	--	--	--	--	--	--	--	--	--	NR	NR	0.7	Bomboi and Hernandez, 1991
Benzo(*ghi*) perylene	United States																
	Arizona																
	Maricopa County	--	--	--	<10	<10	NR	<10	<10	NR	<10	16	NR	--	--	--	Lopes and others, 1995
	Colorado																
	Colorado Springs	--	--	--	<10	<10	--	<10	11	NR	<10	31	NR	--	--	--	von Guerard and Weiss, 1995

Table 7. Concentrations of detected semivolatile and volatile organic compounds in stormwater, suspended sediment, and bottom material, and (or) soil—*Continued*

Compound name	Location	Land use															Reference
		Highway			Residential			Commercial			Industrial			Unspecified			
		Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	
Semivolatile organic compounds, whole water, in micrograms per liter—*Continued*																	
Benzo(*ghi*) perylene	Texas																
	Dallas–Fort Worth	--	--	--	<10	<10	NR	<10	15	NR	<10	25	NR	--	--	--	Baldys and others, 1998
	Summary	--	--	--	--	--	--	--	--	--	--	--	--	0.0024	1.5	NR	Makepeace and others, 1995
	Canada																
	Sault Ste Marie	--	--	--	--	--	--	--	--	--	<0.1	0.466	NR	--	--	--	Boom and Marsalek, 1988
	Japan																
	Tokyo	--	--	--	NR	NR	1.2	--	--	--	--	--	--	--	--	--	Yamane and others, 1990
	Norway																
	Oslo	ND	0.551	NR	--	--	--	--	--	--	--	--	--	--	--	--	Gjessing and others, 1984
	Spain																
	Madrid	--	--	--	--	--	--	--	--	--	--	--	--	NR	NR	0.3	Bomboi and Hernandez, 1991
Benzo(*a*) pyrene	United States																
	Arizona																
	Maricopa County	--	--	--	<10	<10	NR	<10	<10	NR	<10	<10	NR	--	--	--	Lopes and others, 1995
	Colorado																
	Colorado Springs	--	--	--	<10	11	NR	<10	<10	NR	<10	46	NR	--	--	--	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<10	<10	NR	<10	11	NR	<10	20	NR	--	--	--	Baldys and others, 1998
	Summary–NURP	--	--	--	--	--	--	--	--	--	--	--	--	1	10	NR	Cole and others, 1984
	Summary	--	--	--	--	--	--	--	--	--	--	--	--	0.0025	10	NR	Makepeace and others, 1995
	Canada																
	Sault Ste Marie	--	--	--	--	--	--	--	--	--	<0.1	0.558	NR	--	--	--	Boom and Marsalek, 1988
	Germany																
	Bayreuth	--	--	--	--	--	--	--	--	--	--	--	--	NR	NR	52	Herrmann, 1981
	Japan																
	Tokyo	--	--	--	NR	NR	NR	--	--	--	--	--	--	--	--	--	Yamane and others, 1990
	Norway																
	Oslo	ND	0.602	NR	--	--	--	--	--	--	--	--	--	--	--	--	Gjessing and others, 1984

Table 7. Concentrations of detected semivolatile and volatile organic compounds in stormwater, suspended sediment, and bottom material, and (or) soil—*Continued*

Compound name	Location	Land use															Reference
		Highway			Residential			Commercial			Industrial			Unspecified			
		Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	
Semivolatile organic compounds, whole water, in micrograms per liter—*Continued*																	
Benzo(*a*) pyrene	Spain																
	Madrid	--	--	--	--	--	--	--	--	--	--	--	--	NR	NR	1.1	Bomboi and Hernandez, 1991
	Madrid	--	--	--	--	--	--	--	--	--	--	--	--	ND	4.75	NR	Bomboi and others, 1990
Benzo(*e*) pyrene	Summary	--	--	--	--	--	--	--	--	--	--	--	--	0.4	0.609	NR	Makepeace and others, 1995
	Norway																
	Oslo	ND	0.609	NR	--	--	--	--	--	--	--	--	--	--	--	--	Gjessing and others, 1984
Butylbenzyl phthalate	United States																
	Arizona																
	Maricopa County	--	--	--	<5	<5	NR	<5	<5	NR	<5	<5	NR	--	--	--	Lopes and others, 1995
	Colorado																
	Colorado Springs	--	--	--	<5	<5	NR	<5	11	NR	<5	<5	NR	--	--	--	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<5	10	NR	<5	8	NR	<5	14	NR	--	--	--	Baldys and others, 1998
	Summary–NURP	--	--	--	--	--	--	--	--	--	--	--	--	NR	10	NR	Cole and others, 1984
p-Chloro-*m*-cresol	Summary–NURP	--	--	--	--	--	--	--	--	--	--	--	--	NR	1.5	NR	Cole and others, 1984
2-Chloro naphthalene	United States																
	Arizona																
	Maricopa County	--	--	--	<5	<5	NR	<5	<5	NR	<5	<5	NR	--	--	--	Lopes and others, 1995
	Colorado																
	Colorado Springs	--	--	--	<5	<5	NR	<5	<5	NR	<5	<5	NR	--	--	--	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<5	<5	NR	<5	<5	NR	<5	<5	NR	--	--	--	Baldys and others, 1998
	Canada																
	Sault Ste Marie	--	--	--	--	--	--	--	--	--	<0.5	0.5	NR	--	--	--	Boom and Marsalek, 1988
B-Chloro naphthalene	Canada																
	Canadian Great Lakes	--	--	--	--	--	--	--	--	--	--	--	--	NR	NR	0.97	Marsalek and Schroeter, 1988
2-Chloro phenol	United States																
	Arizona																
	Maricopa County	--	--	--	<5	<5	NR	<5	<5	NR	<5	<5	NR	--	--	--	Lopes and others, 1995

Table 7. Concentrations of detected semivolatile and volatile organic compounds in stormwater, suspended sediment, and bottom material, and (or) soil—*Continued*

Compound name	Location	Land use															Reference
		Highway			Residential			Commercial			Industrial			Unspecified			
		Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	
Semivolatile organic compounds, whole water, in micrograms per liter—*Continued*																	
2-Chloro phenol	Colorado																
	Colorado Springs	--	--	--	<5	<5	NR	<5	<5	NR	<5	<5	NR	--	--	--	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<5	<5	NR	<5	<5	NR	<5	<5	NR	--	--	--	Baldys and others, 1998
	Summary–NURP	--	--	--	--	--	--	--	--	--	--	--	--	NR	2	NR	Cole and others, 1984
Chrysene	United States																
	Arizona																
	Maricopa County	--	--	--	<10	<10	NR	<10	17	NR	<10	<10	NR	--	--	--	Lopes and others, 1995
	Colorado																
	Colorado Springs	--	--	--	<10	--	NR	<10	12	NR	<10	61	NR	--	--	--	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<10	<10	NR	<10	23	NR	<10	49	3.2	--	--	--	Baldys and others, 1998
	Summary–NURP	--	--	--	--	--	--	--	--	--	--	--	--	0.6	10	NR	Cole and others, 1984
	Summary	--	--	--	--	--	--	--	--	--	--	--	--	0.0038	10	NR	Makepeace and others, 1995
	Norway																
	Oslo	ND	1.147	NR	--	--	--	--	--	--	--	--	--	--	--	--	Gjessing and others, 1984
	Spain																
	Madrid	--	--	--	--	--	--	--	--	--	--	--	--	NR	NR	1.4	Bomboi and Hernandez, 1991
Dibenzanthracene	United States																
	Texas																
	Dallas–Fort Worth	--	--	--	<10	<10	NR	<10	<10	NR	<10	<10	NR	--	--	--	Baldys and others, 1998
	Norway																
	Oslo	ND	0.214	NR	--	--	--	--	--	--	--	--	--	--	--	--	Gjessing and others, 1984
Dibenz(*a*,*h*) anthracene	Summary	--	--	--	--	--	--	--	--	--	--	--	--	0.0006	0.9	NR	Makepeace and others, 1995
	Spain																
	Madrid	--	--	--	--	--	--	--	--	--	--	--	--	NR	NR	0.5	Bomboi and Hernandez, 1991
Dibenzofuran	Norway																
	Oslo	ND	0.001	NR	--	--	--	--	--	--	--	--	--	--	--	--	Gjessing and others, 1984

Table 7. Concentrations of detected semivolatile and volatile organic compounds in stormwater, suspended sediment, and bottom material, and (or) soil—*Continued*

Compound name	Location	Land use															Reference
		Highway			Residential			Commercial			Industrial			Unspecified			
		Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	
Semivolatile organic compounds, whole water, in micrograms per liter—*Continued*																	
Dibenzothio-phene	Norway																
	Oslo	ND	0.136	NR	--	--	--	--	--	--	--	--	--	--	--	--	Gjessing and others, 1984
1,2-Dichloro benzene	United States																
	Colorado																
	Colorado Springs	--	--	--	<5	<5	NR	<5	<5	NR	<5	<5	NR	--	--	--	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<0.2	<5	NR	<0.2	<5	NR	<0.2	<10	NR	--	--	--	Baldys and others, 1998
	Canada																
	Canadian Great Lakes	--	--	--	--	--	--	--	--	--	--	--	--	NR	NR	0.39	Marsalek and Schroeter, 1988
1,3-Dichloro benzene	United States																
	Arizona																
	Maricopa County	--	--	--	<5	<5	NR	<5	<5	NR	<5	<5	NR	--	--	--	Lopes and others, 1995
	Colorado																
	Colorado Springs	--	--	--	<5	<5	NR	<5	<5	NR	<5	<5	NR	--	--	--	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<0.2	<5	NR	<0.2	<5	NR	<0.2	<10	NR	--	--	--	Baldys and others, 1998
	Canada																
	Canadian Great Lakes	--	--	--	--	--	--	--	--	--	--	--	--	NR	NR	0.0074	Marsalek and Schroeter, 1988
1,4-Dichloro benzene	United States																
	Arizona																
	Maricopa County	--	--	--	<5	<5	NR	<5	<5	NR	<5	<5	NR	--	--	--	Lopes and others, 1995
	Colorado																
	Colorado Springs	--	--	--	<5	<5	NR	<5	<5	NR	<5	<5	NR	--	--	--	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<0.2	<5	NR	<0.2	<5	NR	<0.2	<10	NR	--	--	--	Baldys and others, 1998
	Canada																
	Canadian Great Lakes	--	--	--	--	--	--	--	--	--	--	--	--	NR	NR	0.0089	Marsalek and Schroeter, 1988

Table 7. Concentrations of detected semivolatile and volatile organic compounds in stormwater, suspended sediment, and bottom material, and (or) soil—*Continued*

Compound name	Location	Land use															Reference
		Highway			Residential			Commercial			Industrial			Unspecified			
		Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	
Semivolatile organic compounds, whole water, in micrograms per liter—*Continued*																	
Diethylphthalate	United States																
	Arizona																
	Maricopa County	--	--	--	<5	<5	NR	<5	<5	NR	<5	<5	NR	--	--	--	Lopes and others, 1995
	Colorado																
	Colorado Springs	--	--	--	<5	<5	NR	<5	<5	NR	<5	<5	NR	--	--	--	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<5	<5	NR	<5	<5	NR	<5	<5	NR	--	--	--	Baldys and others, 1998
	Summary–NURP	--	--	--	--	--	--	--	--	--	--	--	--	2	10	NR	Cole and others, 1984
9,10-Dimethyl-anthracene	Summary	--	--	--	--	--	--	--	--	--	--	--	--	1	1.4	NR	Makepeace and others, 1995
	Spain																
	Madrid	--	--	--	--	--	--	--	--	--	--	--	--	NR	NR	1	Bomboi and Hernandez, 1991
2,4-Dimethyl phenol	United States																
	Arizona																
	Maricopa County	--	--	--	<5	<5	NR	<5	<5	NR	<5	<5	NR	--	--	--	Lopes and others, 1995
	Colorado																
	Colorado Springs	--	--	--	<5	<5	NR	<5	<5	NR	<5	<5	NR	--	--	--	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<5	<5	NR	<5	<5	NR	<5	<5	NR	--	--	--	Baldys and others, 1998
	Summary–NURP	--	--	--	--	--	--	--	--	--	--	--	--	NR	10	NR	Cole and others, 1984
Di-n-butyl phthalate	United States																
	Arizona																
	Maricopa County	--	--	--	<5	<5	NR	<5	<5	NR	<5	<5	NR	--	--	--	Lopes and others, 1995
	Colorado																
	Colorado Springs	--	--	--	<5	<5	NR	<5	15	NR	<5	<5	NR	--	--	--	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<5	<5	NR	<5	<5	NR	<5	<5	NR	--	--	--	Baldys and others, 1998
	Summary–NURP	--	--	--	--	--	--	--	--	--	--	--	--	0.5	11	NR	Cole and others, 1984
Di-n-octyl phthalate	United States																
	Arizona																
	Maricopa County	--	--	--	<10	<10	NR	<10	<10	NR	<10	<10	NR	--	--	--	Lopes and others, 1995

Table 7. Concentrations of detected semivolatile and volatile organic compounds in stormwater, suspended sediment, and bottom material, and (or) soil—*Continued*

Compound name	Location	Land use: Highway			Residential			Commercial			Industrial			Unspecified			Reference
		Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	
Semivolatile organic compounds, whole water, in micrograms per liter—*Continued*																	
Di-n-octyl phthalate	Colorado																
	Colorado Springs	--	--	--	<10	11	NR	<10	11	NR	<10	11	NR	--	--	--	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<10	<10	NR	<10	<10	NR	<10	<10	NR	--	--	--	Baldys and others, 1998
	Summary–NURP	--	--	--	--	--	--	--	--	--	--	--	--	0.4	1	NR	Cole and others, 1984
bis(2-Ethyl hexyl) phthalate	United States																
	Arizona																
	Maricopa County	--	--	--	<5	<5	NR	<5	8	NR	<5	9	NR	--	--	--	Lopes and others, 1995
	Colorado																
	Colorado Springs	--	--	--	7	13	NR	11	100	NR	9	24	NR	--	--	--	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<5	24	5.7	<5	20	NR	<5	140	6.9	--	--	--	Baldys and others, 1998
	Summary–NURP	--	--	--	--	--	--	--	--	--	--	--	--	7	39	NR	Cole and others, 1984
Fluoranthene	United States																
	Arizona																
	Maricopa County	--	--	--	<5	<5	NR	<5	18	NR	<5	7	NR	--	--	--	Lopes and others, 1995
	Colorado																
	Colorado Springs	--	--	--	<5	32	NR	10	25	NR	<5	120	NR	--	--	--	von Guerard and Weiss, 1995
	Rhode Island																
	Cranston	--	--	--	--	--	--	NR	0.1609	NR	--	--	--	--	--	--	Hoffman and others, 1984
	Texas																
	Dallas–Fort Worth	--	--	--	<5	13	NR	<5	23	3.6	<5	52	6.5	--	--	--	Baldys and others, 1998
	Summary–NURP	--	--	--	--	--	--	--	--	--	--	--	--	0.3	12	NR	Cole and others, 1984
	Summary	--	--	--	--	--	--	--	--	--	--	--	--	0.03	56	NR	Makepeace and others, 1995
	Canada																
	Canadian Great Lakes	--	--	--	--	--	--	--	--	--	--	--	--	NR	NR	1	Marsalek and Schroeter, 1988
	Sault Ste Marie	--	--	--	--	--	--	--	--	--	<0.5	2.95	NR	--	--	--	Boom and Marsalek, 1988
	Germany																
	Bayreuth	--	--	--	--	--	--	--	--	--	--	--	--	NR	NR	0.106	Herrmann, 1981

Table 7. Concentrations of detected semivolatile and volatile organic compounds in stormwater, suspended sediment, and bottom material, and (or) soil—*Continued*

Compound name	Location	Land use: Highway Min	Highway Max	Highway Mean	Residential Min	Residential Max	Residential Mean	Commercial Min	Commercial Max	Commercial Mean	Industrial Min	Industrial Max	Industrial Mean	Unspecified Min	Unspecified Max	Unspecified Mean	Reference
Semivolatile organic compounds, whole water, in micrograms per liter—*Continued*																	
Fluoranthene	Norway																
	Oslo	4	2.665	NR	--	--	--	--	--	--	--	--	--	--	--	--	Gjessing and others, 1984
	Spain																
	Madrid	--	--	--	--	--	--	--	--	--	--	--	--	NR	NR	2.7	Bomboi and Hernandez, 1991
	Madrid	--	--	--	--	--	--	--	--	--	--	--	--	0.4	10.65	NR	Bomboi and others, 1990
Fluorene	United States																
	Arizona																
	Maricopa County	--	--	--	<5	<5	NR	<5	<5	NR	<5	<5	NR	--	--	--	Lopes and others, 1995
	Colorado																
	Colorado Springs	--	--	--	<5	<5	NR	<5	<5	NR	<5	<5	NR	--	--	--	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<5	<5	NR	<5	<5	NR	<5	<5	NR	--	--	--	Baldys and others, 1998
	Summary–NURP	--	--	--	--	--	--	--	--	--	--	--	--	NR	1	NR	Cole and others, 1984
	Summary	--	--	--	--	--	--	--	--	--	--	--	--	0.096	1	NR	Makepeace and others, 1995
	Canada																
	Sault Ste Marie	--	--	--	--	--	--	--	--	--	<0.05	0.135	NR	--	--	--	Boom and Marsalek, 1988
	Norway																
	Oslo	ND	0.96	NR	--	--	--	--	--	--	--	--	--	--	--	--	Gjessing and others, 1984
Hexachloro benzene	United States																
	Arizona																
	Maricopa County	--	--	--	<5	<5	NR	<5	<5	NR	<5	<5	NR	--	--	--	Lopes and others, 1995
	Colorado																
	Colorado Springs	--	--	--	<5	<5	NR	<5	<5	NR	<5	<5	NR	--	--	--	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<5	--	NR	<5	<5	NR	<5	<5	NR	--	--	--	Baldys and others, 1998
	Canada																
	Canadian Great Lakes	--	--	--	--	--	--	--	--	--	--	--	--	NR	NR	0.00073	Marsalek and Schroeter, 1988
Indene	Canada																
	Sault Ste Marie	--	--	--	--	--	--	--	--	--	<0.05	0.05	NR	--	--	--	Boom and Marsalek, 1988

Table 7. Concentrations of detected semivolatile and volatile organic compounds in stormwater, suspended sediment, and bottom material, and (or) soil—*Continued*

Compound name	Location	Land use															Reference
		Highway			Residential			Commercial			Industrial			Unspecified			
		Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	
Semivolatile organic compounds, whole water, in micrograms per liter—*Continued*																	
Indeno (1,2,3-cd) pyrene	United States																
	Arizona																
	Maricopa County	--	--	--	<10	<10	NR	<10	<10	NR	<10	27	NR	--	--	--	Lopes and others, 1995
	Colorado																
	Colorado Springs	--	--	--	<10	11	NR	<10	13	NR	<10	38	NR	--	--	--	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<10	<10	NR	<10	15	NR	<10	27	NR	--	--	--	Baldys and others, 1998
	Summary	--	--	--	--	--	--	--	--	--	--	--	--	0.31	0.5	NR	Makepeace and others, 1995
	Canada																
	Sault Ste Marie	--	--	--	--	--	--	--	--	--	<0.1	0.496	NR	--	--	--	Boom and Marsalek, 1988
	Spain																
	Madrid	--	--	--	--	--	--	--	--	--	--	--	--	NR	NR	0.2	Bomboi and Hernandez, 1991
1-Methyl anthracene	Norway																
	Oslo	ND	0.133	NR	--	--	--	--	--	--	--	--	--	--	--	--	Gjessing and others, 1984
2-Methyl anthracene	Norway																
	Oslo	ND	0.036	NR	--	--	--	--	--	--	--	--	--	--	--	--	Gjessing and others, 1984
	Spain																
	Madrid	--	--	--	--	--	--	--	--	--	--	--	--	NR	NR	0.7	Bomboi and Hernandez, 1991
1-Methyl naphthalene	Canada																
	Sault Ste Marie	--	--	--	--	--	--	--	--	--	<0.05	0.177	NR	--	--	--	Boom and Marsalek, 1988
	Norway																
	Oslo	ND	0.045	NR	--	--	--	--	--	--	--	--	--	--	--	--	Gjessing and others, 1984
2-Methyl naphthalene	Summary	--	--	--	--	--	--	--	--	--	--	--	--	0.01	1.6	NR	Makepeace and others, 1995
	Canada																
	Canadian Great Lakes	--	--	--	--	--	--	--	--	--	--	--	--	NR	NR	0.95	Marsalek and Schroeter, 1988
	Sault Ste Marie	--	--	--	--	--	--	--	--	--	<0.05	0.251	NR	--	--	--	Boom and Marsalek, 1988
	Norway																
	Oslo	ND	0.025	NR	--	--	--	--	--	--	--	--	--	--	--	--	Gjessing and others, 1984

Table 7. Concentrations of detected semivolatile and volatile organic compounds in stormwater, suspended sediment, and bottom material, and (or) soil—*Continued*

Compound name	Location	Land use															Reference
		Highway			Residential			Commercial			Industrial			Unspecified			
		Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	
Semivolatile organic compounds, whole water, in micrograms per liter—*Continued*																	
Methylphen anthrene	Summary	--	--	--	--	--	--	--	--	--	--	--	--	2.9	3.4	NR	Makepeace and others, 1995
	Spain																
	Madrid	--	--	--	--	--	--	--	--	--	--	--	--	NR	NR	2.9	Bomboi and Hernandez, 1991
Naphthalene	United States																
	Arizona																
	Maricopa County	--	--	--	<5	<5	NR	<5	<5	NR	<5	<5	NR	--	--	--	Lopes and others, 1995
	Colorado																
	Colorado Springs	--	--	--	<5	<5	NR	<5	<5	NR	<5	<5	NR	--	--	--	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<0.2	<5	NR	<0.2	<5	NR	<0.2	<5	NR	--	--	--	Baldys and others, 1998
	Summary–NURP	--	--	--	--	--	--	--	--	--	--	--	--	0.8	2.3	NR	Cole and others, 1984
	Summary	--	--	--	--	--	--	--	--	--	--	--	--	0.036	2.3	NR	Makepeace and others, 1995
	Norway																
	Oslo	ND	0.067	NR	--	--	--	--	--	--	--	--	--	--	--	--	Gjessing and others, 1984
4-Nitrophenol	United States																
	Arizona																
	Maricopa County	--	--	--	<30	<30	NR	<30	<30	NR	<30	<30	NR	--	--	--	Lopes and others, 1995
	Colorado																
	Colorado Springs	--	--	--	<30	<30	NR	<30	<30	NR	<30	<30	NR	--	--	--	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<30	<30	NR	<30	<30	NR	<30	<30	NR	--	--	--	Baldys and others, 1998
	Summary–NURP	--	--	--	--	--	--	--	--	--	--	--	--	1	19	NR	Cole and others, 1984
PAH (total)	Summary	--	--	--	--	--	--	--	--	--	--	--	--	0.24	13	NR	Makepeace and others, 1995
	Germany																
	Obereisesheim	NR	NR	2.97	--	--	--	--	--	--	--	--	--	--	--	--	Stoltz, 1987
	Pleidelsheim	NR	NR	2.61	--	--	--	--	--	--	--	--	--	--	--	--	Stoltz, 1987
	Ulm	NR	NR	2.51	--	--	--	--	--	--	--	--	--	--	--	--	Stoltz, 1987
	United Kingdom																
	NW London	--	--	--	--	--	--	--	--	--	--	--	--	5830	18210	NR	Gavens and others, 1983

Table 7. Concentrations of detected semivolatile and volatile organic compounds in stormwater, suspended sediment, and bottom material, and (or) soil—*Continued*

Compound name	Location	Land use															Reference
		Highway			Residential			Commercial			Industrial			Unspecified			
		Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	
Semivolatile organic compounds, whole water, in micrograms per liter—*Continued*																	
Pentachloro benzene	Canada																
	Canadian Great Lakes	--	--	--	--	--	--	--	--	--	--	--	--	NR	NR	0.001	Marsalek and Schroeter, 1988
Pentachloro phenol	United States																
	Arizona																
	Maricopa County	--	--	--	<30	<30	NR	<30	<30	NR	<30	<30	NR	--	--	--	Lopes and others, 1995
	Colorado																
	Colorado Springs	--	--	--	<30	<30.	NR	<30	<30	NR	<30	<30	NR	--	--	--	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<30	<30	NR	<30	<30	NR	<30	<30	NR	--	--	--	Baldys and others, 1998
	Summary–NURP	--	--	--	--	--	--	--	--	--	--	--	--	1	115	NR	Cole and others, 1984
Perylene	Summary	--	--	--	--	--	--	--	--	--	--	--	--	0.05	0.5	NR	Makepeace and others, 1995
	Spain																
	Madrid	--	--	--	--	--	--	--	--	--	--	--	--	NR	NR	0.5	Bomboi and Hernandez, 1991
Phenanthrene	United States																
	Arizona																
	Maricopa County	--	--	--	<5	<5	NR	<5	<5	NR	<5	<5	NR	--	--	--	Lopes and others, 1995
	Colorado																
	Colorado Springs	--	--	--	<5	23	NR	<5	14	NR	<5	67	NR	--	--	--	von Guerard and Weiss, 1995
	Rhode Island																
	Cranston	--	--	--	--	--	--	NR	0.0906	NR	--	--	--	--	--	--	Hoffman and others, 1984
	Texas																
	Dallas–Fort Worth	--	--	--	<5	10	NR	<5	10	NR	<5	33	3.6	--	--	--	Baldys and others, 1998
	Summary–NURP	--	--	--	--	--	--	--	--	--	--	--	--	0.3	10	NR	Cole and others, 1984
	Summary	--	--	--	--	--	--	--	--	--	--	--	--	0.045	10	NR	Makepeace and others, 1995
	Canada																
	Sault Ste Marie	--	--	--	--	--	--	--	--	--	<0.05	3.56	NR	--	--	--	Boom and Marsalek, 1988
	Norway																
	Oslo	3	1.385	NR	--	--	--	--	--	--	--	--	--	--	--	--	Gjessing and others, 1984

Table 7. Concentrations of detected semivolatile and volatile organic compounds in stormwater, suspended sediment, and bottom material, and (or) soil—*Continued*

Compound name	Location	Land use															Reference
		Highway			Residential			Commercial			Industrial			Unspecified			
		Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	
Semivolatile organic compounds, whole water, in micrograms per liter—*Continued*																	
Phenanthrene	Spain																
	Madrid	--	--	--	--	--	--	--	--	--	--	--	--	NR	NR	2.9	Bomboi and Hernandez, 1991
Phenol	Summary–NURP	--	--	--	--	--	--	--	--	--	--	--	--	3	10	NR	Cole and others, 1984
0-Phenyl enepyrene	Norway																
	Oslo	ND	0.432	NR	--	--	--	--	--	--	--	--	--	--	--	--	Gjessing and others, 1984
Pyrene	United States																
	Arizona																
	Maricopa County	--	--	--	<5	<5	NR	<5	13	NR	<5	<5	NR	--	--	--	Lopes and others, 1995
	Colorado																
	Colorado Springs	--	--	--	<5	24	NR	8	19	NR	<5	94	NR	--	--	--	von Guerard and Weiss, 1995
	Rhode Island																
	Cranston	--	--	--	--	--	--	NR	0.1367	NR	--	--	--	--	--	--	Hoffman and others, 1984
	Texas																
	Dallas–Fort Worth	--	--	--	<5	10	NR	<5	18	NR	<5	43	5.4	--	--	--	Baldys and others, 1998
	Summary–NURP	--	--	--	--	--	--	--	--	--	--	--	--	0.3	10	NR	Cole and others, 1984
	Summary	--	--	--	--	--	--	--	--	--	--	--	--	0.045	10	NR	Makepeace and others, 1995
	Canada																
	Canadian Great Lakes	--	--	--	--	--	--	--	--	--	--	--	--	NR	NR	1	Marsalek and Schroeter, 1988
	Sault Ste Marie	--	--	--	--	--	--	--	--	--	<0.05	3.75	NR	--	--	--	Boom and Marsalek, 1988
	Norway																
	Oslo	5	2.002	NR	--	--	--	--	--	--	--	--	--	--	--	--	Gjessing and others, 1984
	Spain																
	Madrid	--	--	--	--	--	--	--	--	--	--	--	--	NR	NR	1.9	Bomboi and Hernandez, 1991
	Madrid	--	--	--	--	--	--	--	--	--	--	--	--	0.5	8.5	NR	Bomboi and others, 1990
Quinoline	Canada																
	Sault Ste Marie	--	--	--	--	--	--	--	--	--	<0.05	0.124	NR	--	--	--	Boom and Marsalek, 1988
1,2,3,4-Tetra hydronaphthalene	Canada																
	Sault Ste Marie	--	--	--	--	--	--	--	--	--	<0.05	0.05	NR	--	--	--	Boom and Marsalek, 1988

Table 7. Concentrations of detected semivolatile and volatile organic compounds in stormwater, suspended sediment, and bottom material, and (or) soil—*Continued*

Compound name	Location	Land use															Reference
		Highway			Residential			Commercial			Industrial			Unspecified			
		Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	
Semivolatile organic compounds, whole water, in micrograms per liter—*Continued*																	
1,2,4-Trichloro benzene	United States																
	Colorado																
	Colorado Springs	--	--	--	<5	<5	NR	<5	<5	NR	<5	<5	NR	--	--	--	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<0.2	<5	NR	<0.2	<5	NR	<0.2	<10	NR	--	--	--	Baldys and others, 1998
	Canada																
	Canadian Great Lakes	--	--	--	--	--	--	--	--	--	--	--	--	NR	NR	0.0015	Marsalek and Schroeter, 1988
1,3,5,-Trichloro benzene	Canada																
	Canadian Great Lakes	--	--	--	--	--	--	--	--	--	--	--	--	NR	NR	0.00099	Marsalek and Schroeter, 1988
Semivolatile organic compounds, filtered/centrigured water, in micrograms per liter																	
Fluoranthrene	United States																
	Rhode Island																
	Cranston	--	--	--	--	--	--	NR	0.0034	NR	--	--	--	--	--	--	Hoffman and others, 1984
Phenanthrene	United States																
	Rhode Island																
	Cranston	--	--	--	--	--	--	NR	0.0263	NR	--	--	--	--	--	--	Hoffman and others, 1984
Pyrene	United States																
	Rhode Island																
	Cranston	--	--	--	--	--	--	NR	0.0056	NR	--	--	--	--	--	--	Hoffman and others, 1984
Semivolatile organic compounds, suspended sediment, in micrograms per gram																	
Acenaphthylene	Canada																
	Canadian Great Lakes	--	--	--	--	--	--	--	--	--	--	--	--	NR	NR	0.7	Marsalek and Schroeter, 1988
Benzo(*b*) fluoranthene	United States																
	Washington																
	Columbia River	--	--	--	--	--	--	--	--	--	--	--	--	0.021	0.35	0.07	Prahl and others, 1984
Benzo(*k*) fluorenthene	United States																
	Washington																
	Columbia River	--	--	--	--	--	--	--	--	--	--	--	--	0.008	0.14	NR	Prahl and others, 1984

Table 7. Concentrations of detected semivolatile and volatile organic compounds in stormwater, suspended sediment, and bottom material, and (or) soil—*Continued*

Compound name	Location	Land use															Reference
		Highway			Residential			Commercial			Industrial			Unspecified			
		Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	
Semivolatile organic compounds, suspended sediment, in micrograms per gram—*Continued*																	
Benzo(*ghi*) perylene	United States																
	Washington																
	Columbia River	--	--	--	--	--	--	--	--	--	--	--	--	0.007	0.15	0.019	Prahl and others, 1984
Benzo(*a*) pyrene	United States																
	Rhode Island																
	Cranston	0.28	7.78	1.35	--	--	--	--	--	--	--	--	--	--	--	--	Hoffman and others, 1985
	Washington																
	Columbia River	--	--	--	--	--	--	--	--	--	--	--	--	0.005	0.097	0.016	Prahl and others, 1984
1,2-Dichloro benzene	Canada																
	Canadian Great Lakes	--	--	--	--	--	--	--	--	--	--	--	--	NR	NR	0.12	Marsalek and Schroeter, 1988
1,3-Dichloro benzene	Canada																
	Canadian Great Lakes	--	--	--	--	--	--	--	--	--	--	--	--	NR	NR	0.027	Marsalek and Schroeter, 1988
1,4-Dichloro benzene	Canada																
	Canadian Great Lakes	--	--	--	--	--	--	--	--	--	--	--	--	NR	NR	0.4	Marsalek and Schroeter, 1988
Fluoranthene	United States																
	Rhode Island																
	Cranston	3.2	45.7	12	--	--	--	--	--	--	--	--	--	--	--	--	Hoffman and others, 1985
	Cranston	--	--	--	--	--	--	NR	3.32	NR	--	--	--	--	--	--	Hoffman and others, 1984
	Washington																
	Columbia River	--	--	--	--	--	--	--	--	--	--	--	--	0.025	0.38	0.052	Prahl and others, 1984
	Canada																
	Canadian Great Lakes	--	--	--	--	--	--	--	--	--	--	--	--	NR	NR	2.4	Marsalek and Schroeter, 1988
Hexachloro benzene	Canada																
	Canadian Great Lakes	--	--	--	--	--	--	--	--	--	--	--	--	NR	NR	0.075	Marsalek and Schroeter, 1988
Indene	Canada																
	Canadian Great Lakes	--	--	--	--	--	--	--	--	--	--	--	--	NR	NR	0.44	Marsalek and Schroeter, 1988
2-Methylnaph-thalene	Canada																
	Canadian Great Lakes	--	--	--	--	--	--	--	--	--	--	--	--	NR	NR	0.53	Marsalek and Schroeter, 1988

Table 7. Concentrations of detected semivolatile and volatile organic compounds in stormwater, suspended sediment, and bottom material, and (or) soil—*Continued*

Compound name	Location	Land use															Reference
		Highway			Residential			Commercial			Industrial			Unspecified			
		Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	
Semivolatile organic compounds, suspended sediment, in micrograms per gram—*Continued*																	
Pentachloro benzene	Canada																
	Canadian Great Lakes	--	--	--	--	--	--	--	--	--	--	--	--	NR	NR	0.0098	Marsalek and Schroeter, 1988
Perylene	United States																
	Washington																
	Columbia River	--	--	--	--	--	--	--	--	--	--	--	--	0.021	0.17	0.051	Prahl and others, 1984
Phenanthrene	United States																
	Rhode Island																
	Cranston	--	--	--	--	--	--	NR	1.35	NR	--	--	--	--	--	--	Hoffman and others, 1984
Phenanthrene	Canada																
	Canadian Great Lakes	--	--	--	--	--	--	--	--	--	--	--	--	NR	NR	1.7	Marsalek and Schroeter, 1988
Pyrene	United States																
	Rhode Island																
	Cranston	--	--	--	--	--	--	NR	2.76	NR	--	--	--	--	--	--	Hoffman and others, 1984
	Washington																
	Columbia River	--	--	--	--	--	--	--	--	--	--	--	--	0.026	0.41	0.056	Prahl and others, 1984
	Canada																
	Canadian Great Lakes	--	--	--	--	--	--	--	--	--	--	--	--	NR	NR	2.2	Marsalek and Schroeter, 1988
1,2,3,5-Tetra chloro benzene	Canada																
	Canadian Great Lakes	--	--	--	--	--	--	--	--	--	--	--	--	NR	NR	0.005	Marsalek and Schroeter, 1988
1,2,3,4-Tetra chloro benzene	Canada																
	Canadian Great Lakes	--	--	--	--	--	--	--	--	--	--	--	--	NR	NR	0.0044	Marsalek and Schroeter, 1988
1,2,4,5-Tetra chloro benzene	Canada																
	Canadian Great Lakes	--	--	--	--	--	--	--	--	--	--	--	--	NR	NR	0.005	Marsalek and Schroeter, 1988
1,2,3-Trichloro benzene	Canada																
	Canadian Great Lakes	--	--	--	--	--	--	--	--	--	--	--	--	NR	NR	0.0076	Marsalek and Schroeter, 1988
1,2,4-Trichloro benzene	Canada																
	Canadian Great Lakes	--	--	--	--	--	--	--	--	--	--	--	--	NR	NR	0.0085	Marsalek and Schroeter, 1988
1,3,5-Trichloro benzene	Canada																
	Canadian Great Lakes	--	--	--	--	--	--	--	--	--	--	--	--	NR	NR	0.019	Marsalek and Schroeter, 1988

Table 7. Concentrations of detected semivolatile and volatile organic compounds in stormwater, suspended sediment, and bottom material, and (or) soil—*Continued*

Compound name	Location	Land use															Reference
		Highway			Residential			Commercial			Industrial			Unspecified			
		Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	
Semivolatile organic compounds, bottom material/soil, in micrograms per gram																	
Anthracene	Norway																
	Olso	ND	0.16	NR	--	--	--	--	--	--	--	--	--	--	--	--	Gjessing and others, 1984
	United Kingdom																
	N.W. London	--	--	--	--	--	--	--	--	--	--	--	--	0.25	2.1	NR	Ellis and others, 1985
Benzo(*a*) anthracene	Japan																
	Tokyo	--	--	--	NR	NR	0.075	--	--	--	--	--	--	--	--	--	Yamane and others, 1990
	United Kingdom																
	Midlands	0.169	2.97	1.165	--	--	--	--	--	--	--	--	--	--	--	--	Butler and others, 1984
Benzo(*b*)fluor anthene	Norway																
	Olso	0.03	0.096	NR	--	--	--	--	--	--	--	--	--	--	--	--	Gjessing and others, 1984
	United Kingdom																
	N.W. London	--	--	--	--	--	--	--	--	--	--	--	--	0.5	4	NR	Ellis and others, 1985
Benzo(*k*)fluor anthene	Japan																
	Tokyo	--	--	--	NR	NR	0.14	--	--	--	--	--	--	--	--	--	Yamane and others, 1990
	United Kingdom																
	N.W. London	--	--	--	--	--	--	--	--	--	--	--	--	0.5	4	NR	Ellis and others, 1985
Benzo(*ghi*) perylene	Japan																
	Tokyo	--	--	--	NR	NR	0.42	--	--	--	--	--	--	--	--	--	Yamane and others, 1990
	United Kingdom																
	N.W. London	--	--	--	--	--	--	--	--	--	--	--	--	0.1	4.5	NR	Ellis and others, 1985
Benzo(*a*) pyrene	US–summary	--	--	--	--	--	--	--	--	--	--	--	--	0.04	7	NR	Edwards, 1983
	Canada–summary	NR	0.866	NR	--	--	--	--	--	--	--	--	--	--	--	--	Edwards, 1983
	Czechoslovakia–summary	--	--	--	--	--	--	--	--	--	--	--	--	0.0083	0.0421	--	Edwards, 1983
	Germany–summary	--	--	--	--	--	--	--	--	--	0.8	650	NR	0.0015	0.004	NR	Edwards, 1983
	Japan																
	Tokyo	--	--	--	NR	NR	0.08	--	--	--	--	--	--	--	--	--	Yamane and others, 1990
	Russia																
	Moscow–summary	--	--	--	--	--	--	--	--	--	0.058	0.2997	NR	ND	200	--	Edwards, 1983
	Switzerland																
	Greifebsee	--	--	--	--	--	--	--	--	--	--	--	--	ND	2	NR	Wakeham and others, 1980
	United Kingdom																
	N.W. London	--	--	--	--	--	--	--	--	--	--	--	--	0.2	2.9	NR	Ellis and others, 1985

Table 7. Concentrations of detected semivolatile and volatile organic compounds in stormwater, suspended sediment, and bottom material, and (or) soil—*Continued*

Compound name	Location	Land use															Reference
		Highway			Residential			Commercial			Industrial			Unspecified			
		Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	
Semivolatile organic compounds, bottom material/soil, in micrograms per gram—*Continued*																	
Benzo(*a*) pyrene	Midlands	0.165	3.196	0.781	--	--	--	--	--	--	--	--	--	--	--	--	Butler and others, 1984
	Yugoslavia–summary	--	--	--	--	--	--	--	--	--	--	--	--	0.029	0.9	--	Edwards, 1983
Benzo(*e*) pyrene	Norway																
	Olso	ND	0.8	NR	--	--	--	--	--	--	--	--	--	--	--	--	Gjessing and others, 1984
	United Kingdom																
	Midlands	0.164	2.293	0.731	--	--	--	--	--	--	--	--	--	--	--	--	Butler and others, 1984
Chrysene	Norway																
	Olso	0.02	0.1	NR	--	--	--	--	--	--	--	--	--	--	--	--	Gjessing and others, 1984
	United Kingdom																
	Midlands	0.251	2.703	1.949	--	--	--	--	--	--	--	--	--	--	--	--	Butler and others, 1984
Coronene	United Kingdom																
	Midlands	0.032	0.322	0.117	--	--	--	--	--	--	--	--	--	--	--	--	Butler and others, 1984
Fluoranthene	Norway																
	Olso	0.066	0.248	NR	--	--	--	--	--	--	--	--	--	--	--	--	Gjessing and others, 1984
	Switzerland																
	Greifebsee	--	--	--	--	--	--	--	--	--	--	--	--	ND	3.5	NR	Wakeham and others, 1980
	United Kingdom																
	Midlands	0.2	3.734	1.313	--	--	--	--	--	--	--	--	--	--	--	--	Butler and others, 1984
Fluorene	United Kingdom																
	N.W. London	--	--	--	--	--	--	--	--	--	--	--	--	0.3	3.9	NR	Ellis and others, 1985
PAH (total)	United States																
	Washington																
	Lake Washington	--	--	--	--	--	--	--	--	--	--	--	--	1	6.5	NR	Wakeham and others, 1980
	Canada–summary	--	--	--	--	--	--	--	--	--	--	--	--	NR	1.109	NR	Edwards, 1983
	Switzerland																
	Greifensee	--	--	--	--	--	--	--	--	--	--	--	--	0.3	6	NR	Wakeham and others, 1980
	Lake Lucerne	--	--	--	--	--	--	--	--	--	--	--	--	1	5.5	NR	Wakeham and others, 1980
	Lake Zurich	--	--	--	--	--	--	--	--	--	--	--	--	0.4	15	NR	Wakeham and others, 1980

Table 7. Concentrations of detected semivolatile and volatile organic compounds in stormwater, suspended sediment, and bottom material, and (or) soil—*Continued*

Compound name	Location	Land use															Reference
		Highway			Residential			Commercial			Industrial			Unspecified			
		Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	
Semivolatile organic compounds, bottom material/soil, in micrograms per gram—*Continued*																	
PAH (total)	Summary	5	300	NR	--	--	--	--	--	--	--	--	--	4	8	NR	Edwards, 1983
	United Kingdom																
	Derwent River	1.51	26.76	8.32	0.02	2.45	0.58	2.65	63.75	34.55	2.91	209.59	25.75	--	--	--	Evans and others, 1990
	NW London	--	--	--	--	--	--	--	--	--	--	--	--	310	1100	NR	Gavens and others, 1983
Phenanthracene	Norway																
	Olso	0.07	0.18	NR	--	--	--	--	--	--	--	--	--	--	--	--	Gjessing and others, 1984
	Switzerland																
	Greifebsee	--	--	--	--	--	--	--	--	--	--	--	--	ND	5	NR	Wakeham and others, 1980
Pyrene	Norway																
	Olso	0.11	0.122	NR	--	--	--	--	--	--	--	--	--	--	--	--	Gjessing and others, 1984
	United Kingdom																
	N.W. London	--	--	--	--	--	--	--	--	--	--	--	--	0.1	3.3	NR	Ellis and others, 1985
	Midlands	0.145	4.515	1.386	--	--	--	--	--	--	--	--	--	--	--	--	Butler and others, 1984
Extractable organic compounds, whole water, in milligrams per liter																	
Hydrocarbons	United States																
	California																
	Los Angeles	--	--	--	--	--		--	--	--	--	--	--	0.99	19.5	NR	Eganhoues and Kaplan. 1981
	San Francisco Bay	--	--	--	--	--	--	--	--	--	2.98	9.75	NR	1.606	10.83	NR	Fam and others, 1987
	Florida																
	Tallahassee	--	--	--	--	--	--	0.064	16.4	3.44	--	--	--	0.17	1.35	0.58	Hoffman and Qunin, 1987
	Pennsylvania																
	Philadelphia	--	--	--	--	--	--	--	--	--	--	--	--	2.18	5.3	3.69	Hunter and others, 1979
	Rhode Island	0.03	6.85	3.28	0.02	1.95	1.09	0.04	5.71	0.99	0.32	58.4	19.82	--	--	--	Hoffman and Qunin, 1987
	Cranston	2	6	NR	--	--	--	--	--	--	--	--	--	--	--	--	Hoffman and others, 1983
	Cranston	--	--	--	--	--	--	--	1.14	--	--	--	--	--	--	--	Hoffman and others, 1984
	Washington																
	Seattle	--	--	--	--	--	--	--	--	--	--	--	--	6	24	NR	Hoffman and Qunin, 1987

Table 7. Concentrations of detected semivolatile and volatile organic compounds in stormwater, suspended sediment, and bottom material, and (or) soil—*Continued*

Compound name	Location	Land use															Reference
		Highway			Residential			Commercial			Industrial			Unspecified			
		Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	
Extractable organic compounds, whole water, in milligrams per liter—*Continued*																	
Hydrocarbons	Summary	--	--	--	--	--	--	--	--	--	--	--	--	0.64	19.71	NR	Makepeace and others, 1995
	Japan																
	Tokyo	--	--	--	NR	NR	0.75	--	--	--	--	--	--	--	--	--	Yamane and others, 1990
	Spain																
	Madrid	--	--	--	--	--	--	--	--	--	--	--	--	NR	NR	1.154	Bomboi and Hernandez, 1991
	Switzerland	1.7	10	3.9	--	--	--	--	--	--	--	--	--	--	--	--	Hoffman and Qunin, 1987
	United Kingdom																
	NW London	--	--	--	--	--	--	--	--	--	--	--	--	0.36	1.1	NR	Gavens and others, 1983
Extractable organic compounds, filtered/centrigured water, in milligrams per liter																	
	United States																
	California																
	Los Angeles	--	--	--	--	--	--	--	--	--	--	--	--	0.302	0.49	NR	Eganhouse and Kaplan, 1981
	San Francisco Bay	--	--	--	--	--	--	--	--	--	1.29	4.32	NR	1.18	3.98	NR	Fam and others, 1987
	Pennsylvania																
	Philadelphia	--	--	--	--	--	--	--	--	--	--	--	--	0.67	0.16	0.4	Hunter and others, 1979
	Rhode Island																
	Cranston	ND	0.5	NR	--	--	--	--	--	--	--	--	--	--	--	--	Hoffman and others, 1983
	Cranston	--	--	--	--	--	--	--	0.0954	--	--	--	--	--	--	--	Hoffman and others, 1984
Extractable organic compounds, suspended sediment, in micrograms per gram																	
	United States																
	Rhode Island	8,750	51,800	24,800	15,700	59,800	42,000	16,400	34,000	24,800	61,900	507,000	211,000	--	--	--	Latimer and others, 1990
	Cranston	--	--	--	--	--	--	--	21,900	--	--	--	--	--	--	--	Hoffman and others, 1984
	Summary	--	--	--	--	--	--	--	--	--	--	--	--	8.75	507	NR	Makepeace and others, 1995

Table 7. Concentrations of detected semivolatile and volatile organic compounds in stormwater, suspended sediment, and bottom material, and (or) soil—*Continued*

Compound name	Location	Land use															Reference
		Highway			Residential			Commercial			Industrial			Unspecified			
		Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	
Extractable organic compounds, bottom material/soil, in micrograms per gram																	
Hydrocarbons	United States																
	Florida																
	Tampa	--	--	--	--	--	--	--	--	--	--	--	--	152	485	258	Brown and others, 1985
	Japan																
	Tokyo	--	--	--	--	--	--	--	--	--	--	--	--	NR	NR	69	Yamane and others, 1990
	United Kingdom																
	NW London	--	--	--	--	--	--	--	--	--	--	--	--	43	690	NR	Gavens and others, 1983
Extractable organic compounds, whole water, in milligrams per liter																	
Oil and grease	United States																
	Arizona																
	Maricopa County	--	--	--	<1	10	NR	<1.0	5	NR	<1	6	NR	<1	8	NR	Lopes and Fossum, 1995
	California																
	Richmond	4.2	89.09	16.05	0.57	24.55	3.92	1.98	--	10.9	1.49	21.11	7.26	2.1	71.97	7.87	Stenstrom and others, 1984
	Colorado																
	Boulder	--	--	--	1.7	25.9	NR	8.9	155	NR	--	--	--	--	--	--	Hoffman and Qunin, 1987
	Colorado Springs	--	--	--	<1	10	NR	<1.0	10	NR	<1	6	NR	--	--	--	von Guerard and Weiss, 1995
	Michigan																
	Southeast Michigan	--	--	--	--	--	--	--	--	--	--	--	--	ND	0.28	NR	Hoffman and Qunin, 1987
	North Carolina	--	--	--	--	--	--	--	--	--	<5	51	6	--	--	--	Line and others, 1997
	Texas																
	Austin	1.4	7.8	3.65	--	--	--	--	--	--	--	--	--	--	--	--	Wiland and Malima, 1976
	Dallas–Fort Worth	--	--	--	<1	19	2.2	<1.0	8	2.3	1	1.2	3.5	--	--	--	Baldys and others, 1998
	Washington																
	Seattle	146	480	NR	--	--	--	--	--	--	--	--	--	--	--	--	Zawlocki and others, 1980
	Wisconson																
	Milwaukee	1	20	NR	--	--	--	--	--	--	--	--	--	--	--	--	Gupta, 1981
	Summary	--	--	--	--	--	--	--	--	--	--	--	--	0.001	110	NR	Makepeace and others, 1995
	Summary	--	--	--	--	--	--	--	--	--	--	--	--	2.7	27	NR	Barrett and others, 1993

Table 7. Concentrations of detected semivolatile and volatile organic compounds in stormwater, suspended sediment, and bottom material, and (or) soil—*Continued*

Compound name	Location	Land use															Reference
		Highway			Residential			Commercial			Industrial			Unspecified			
		Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	
Extractable organic compounds, bottom material/soil, in micrograms per gram																	
Oil and grease	United States																
	Arizona																
	Maricopa County	--	--	--	--	--	--	--	--	--	--	--	--	<100	2,200	NR	Lopes and Fossum, 1995
Volatile organic compounds, whole water, in micrograms per liter																	
Benzene	United States																
	Arizona																
	Maricopa County	--	--	--	<0.2	<0.2	NR	<0.2	<0.2	NR	<0.2	<0.2	NR	--	--	--	Lopes and others, 1995
	Colorado																
	Colorado Springs	--	--	--	<0.2	<0.2	NR	<0.2	0.4	NR	<0.2	<0.2	NR	--	--	--	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<0.2	<0.2	NR	<0.2	0.8	0.12	<0.2	0.6	NR	--	--	--	Baldys and others, 1998
	Summary–NURP	--	--	--	--	--	--	--	--	--	--	--	--	3.5	13	NR	Cole and others, 1984
Bromodichloromethane	United States																
	Colorado																
	Colorado Springs	--	--	--	<0.2	<0.2	NR	<0.2	<0.2	NR	<0.2	<0.2	NR	--	--	--	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<0.2	0.2	NR	<0.2	<10	NR	<0.2	0.5	NR	--	--	--	Baldys and others, 1998
	Summary–NURP	--	--	--	--	--	--	--	--	--	--	--	--	NR	2	NR	Cole and others, 1984
	Summary–NPDES	--	--	--	--	--	--	--	--	--	--	--	--	<0.2	2.8	NR	Delzer and others, 1996
n-Butylbenzene	United States																
	Arizona																
	Maricopa County	--	--	--	<0.2	<0.2	NR	<0.2	<0.2	NR	<0.2	<0.2	NR	--	--	--	Lopes and others, 1995
	Colorado																
	Colorado Springs	--	--	--	<0.2	<0.2	NR	<0.2	0.4	NR	<0.2	<0.2	NR	--	--	--	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<0.2	0.2	NR	<0.2	<10	NR	<0.2	<10	NR	--	--	--	Baldys and others, 1998
Chlorobenzene	United States																
	Arizona																
	Maricopa County	--	--	--	<0.2	<0.2	NR	<0.2	<0.2	NR	<0.2	<0.2	NR	--	--	--	Lopes and others, 1995

Table 7. Concentrations of detected semivolatile and volatile organic compounds in stormwater, suspended sediment, and bottom material, and (or) soil—*Continued*

Compound name	Location	Land use															Reference
		Highway			Residential			Commercial			Industrial			Unspecified			
		Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	
Volatile organic compounds, whole water, in micrograms per liter—*Continued*																	
Chlorobenzene	Colorado																
	Colorado Springs	--	--	--	<0.2	<0.2	NR	<0.2	<0.2	NR	<0.2	<0.2	NR	--	--	--	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<0.2	<5	NR	<0.2	<10	NR	<0.2	<10	NR	--	--	--	Baldys and others, 1998
	Summary–NURP	--	--	--	--	--	--	--	--	--	--	--	--	1	10	NR	Cole and others, 1984
Chloroethene (vinyl chloride)	United States																
	Arizona																
	Maricopa County	--	--	--	<0.2	<0.2	NR	<0.2	<0.2	NR	<0.2	<0.2	NR	--	--	--	Lopes and others, 1995
	Colorado																
	Colorado Springs	--	--	--	--	--	--	<0.2	<0.2	NR	<0.2	<0.2	NR	--	--	--	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<0.2	<5	NR	<0.2	<10	NR	<0.2	110	NR	--	--	--	Baldys and others, 1998
1,2-Chloro toluene	United States																
	Texas																
	Dallas–Fort Worth	--	--	--	<0.2	<5	NR	<0.2	<10	NR	<0.2	0.2	NR	--	--	--	Baldys and others, 1998
1,4-Chloro toluene	United States																
	Texas																
	Dallas–Fort Worth	--	--	--	<0.2	<5	NR	<0.2	<10	NR	<0.2	0.2	NR	--	--	--	Baldys and others, 1998
Dibromochloro-methane (chloro dibromo-methane)	United States																
	Arizona																
	Maricopa County	--	--	--	<0.2	<0.2	NR	<0.2	<0.2	NR	<0.2	<0.2	NR	--	--	--	Lopes and others, 1995
	Colorado																
	Colorado Springs	--	--	--	<0.2	<0.2	NR	<0.2	<0.2	NR	<0.2	<0.2	NR	--	--	--	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<0.2	<0.2	NR	<0.2	<10	NR	<0.2	<10	NR	--	--	--	Baldys and others, 1998
	Summary–NURP	--	--	--	--	--	--	--	--	--	--	--	--	2	2	NR	Cole and others, 1984
Dibromo methane	United States																
	Arizona																
	Maricopa County	--	--	--	<0.2	<0.2	NR	<0.2	<0.2	NR	<0.2	<0.2	NR	--	--	--	Lopes and others, 1995

Table 7. Concentrations of detected semivolatile and volatile organic compounds in stormwater, suspended sediment, and bottom material, and (or) soil—*Continued*

Compound name	Location	Land use															Reference
		Highway			Residential			Commercial			Industrial			Unspecified			
		Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	
Volatile organic compounds, whole water, in micrograms per liter—*Continued*																	
Dibromo methane	Colorado																
	Colorado Springs	--	--	--	<0.2	<0.2	NR	<0.2	<0.2	NR	<0.2	<0.2	NR	--	--	--	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<0.2	0.2	NR	<0.2	0.4	NR	<0.2	0.7	NR	--	--	--	Baldys and others, 1998
1,1-Dichloro ethane	United States																
	Arizona																
	Maricopa County	--	--	--	<0.2	<0.2	NR	<0.2	<0.2	NR	<0.2	<0.2	NR	--	--	--	Lopes and others, 1995
	Colorado																
	Colorado Springs	--	--	--	<0.2	<0.2	NR	<0.2	<0.2	NR	<0.2	<0.2	NR	--	--	--	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<0.2	<5	NR	<0.2	<10	NR	<0.2	8.3	NR	--	--	--	Baldys and others, 1998
	Summary–NURP	--	--	--	--	--	--	--	--	--	--	--	--	1.5	3	NR	Cole and others, 1984
1,2-Dichloro ethane	United States																
	Arizona																
	Maricopa County	--	--	--	<0.2	<0.2	NR	<0.2	0.2	NR	<0.2	<0.2	NR	--	--	--	Lopes and others, 1995
	Colorado																
	Colorado Springs	--	--	--	<0.2	<0.2	NR	<0.2	0.2	NR	<0.2	<0.2	NR	--	--	--	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<0.2	<5	NR	<0.2	<10	NR	<0.2	<10	NR	--	--	--	Baldys and others, 1998
	Summary–NURP	--	--	--	--	--	--	--	--	--	--	--	--	NR	4	NR	Cole and others, 1984
1,1-Dichloro ethene (1,1-Dichloro ethylene)	United States																
	Arizona																
	Maricopa County	--	--	--	<0.2	<0.2	NR	<0.2	<0.2	NR	<0.2	<0.2	NR	--	--	--	Lopes and others, 1995
	Colorado																
	Colorado Springs	--	--	--	<0.2	<0.2	NR	<0.2	<0.2	NR	<0.2	<0.2	NR	--	--	--	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<0.2	5.9	NR	<0.2	<10	NR	<0.2	13	NR	--	--	--	Baldys and others, 1998
	Summary–NURP	--	--	--	--	--	--	--	--	--	--	--	--	1.5	4	NR	Cole and others, 1984
	Summary	--	--	--	--	--	--	--	--	--	--	--	--	1.5	4	NR	Makepeace and others, 1995

Table 7. Concentrations of detected semivolatile and volatile organic compounds in stormwater, suspended sediment, and bottom material, and (or) soil—*Continued*

Compound name	Location	Land use															Reference
		Highway			Residential			Commercial			Industrial			Unspecified			
		Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	
Volatile organic compounds, whole water, in micrograms per liter—*Continued*																	
cis-1,2-Dichloro ethene	United States																
	Arizona																
	Maricopa County	--	--	--	<0.2	<0.2	NR	<0.2	<0.2	NR	<0.2	<0.2	NR	--	--	--	Lopes and others, 1995
	Colorado																
	Colorado Springs	--	--	--	<0.2	<0.2	NR	<0.2	<0.2	NR	<0.2	<0.2	NR	--	--	--	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<0.2	<5	NR	<0.2	<10	NR	<0.2	1200	25.7	--	--	--	Baldys and others, 1998
trans-1,2-Dichloro ethene (*trans*-1,2-Dichloro ethylene)	United States																
	Arizona																
	Maricopa County	--	--	--	<0.2	<0.2	NR	<0.2	<0.2	NR	<0.2	<0.2	NR	--	--	--	Lopes and others, 1995
	Colorado																
	Colorado Springs	--	--	--	<0.2	<0.2	NR	<0.2	<0.2	NR	<0.2	<0.2	NR	--	--	--	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<0.2	<5	NR	<0.2	<10	NR	<0.2	27	NR	--	--	--	Baldys and others, 1998
	Summary–NURP	--	--	--	--	--	--	--	--	--	--	--	--	1	3	NR	Cole and others, 1984
	Summary	--	--	--	--	--	--	--	--	--	--	--	--	1	3	NR	Makepeace and others, 1995
Dichloro methane (methylene chloride)	United States																
	Arizona																
	Maricopa County	--	--	--	<0.2	<0.2	NR	<0.2	<20	NR	<0.2	0.2	NR	--	--	--	Lopes and others, 1995
	Colorado																
	Colorado Springs	--	--	--	--	--	--	<0.2	<0.2	NR	<0.2	<0.2	NR	--	--	--	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<0.2	0.8	NR	<0.2	<0.2	NR	<0.2	0.09	0.09	--	--	--	Baldys and others, 1998
	Summary–NURP	--	--	--	--	--	--	--	--	--	--	--	--	4	14.5	NR	Cole and others, 1984
	Summary–NPDES	--	--	--	--	--	--	--	--	--	--	--	--	<0.2	13	NR	Baldys and others, 1998
1,2-Dichloro propane	United States																
	Arizona																
	Maricopa County	--	--	--	<0.2	<0.2	NR	<0.2	<0.2	NR	<0.2	<0.2	NR	--	--	--	Lopes and others, 1995

Table 7. Concentrations of detected semivolatile and volatile organic compounds in stormwater, suspended sediment, and bottom material, and (or) soil—*Continued*

Compound name	Location	Land use															Reference
		Highway			Residential			Commercial			Industrial			Unspecified			
		Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	
Volatile organic compounds, whole water, in micrograms per liter—*Continued*																	
1,2-Dichloro propane	Colorado																
	Colorado Springs	--	--	--	<0.2	<0.2	NR	<0.2	<0.2	NR	<0.2	<0.2	NR	--	--	--	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<0.2	<5	NR	<0.2	<10	NR	<0.2	<10	NR	--	--	--	Baldys and others, 1998
	Summary–NPDES	--	--	--	--	--	--	--	--	--	--	--	--	NR	3	NR	Cole and others, 1984
1,3-Dichloro propene (isomer not specified)	Summary–NURP	--	--	--	--	--	--	--	--	--	--	--	--	1	2	NR	Cole and others, 1984
Ethenyl benzene (Styrene)	United States																
	Arizona	--	--	--	<0.2	<0.2	NR	<0.2	<20	NR	<0.2	0.5	NR	--	--	--	Lopes and others, 1995
	Maricopa County																
	Colorado																
	Colorado Springs	--	--	--	--	--	--	<0.2	<0.2	NR	<0.2	<0.2	NR	--	--	--	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<0.2	<5	NR	<0.2	0.6	NR	<0.2	<10	NR	--	--	--	Baldys and others, 1998
Ethylbenzene	United States																
	Arizona	--	--	--	<0.2	<0.2	NR	<0.2	<20	NR	<0.2	<0.2	NR	--	--	--	Lopes and others, 1995
	Maricopa County																
	Colorado																
	Colorado Springs	--	--	--	<0.2	<0.2	NR	<0.2	<0.2	NR	<0.2	<0.2	NR	--	--	--	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<0.2	0.6	NR	<0.2	0.6	NR	<0.2	1.5	NR	--	--	--	Baldys and others, 1998
	Summary–NURP	--	--	--	--	--	--	--	--	--	--	--	--	1	2	NR	Cole and others, 1984
	Summary–NPDES	--	--	--	--	--	--	--	--	--	--	--	--	<0.2	2	NR	Delzer and others, 1996
Isopropyl benzene	United States																
	Arizona	--	--	--	<0.2	<0.2	NR	<0.2	<20	NR	<0.2	<0.2	NR	--	--	--	Lopes and others, 1995
	Maricopa County																
	Colorado																
	Colorado Springs	--	--	--	<0.2	<0.2	NR	<0.2	<0.2	NR	<0.2	<0.2	NR	--	--	--	von Guerard and Weiss, 1995

Table 7. Concentrations of detected semivolatile and volatile organic compounds in stormwater, suspended sediment, and bottom material, and (or) soil—*Continued*

Compound name	Location	Land use															Reference
		Highway			Residential			Commercial			Industrial			Unspecified			
		Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	
Volatile organic compounds, whole water, in micrograms per liter—*Continued*																	
Isopropyl benzene	Texas																
	Dallas–Fort Worth	--	--	--	<0.2	--	NR	<0.2	<10	NR	<0.2	4.6	NR	--	--	--	Baldys and others, 1998
1-Isopropyl-4-methyl benzene (P-isopropyltoluene)	United States																
	Arizona																
	Maricopa County	--	--	--	<0.2	<0.2	NR	<0.2	<20	NR	<0.2	0.7	NR	--	--	--	Lopes and others, 1995
	Colorado																
	Colorado Springs	--	--	--	<0.2	<0.2	NR	<0.2	<10	NR	<0.2	<10	NR	--	--	--	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<0.2	<5	NR	<0.2	0.9	NR	<0.2	0.2	NR	--	--	--	Baldys and others, 1998
Methyl benzene (Toluene)	United States																
	Arizona																
	Maricopa County	--	--	--	<0.2	<0.2	NR	<1	0.2	NR	<0.2	0.3	NR	--	--	--	Lopes and others, 1995
	Colorado																
	Colorado Springs	--	--	--	<0.2	1.2	NR	<0.2	1.7	NR	<0.2	0.4	NR	--	--	--	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<0.2	1.8	0.08	<0.2	2.4	0.25	<0.2	1.8	0.11	--	--	--	Baldys and others, 1998
	Summary–NURP	--	--	--	--	--	--	--	--	--	--	--	--	9	12	NR	Cole and others, 1984
	Summary–NPDES	--	--	--	--	--	--	--	--	--	--	--	--	<0.2	6.6	NR	Delzer and others, 1996
2-Methoxy-2-methyl-propane (Methyl *tert*-butyl ether)	United States																
	Alabama																
	Birmingham	--	--	--	--	--	--	--	--	--	--	--	--	<0.2	1.9	NR	Delzer and others, 1996
	Arizona																
	Maricopa County	--	--	--	<0.2	<0.2	NR	<5	2.5	NR	<0.2	0.3	NR	--	--	--	Lopes and others, 1995
	Phoenix	--	--	--	--	--	--	--	--	--	--	--	--	<0.2	2.5	NR	Delzer and others, 1996
	Colorado																
	Colorado Springs	--	--	--	--	--	--	--	--	--	--	--	--	<0.2	3	NR	Delzer and others, 1996
	Denver	--	--	--	--	--	--	--	--	--	--	--	--	<0.2	1.5	NR	Delzer and others, 1996

Table 7. Concentrations of detected semivolatile and volatile organic compounds in stormwater, suspended sediment, and bottom material, and (or) soil—*Continued*

Compound name	Location	Land use															Reference
		Highway			Residential			Commercial			Industrial			Unspecified			
		Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	
Volatile organic compounds, whole water, in micrograms per liter—*Continued*																	
2-Methoxy-2-methyl-propane (Methyl *tert*-butyl ether)	Georgia																
	Atlanta	--	--	--	--	--	--	--	--	--	--	--	--	<0.2	1.5	NR	Delzer and others, 1996
	Louisana																
	Baton Rouge	--	--	--	--	--	--	--	--	--	--	--	--	<0.2	0.4	NR	Delzer and others, 1996
	Texas																
	Dallas–Fort Worth	--	--	--	<1	<25	NR	<1	8.7	1.2	<0.2	5.4	NR	--	--	--	Baldys and others, 1998
	San Antonio	--	--	--	--	--	--	--	--	--	--	--	--	<0.2	1.8	NR	Delzer and others, 1996
	Summary–NPDES	--	--	--	--	--	--	--	--	--	--	--	--	<0.2	8.7	NR	Delzer and others, 1996
Naphthalene	United States																
	Colorado																
	Colorado Springs	--	--	--	<0.2	0.4	NR	<0.2	--	NR	<0.2	1.1	NR	--	--	--	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<0.2	0.6	NR	<0.2	<5	NR	<0.2	1.3	NR	--	--	--	Baldys and others, 1998
	Summary–NPDES	--	--	--	--	--	--	--	--	--	--	--	--	<0.2	5.1	NR	Delzer and others, 1996
n-Propyl benzene	United States																
	Arizona																
	Maricopa County	--	--	--	<0.2	<0.2	NR	<0.2	<0.2	NR	<0.2	<0.2	NR	--	--	--	Lopes and others, 1995
	Colorado																
	Colorado Springs	--	--	--	--	--	--	<0.2	<0.2	NR	<0.2	<0.2	NR	--	--	--	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<0.2	<5	NR	<0.2	<10	NR	<0.2	0.5	NR	--	--	--	Baldys and others, 1998
1,1,2,2-Tetra chloro ethane	United States																
	Arizona																
	Maricopa County	--	--	--	<0.2	<0.2	NR	<0.2	<0.2	NR	<0.2	<0.2	NR	--	--	--	Lopes and others, 1995
	Colorado																
	Colorado Springs	--	--	--	--	--	--	<0.2	<0.2	NR	<0.2	<0.2	NR	--	--	--	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<0.2	<5	NR	<0.2	<10	NR	<0.2	<01	NR	--	--	--	Baldys and others, 1998
	Summary–NURP	--	--	--	--	--	--	--	--	--	--	--	--	2	3	NR	Cole and others, 1984

Table 7. Concentrations of detected semivolatile and volatile organic compounds in stormwater, suspended sediment, and bottom material, and (or) soil—*Continued*

Compound name	Location	Land use															Reference
		Highway			Residential			Commercial			Industrial			Unspecified			
		Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	
Volatile organic compounds, whole water, in micrograms per liter—*Continued*																	
Tetrachloro ethene (Tetrachlor- oethylene)	United States																
	Arizona																
	Maricopa County	--	--	--	<0.2	<0.2	NR	<0.2	<0.2	NR	<0.2	<0.2	NR	--	--	--	Lopes and others, 1995
	Colorado																
	Colorado Springs	--	--	--	--	--	--	<0.2	<0.2	NR	<0.2	<0.2	NR	--	--	--	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<0.2	<5	NR	<0.2	<10	NR	<0.2	42	1.2	--	--	--	Baldys and others, 1998
	Summary–NURP	--	--	--	--	--	--	--	--	--	--	--	--	4.5	43	NR	Cole and others, 1984
	Summary–NPDES	--	--	--	--	--	--	--	--	--	--	--	--	<0.2	42	NR	Delzer and others, 1996
Tetrachloro methane (Carbon tetra chloride)	United States																
	Arizona																
	Maricopa County	--	--	--	<0.2	<0.2	NR	<0.2	<0.2	NR	<0.2	<0.2	NR	--	--	--	Lopes and others, 1995
	Colorado																
	Colorado Springs	--	--	--	<0.2	<0.2	NR	<0.2	<0.2	NR	<0.2	<0.2	NR	--	--	--	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<0.2	<5	NR	<0.2	<10	NR	<0.2	<10	NR	--	--	--	Baldys and others, 1998
	Summary–NURP	--	--	--	--	--	--	--	--	--	--	--	--	1	2	NR	Cole and others, 1984
Tribromo methane (Bromo form)	United States																
	Arizona																
	Maricopa County	--	--	--	<0.2	<0.2	NR	<0.2	<0.2	NR	<0.2	<0.2	NR	--	--	--	Lopes and others, 1995
	Colorado																
	Colorado Springs	--	--	--	<0.2	<0.2	NR	<0.2	<0.2	NR	<0.2	<0.2	NR	--	--	--	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<0.2	<5	NR	<0.2	<10	NR	<0.2	<10	NR	--	--	--	Baldys and others, 1998
	Summary–NURP	--	--	--	--	--	--	--	--	--	--	--	--	NR	1	NR	Cole and others, 1984
1,1,1-Trichloro ethane	United States																
	Arizona																
	Maricopa County	--	--	--	<0.2	<0.2	NR	<0.2	<0.2	NR	<0.2	<0.2	NR	--	--	--	Lopes and others, 1995
	Colorado																
	Colorado Springs	--	--	--	--	--	--	<0.2	0.7	NR	<0.2	<0.2	NR	--	--	--	von Guerard and Weiss, 1995

Table 7. Concentrations of detected semivolatile and volatile organic compounds in stormwater, suspended sediment, and bottom material, and (or) soil—*Continued*

Compound name	Location	Land use															Reference
		Highway			Residential			Commercial			Industrial			Unspecified			
		Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	
Volatile organic compounds, whole water, in micrograms per liter—*Continued*																	
1,1,1-Trichloro ethane	Texas																
	Dallas–Fort Worth	--	--	--	<0.2	<0.2	NR	<0.2	0.2	NR	<0.2	5.4	<0.24	--	--	--	Baldys and others, 1998
	Summary–NURP	--	--	--	--	--	--	--	--	--	--	--	--	1.6	10	NR	Cole and others, 1984
1,1,2-Trichloro ethane	United States																
	Arizona																
	Maricopa County	--	--	--	<0.2	<0.2	NR	<0.2	<0.2	NR	<0.2	<0.2	NR	--	--	--	Lopes and others, 1995
	Colorado																
	Colorado Springs	--	--	--	--	--	--	<0.2	<0.2	NR	<0.2	<0.2	NR	--	--	--	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<0.2	<5	NR	<0.2	<10	NR	<0.2	<0.2	NR	--	--	--	Baldys and others, 1998
	Summary–NURP	--	--	--	--	--	--	--	--	--	--	--	--	2	3	NR	Cole and others, 1984
Trichloro ethene (Trichloro ethylene)	United States																
	Arizona																
	Maricopa County	--	--	--	<0.2	<0.2	NR	<0.2	<0.2	NR	<0.2	<0.2	NR	--	--	--	Lopes and others, 1995
	Colorado																
	Colorado Springs	--	--	--	--	--	--	<0.2	<0.2	NR	<0.2	<0.2	NR	--	--	--	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<0.2	0.2	NR	<0.2	<10	NR	<0.2	28	1.3	--	--	--	Baldys and others, 1998
	Summary–NURP	--	--	--	--	--	--	--	--	--	--	--	--	0.3	10	NR	Cole and others, 1984
	Summary	--	--	--	--	--	--	--	--	--	--	--	--	0.3	10	NR	Makepeace and others, 1995
Trichloro fluoro methane	United States																
	Arizona																
	Maricopa County	--	--	--	<0.2	<0.2	NR	<0.2	<0.2	NR	<0.2	<0.2	NR	--	--	--	Lopes and others, 1995
	Colorado																
	Colorado Springs	--	--	--	--	--	--	<0.2	<0.2	NR	<0.2	<0.2	NR	--	--	--	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<0.5	<13	NR	<0.5	<25	NR	<0.2	<25	NR	--	--	--	Baldys and others, 1998
	Summary–NURP	--	--	--	--	--	--	--	--	--	--	--	--	0.6	0.27	NR	Cole and others, 1984

Table 7. Concentrations of detected semivolatile and volatile organic compounds in stormwater, suspended sediment, and bottom material, and (or) soil—*Continued*

Compound name	Location	Land use															Reference
		Highway			Residential			Commercial			Industrial			Unspecified			
		Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	
Volatile organic compounds, whole water, in micrograms per liter—*Continued*																	
Trichloro methane Chloroform	United States																
	Arizona																
	Maricopa County	--	--	--	<0.2	<0.2	NR	<0.2	<0.2	NR	<0.2	<0.2	NR	--	--	--	Lopes and others, 1995
	Colorado																
	Colorado Springs	--	--	--	<0.2	<0.2	NR	<0.2	2.1	NR	<0.2	<0.2	NR	--	--	--	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<0.2	0.7	0.06	<0.2	1.1	NR	<0.2	0.7	0.15	--	--	--	Baldys and others, 1998
	Summary–NURP	--	--	--	--	--	--	--	--	--	--	--	--	0.2	12	NR	Cole and others, 1984
	Summary–NPDES	--	--	--	--	--	--	--	--	--	--	--	--	<0.2	7	NR	Delzer and others, 1996
1,1,2-Trichloro-1,2,2-trifluoro ethane	United States																
	Texas																
	Dallas–Fort Worth	--	--	--	<0.2	0.4	NR	<0.2	<10	NR	<0.2	<0.2	NR	--	--	--	Baldys and others, 1998
1,2,4-Trimethyl benzene	United States																
	Colorado																
	Colorado Springs	--	--	--	<0.2	0.9	NR	<0.2	2.8	NR	<0.2	0.4	NR	--	--	--	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<0.2	2	NR	<0.2	0.4	NR	<0.2	15	NR	--	--	--	Baldys and others, 1998
1,3,5-Trimethyl benzene	United States																
	Colorado																
	Colorado Springs	--	--	--	<0.2	<0.2	NR	<0.2	0.9	NR	<0.2	<0.2	--	--	--	--	von Guerard and Weiss, 1995
	Texas																
	Dallas–Fort Worth	--	--	--	<0.2	<0.2	NR	<0.2	<10	NR	<0.2	6.3	NR	--	--	--	Baldys and others, 1998
Trimethyl benzene	Summary–NPDES	--	--	--	--	--	--	--	--	--	--	--	--	<0.2	15	NR	Delzer and others, 1996
Dimethyl benzene (total xylenes) (isomer not specified)	United States																
	Arizona																
	Maricopa County	--	--	--	<0.2	<0.2	NR	<1	0.3	NR	<0.2	0.2	NR	--	--	--	Lopes and others, 1995
	Colorado																
	Colorado Springs	--	--	--	<0.2	1.5	NR	<0.2	4.4	NR	<0.2	0.7	NR	--	--	--	von Guerard and Weiss, 1995

Table 7. Concentrations of detected semivolatile and volatile organic compounds in stormwater, suspended sediment, and bottom material, and (or) soil—*Continued*

Compound name	Location	Land use															Reference
		Highway			Residential			Commercial			Industrial			Unspecified			
		Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	
Volatile organic compounds, whole water, in micrograms per liter—*Continued*																	
Dimethyl benzene (total xylenes) (isomer not specified)	Texas																
	Dallas–Fort Worth	--	--	--	<0.2	3.7	0.12	<0.2	1.9	0.23	<0.2	<0.2	0.43	--	--	--	Baldys and others, 1998
	Summary–NPDES	--	--	--	--	--	--	--	--	--	<0.2	10	--	<0.2	15	NR	Delzer and others, 1996
Volatile organic compounds, suspended sediment, in micrograms per gram																	
Benzene	United States																
	New York																
	Love Canal	--	--	--	--	--	--	--	--	--	--	--	--	NR	0.232	NR	Makepeace and others, 1995

Chapter 8. Assessing Biological Effects from Highway-Runoff Constituents

By DENNY R. BUCKLER and GREGORY E. GRANATO

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Assessing Biological Effects from Highway-Runoff Constituents

By Denny R. Buckler *and* Gregory E. Granato

Abstract

Increased emphasis on evaluation of nonpoint-source pollution has intensified the need for techniques that can be used to discern the toxicological effects of complex chemical mixtures. In response, the use of biological assessment techniques is receiving increased regulatory emphasis. When applied with documented habitat assessment and chemical analysis, these techniques can increase our understanding of the influence of environmental contaminants on the biological integrity and ecological function of aquatic communities.

The contaminants of greatest potential concern in highway runoff are those that arise from highway construction, maintenance, and use. The major contaminants of interest are deicers; nutrients; metals; petroleum-related organic compounds, such as polycyclic aromatic hydrocarbons (PAHs), benzene, toluene, ethylbenzene, and xylene (BTEX), and methyl *tert*-butyl ether (MTBE); sediment washed off the road surface; and agricultural chemicals used in highway maintenance.

Hundreds, if not thousands, of biological endpoints (measurable responses of living organisms) may be either directly or associatively affected by contaminant exposure. Measurable effects can occur throughout ecosystem processes across the wide range of biological complexity, ranging from responses at the biochemical level to the community level.

The challenge to the environmental scientist is to develop an understanding of the relationship of effects at various levels of biological organization in order to determine whether a causal relationship exists between chemical exposure and substantial ecological impairment. This report provides a brief history of the evolution of biological assessment techniques, a description of the major classes of contaminants that are of particular interest in highway runoff, an overview of representative biological assessment techniques, and a discussion of data-quality considerations.

Published reports with a focus on the effects of highway runoff on the local ecosystem were reviewed to provide information on (1) the suitability of the existing data for a quantitative national synthesis, (2) the methods available to study the effects of highway runoff on local ecosystems, and (3) the potential for adverse effects on the roadside environment and receiving waters. Although many biological studies have been done, the use of different methods and a general lack of sufficient documentation precludes a quantitative national synthesis on the basis of the existing data. The Federal Highway Administration, the U.S. Environmental Protection Agency, the U.S. Geological Survey, the Intergovernmental Task Force on Monitoring Water Quality, and the National Resources Conservation Service all have developed and documented methods for assessing the effects of contaminants on ecosystems in receiving waters. These published methods can be used to formulate a set of protocols to provide consistent information from highway-runoff studies.

Review of the literature indicates (qualitatively) that highway runoff (even from highways with high traffic volume) may not usually be acutely toxic. Tissue analysis and community assessments, however, indicate effects from highway-runoff sediments near discharge points (even from sites near highways with relatively low traffic

volumes). At many sites, elevated concentrations of highway-runoff constituents were measured in tissues of species associated with aquatic sediments. Community assessments also indicate decreases in the diversity and productivity of aquatic ecosystems at some sites receiving highway runoff. These results are not definitive, however, and depend on many site-specific criteria that were not sufficiently documented in most of the studies reviewed.

INTRODUCTION

Biological effects are an important component of studies of the effects of highway runoff on water quality. The sensitivity of biota to changes in water quality, coupled with a high degree of public interest in their welfare, as well as legal requirements, make consideration of biological effects a high priority. The Clean Water Act (Federal Water Pollution Control Act of 1972, 33 USC §§ 1251 et seq.) and its amendments and revisions represent the primary Federal legislative actions directed toward the protection and restoration of the physical, chemical, and biological integrity of the Nation's waters. More recently, the States have been integrating biological criteria into the development and enforcement of their water-quality standards (Davis and others, 1996). The intended use of biological criteria is to evaluate the effects of anthropogenic activities on the biological integrity and ecological function of aquatic communities. Because of these factors, biological assessment of the effects of nonpoint-source pollution has gained increased regulatory and scientific attention in recent years.

Background

The complexity of mixtures of chemical contaminants has, in part, lead to an increased regulatory emphasis on biological endpoints (using the responses of living organisms as indicators of contaminant presence and effects). Chemical measurements commonly do not allow prediction of the complex interactions that can occur in biological organisms. Scientific advances in the development and application of biological evaluation procedures also have lead to increased use of biological endpoints. These advances are a result of technological improvements in the area of environmental toxicology and chemistry. The early history of aquatic toxicology was a period in which the biological responses of organisms in the field were used to assess the extent of aquatic pollution. During this period, analytical chemistry methods for measuring environmentally relevant concentrations of contaminants were available for relatively few compounds. At this stage in the development of the science, the organism provided the most sensitive measure of environmental contaminants.

Over the past 15 to 20 years, major advances in analytical chemistry have made it possible to measure very low concentrations of many contaminants in environmental samples. These technological advances stimulated a period in which the regulation and monitoring of environmental contaminants were driven largely by the measurement of chemical concentrations in water, soil, or organisms. Water-quality criteria were developed for a wide range of contaminants by using information from laboratory toxicity studies to estimate acceptable environmental concentrations, but enforcement of water-pollution regulations was based largely upon the measurement of chemicals. During this period, efforts were made to develop models to predict biological effects from highway-runoff chemistry data and regulatory drinking water and aquatic life standards (Horner and Mar, 1985). It was recognized, however, that these planning-level estimates were specific to the area for which they were developed. Monitoring and assessment programs also were based on measuring chemical residues in water, sediments, and biota. Although these individual chemical-based approaches have served as the foundation for advancements in point-source pollution control, they also have drawn attention to the difficulties associated with collecting, analyzing, and interpreting the significance of complex mixtures of contaminants that can now be measured.

The most recent trend in environmental pollution assessment has been to return to the use of biological responses as measures of pollutant effects. However, current approaches usually are coupled tightly with analytical chemistry for measuring pollutant exposure. This integration of the biological and physical sciences is particularly important in the arena of nonpoint-source pollution, where the goal is to understand the environmental significance of complex mixtures of diverse arrays of contaminants. In this manner, the scientist or regulator can take advantage of current capabilities to measure low levels of myriad environmental contaminants, while relying upon data from the biota to integrate the cumulative biological effects of such exposure.

Purpose and Scope

The purpose of this report is to survey tools and techniques commonly used for the assessment of the biological effects from contaminants in stormwater runoff that are available for the study of highway runoff, and other sources of nonpoint-source pollution. This report describes the types of contaminants that are of particular interest to the study of highway runoff, discusses an array of biological assessment techniques that are appropriate for use in evaluating the effects of these contaminants, and evaluates data-quality issues for biological assessment techniques. A review of reports that focus on the effects of highway runoff on the local ecosystems provides information on (1) the suitability of the existing data for a quantitative national synthesis, (2) available methods to study the effects of highway runoff on local ecosystems, and (3) information about the potential for adverse effects on the roadside environment and receiving waters.

FACTORS FOR ASSESSING BIOLOGICAL EFFECTS

Factors of particular interest in the study of highway runoff are logically those that arise from construction, maintenance, and use of the highway system. Asphalt, concrete, rock, and steel are the primary highway-construction materials. Road oils, deicers, abrasives, solvents, paints, and vegetation-control agents are the primary highway-maintenance materials. Highway use results in the introduction of metals, fuels, combustion products, and toxic chemical spills as potential environmental contaminants. Finally, physical habitat disturbance resulting from construction, maintenance, and use of the highway system may also affect biota. General descriptions of the major classes of the factors associated with these activities are provided below.

Contaminants of Interest

Many of the contaminants normally associated with runoff from the Nation's highways have the potential for biological effects. Different contaminants will have varying biological effects depending on the physical and chemical properties of each constituent, the concentrations found in an environmental system, the sensitivities of organisms to adverse physical and chemical characteristics of the runoff, and the ability of the system and the individual organism to assimilate a given constituent or a given mixture of constituents. Highway-runoff contaminants of particular interest throughout the United States include deicers, nutrients, metals, industrial/urban-organic chemicals, sediment, and agricultural chemicals from industrial, commercial, residential, agricultural, and highway sources.

Deicers are chemicals used to remove ice and snow from roadways in the winter. Typically, salts such as sodium chloride and(or) calcium chloride are used. However, other compounds such as calcium magnesium acetate (CMA) are sometimes used in areas where the inorganic salts are a perceived problem. Loads of deicing chemicals per area of the road surface can be substantial on an annual basis, and they can change the geochemical conditions normally found in local receiving waters (Granato, 1996; Bricker, 1999).

Nutrients are constituents that are assimilated by organisms and that promote growth. In water-quality studies, the term generally applies to a number of measured constituents that contain nitrogen or phosphorus. Depending on the geochemistry of the runoff and the receiving water, nitrogen may occur as a nutrient in water as nitrite or nitrate anions, the ammonium cation, and(or) a number of natural organic compounds (Hem, 1992; Bricker, 1999). Phosphorus may occur as phosphoric acid, anionic forms including orthophosphate, or as a component of organic compounds. Phosphorus is generally believed to be the limiting nutrient in many aquatic systems because natural geochemical processes (Hem, 1992; Bricker, 1999) more readily control phosphorus compounds. Loads of these nutrients and resultant effects on aquatic biota from stormwater can be substantial (Grizzard and others, 1980).

Metals are considered ubiquitous contaminants today, but were much less abundant on the surface before man began to disturb the Earth’s crust. There are a variety of biological mechanisms for sequestering and managing metals in the body because many metals are essential nutrients. The blood and tissues have a variety of carrier proteins, such as metallothionein (Suzuki, 1982), that regulate required inorganic nutrients, and metals generally show less tendency to accumulate in the body than many organic compounds. Metals, however, can pose important environmental concerns. One mechanism by which inorganic forms of metals tend to cause toxicological problems is known as isomorphic substitution—a process through which one element substitutes for another but may not be able to serve the same function. Organometallics, such as methylmercury, may interact with organisms in a manner that is similar to organic contaminants. Highway-related sources of metals include mobilization by excavation; vehicle wear; combustion of petroleum products; historic fuel additives, such as lead (Pb); maintenance materials, such as salts and deicers; abrasives; and catalytic-converter emissions.

Organic compounds in highway and road runoff that are derived from exhaust, fuel, lubricants, asphalt, and other synthetic chemicals are recognized as an environmental concern in many highway- and urban-runoff studies conducted over the last 20 years (Lopes and Dionne, 1998). These compounds are generally classified as semivolatile organic compounds (SVOCs) and volatile organic compounds (VOCs). Petroleum hydrocarbons, oil and grease, and polycyclic aromatic hydrocarbons (PAHs) are generally classified as SVOCs. Mono-aromatic petroleum compounds and the fuel additive Methyl *tert*-butyl ether are generally classified as VOCs.

Polycyclic aromatic hydrocarbons (PAHs) are a group of organic compounds that can be formed during incomplete combustion of a variety of organic substances, including petroleum. Although some PAHs are manufactured for specific uses, such as in pharmaceuticals, the source of most environmental PAHs is from natural or anthropogenic combustion. This group of compounds includes more than 100 individual chemicals that are usually found as complex mixtures in the environment (Agency for Toxic Substances and Disease Registry, 1995). As their name implies, chemicals in this group are composed of more than one aromatic ring. PAHs are of relatively low molecular weight and generally are volatile and relatively hydrophobic, with a tendency to accumulate on airborne particulate matter or to associate with aquatic sediments. Common examples of individual compounds in this group include naphthalene, anthracene, phenanthrene, chrysene, and benzo(a)pyrene.

The mono-aromatic compounds benzene, toluene, ethylbenzene, and xylene (BTEX) are common constituents of crude oil and petroleum products. They also are produced as industrial solvents and as precursors for pesticides, plastics, and synthetic fibers (Harwood and Gibson, 1997). The primary sources of BTEX compounds relative to highway pollution are from spills and leakage of gasoline and other petroleum products. Similar to the PAHs, the BTEX compounds generally are volatile and relatively hydrophobic, but tend to be associated with storm-runoff sediments and ground-water contamination.

Methyl *tert*-butyl ether (MTBE) is an oxygenate compound that is added to gasoline to improve combustion and to reduce the levels of carbon monoxide emissions from automobiles. The total emission of MTBE from all sources into the environment in the U.S. in 1992 was estimated to be 3 million pounds (U.S. Environmental Protection Agency, 1994). Levels can be expected to increase as a result of the 1990 Amendments to the Clean Air Act, which require the addition of oxygenates to gasoline sold in urban areas that are not meeting target levels for carbon monoxide emissions. In a summary of urban stormwater in 16 cities and metropolitan areas, MTBE was the 7th most frequently detected VOC. MTBE was detected in about 7 percent of the 592 stormwater samples collected from the 16 cities and was detected at a rate of from 22 to 66 percent of samples taken in places where MTBE was in current use as a gasoline additive (Delzer and others, 1996). MTBE is quite volatile and would be expected to dissipate rapidly from soil or water surfaces (U.S. Environmental Protection Agency, 1993a). However, MTBE is about 40 times more soluble than the BTEX compounds and is less biodegradable than many common gasoline hydrocarbons. As a result, it is expected to be comparatively more persistent in ground water and in the shallow, fast-moving streams that are typical of urban and highway-runoff conveyances (Delzer and others, 1996). MTBE has been found in ground-water supplies at levels in excess of 200 milligrams per liter (mg/L) in some locations (U.S. Environmental Protection Agency, 1993b), posing a potential exposure risk to humans and aquatic life.

Sediment comprises inorganic and organic material and can be transported by, suspended in, or deposited by stormwater. Suspended sediment is generally considered to be one of the most substantial nonpoint-source contaminants (Waters, 1995; Crawford and Mansue, 1996). Studies across the Nation have documented that sediment can have large effects on the biology of receiving waters, ranging from the burial of fish eggs to the destruction of the entire aquatic food chain (Waters, 1995; Simmons, 1993). Many contaminants, including some metal ions, organic chemicals, and nutrients, are transported by sediment (Crawford and Mansue, 1996). Sediments have been associated with the destruction of aquatic habitat and a decrease in aquatic populations. Even relatively moderate sediment loading to an otherwise healthy stream can reduce the variety and abundance of aquatic life (Waters, 1995; Crawford and Mansue, 1996; Simmons, 1993). Sediment loads can also cause engineering problems by decreasing the capacity of channels and impoundments.

Although they receive only limited use in vegetation control for highway maintenance, herbicides and other agricultural chemicals are frequent components of nonpoint-source pollution. When a specific product is used intentionally for highway-maintenance activities, it is a relatively straightforward process to estimate the risk associated with the use of that product. Regardless of the actual sources, herbicides, pesticides, and other agricultural products frequently occur in surface-water runoff and should be given consideration in evaluations of nonpoint-source pollution.

Other Factors

Although outside the scope of this report, other factors may influence the health and abundance of individual organisms and biotic communities at a study site, such as spills of hazardous substances, physical habitat disturbance, and thermal pollution. Other factors of particular interest to the study and interpretation of apparent biological effects of highway-runoff quality are contamination and habitat disturbance caused by periodic highway construction and maintenance, hazardous substance spills, and other construction/development in the study area. Knowledge of the potential biological effects caused by these factors is important to assess results of a study to be included in a national or regional characterization of highway runoff. The effects caused by a spill or habitat disturbance from upstream development could potentially overshadow effects caused by highway-runoff discharges into receiving waters.

The high concentrations of chemicals caused by episodic spills of fuel, lubricants, coolant, and other chemicals are not normally considered to be characteristic of highway-runoff constituent concentrations. Spills, however, should be documented because a spill can affect measured water quality, and can affect biota in receiving waters. Unlike vehicle emissions or chemicals that are intentionally applied during highway construction and maintenance, the entry of contaminants into the environment from spills of hazardous substances is much less predictable. Large amounts of a wide array of hazardous materials are routinely transported on the Nation’s highways. Examples include fuels, agricultural chemicals, industrial compounds, and hazardous-waste products. About 2,400 chemical spills on the Nation's highways are reported to Federal authorities each year (National Response Center, 1999), and about 7,000,000 traffic accidents are reported by police to the National Highway Safety Administration each year (Cerrelli, 1998, 1997). McNeill and Olley (1998) noted the effects of small "routine spills"caused by traffic accidents on highway-runoff water quality, and upon stream biota at sites in their study area, and concluded that runoff best-management practice (BMP) structures should be designed to retain these small spills for cleanup. Because both minor and major spills can bias interpretations about the quality of highway runoff and the effects of highway runoff on biota, such events should be tracked and noted as explanatory variables for the data set collected at a given site. Once an accident occurs, the volume and types of contaminants that were released can usually be readily defined and appropriate measures for evaluating the nature and extent of the problem can be identified.

Although it is not specifically an environmental-contaminant concern, the potential for physical habitat disturbance in a highway-runoff study area is of great interest for site selection. Sedimentation and soil erosion, loss and changes in vegetation, physical habitat alteration, and disturbance of wildlife transport corridors are all potential concerns. Some of the most substantial biological changes caused by development are directly or indirectly related to altered hydrology. Despite efforts to use BMPs to attenuate the hydrologic effects of development, increased peak flows and more flashy runoff will cause physical modifications to the channel shape, bed substrate, and banks of receiving waters, with corresponding effects on aquatic habitat and biota. Loss of forest canopy, increases in paved area, and shallow and (or) muddy detention areas also may cause thermal pollution problems, which can exacerbate chemical stressors on aquatic organisms in receiving waters. All these factors will vary from site to site, and will affect interpretation of cause-and-effect relations between highway-runoff quality and the health and abundance of aquatic organisms in receiving waters.

BIOLOGICAL ASSESSMENT TECHNIQUES

The presence of measurable quantities of contaminants in the environment is an indicator of potential exposure. Contaminant presence alone, however, does not necessarily indicate the occurrence of deleterious biological effects. Measures of exposure must be linked to measures of effect in order to establish a causal relationship. Biological responses to contaminant exposure are the result of a progression of events that can be described as follows: The contaminant must first be released into the environment. This may be the result of intentional discharge, emission, or application. Contaminant input may also be due to unintentional releases such as spills, leakages, or other accidents. A variety of physical, chemical, and biological processes then come into play to determine the ultimate distribution, longevity, availability, and chemical form of the contaminant in the environment. The first interaction of the contaminant with an organism occurs at the biomolecular level. If the degree of exposure is sufficient to elicit a biochemical response, then there is the potential for effects at the tissue, organ, whole-organism, population, and community levels of biological organization.

Each level of biological organization has a resiliency, or assimilative capacity, that allows it to mitigate injury. In order for a contaminant to elicit an effect at the higher levels of organization (e.g., population or community levels), it must first exceed the ability of the lower levels to attenuate the response. For example, a 10 percent inhibition of an enzyme may or may not cause an observable response at the tissue, organ, or whole-organism level. The loss of a finite number of individuals may or may not be observable as an adverse effect on population status for some species. And finally, due to redundancy of function, the decline or loss of some populations may, or may not, observably affect the community if other species are able to fill those functional voids.

These relationships and interdependencies provide both promise and challenge to the use of biological responses as indicators of environmental health. Biochemical changes are the first biological responses that occur, therefore, they may be useful as early warning signals of contaminant problems. Effects at the biochemical level, however, may or may not result in measurable responses at the higher levels of biological organization. At the other end of the spectrum, many different physical, chemical, or ecological stressors can elicit apparently similar changes at the community level. As a result, it is often difficult to establish cause and effect at the higher levels of organization. The challenge facing the environmental scientist is to use the comparative specificity of responses at the lower levels of biological organization to help establish causal relationships with the more ecologically meaningful community levels. Measurement of effects at several levels of biological organization can provide a better understanding of the significance of a contaminant's presence, and can help determine whether a causal relationship exists.

In the remainder of this section, a variety of biological assessment techniques are discussed. No attempt has been made to provide an exhaustive review. Literally hundreds, if not thousands, of biological endpoints may be either directly, or associatively, affected by contaminant exposure. The techniques discussed below should be viewed simply as examples of biological tools that have been shown to be useful in evaluating environmental contaminants. Each technique has advantages and drawbacks that must be carefully considered in terms of its suitability to meet information needs for local, regional, and national studies. A number of the techniques are applicable to on-site use in receiving waters, whereas others are applied in the laboratory to samples collected in the field. In most situations, habitat assessments and analytical chemistry determinations should be made and documented in concert with biological measures to maximize opportunities for establishing cause and effect.

Biochemical, Physiological, and Histological Techniques

The principle underlying the use of subcellular biological indicators is that in order to elicit a toxic response, a chemical must first reach and interact with its biomolecular site of action. Whether that receptor site is a pore in a membrane, a transport protein on a fish gill, an enzyme in the liver of a bird, or any of a host of other possibilities, toxicity is always initiated on a molecular basis. Toxicants can interact with organisms on the molecular level in a wide variety of ways that challenge the maintenance of homeostasis (physiological stability). Metals can bind to various proteins disrupting membrane integrity, ion transport, and cellular metabolism. For example, mercury can bind to sulfhydryl groups on structural proteins (Donaldson, 1980), thereby disrupting membrane integrity. Copper (Cu) can interfere with ion regulation in fishes by affecting gill ATPase activity (Lorz and McPherson, 1976). Lead can deactivate δ-aminolevulinic acid dehydratase (ALAD), disrupting red blood cell metabolism (Goering, 1993). Organic contaminants also interact with organisms on the molecular level by disrupting membrane integrity and function, by displacing endogenous substrates of enzymes, or by diminishing energy reserves through increased demands on detoxification mechanisms. For example, pentachlorophenol can uncouple oxidative phosphorylation by interacting with the mitochondrial membrane (Moreland, 1980). Organophosphates and carbamates can displace acetylcholine and inhibit its hydrolytic cleavage by acetylcholinesterase (ACHe), thereby affecting nerve transmission (O'Brien, 1976). Widdows and Donkin (1991) report a variety of ways by which toxicants can diminish the energy reserves of an organism to the detriment of survival.

A wide range of biochemical and physiological parameters are known to be responsive to chemical exposure. However, relatively few of the measurable biochemical and physiological responses are specific to certain chemical classes (for example, ACHe inhibition by organophosphates and carbamates; ALAD inhibition by lead). The majority of responses are sensitive to a wide variety of chemical compounds and other environmental stressors. Thus, with a few exceptions, most biochemical and physiological measures are more useful as general indicators of organism health rather than specific indicators of individual chemical exposure. In order to establish cause and effect, responses that are general indicators of organism health must be used with other measures of chemical exposure, such as chemical residue analysis. The following descriptions address examples of biochemical, physiological, and histological techniques that have been shown to be useful in evaluating environmental contaminants.

Metal Sequestration and Regulation

Metallothioneins are a class of metal-binding proteins that are found in a wide variety of organisms (Roesijadi, 1992) that are inducible after exposure to Cadmium (Cd), Copper (Cu), Mercury (Hg), and Zinc (Zn) (Noel-Lambot and others, 1978). Metallothioneins are thought to reduce the toxicity of heavy-metal exposure by sequestration (Hamilton and Mehrle, 1986), with toxicity occurring only after its binding capacity is exceeded (Brown and Parsons, 1978). Hepatic metallothionein levels in feral fishes from lakes contaminated with Cu, Zn, and Cd have been closely correlated to metals exposure (Roch and others, 1982). The inducible nature of metallothioneins suggests that they represent a regulatory mechanism and, as such, provide a useful indicator of exposure to certain metals. Other metal-binding proteins, such as ferritin (Fe) and copper-chelatin (Cu), have been less thoroughly studied in aquatic organisms.

Oxidative Metabolism

In organisms composed of more than one cell, oxidative metabolism is important for catabolic-energy production, reduction of oxygen radicals and maintenance of oxidative homeostasis within cells, and foreign compound (xenobiotic) metabolism. The cytochrome P450 monooxygenase (MO) system is one of the most extensively studied biochemical indicators of contaminant exposure and effects in fish and wildlife species (Stegeman and others, 1992). This inducible enzyme system has been shown to be responsive to a variety of environmental contaminants, including PAHs. The MO system plays a central role in detoxification of xenobiotic compounds by modifying their structure to a more readily eliminated form. The use of markers of oxidative metabolism in biological monitoring studies has been reviewed for aquatic organisms

(Payne and others, 1987; Goksøyr and Förlin, 1992) and wildlife (Rattner and others, 1989). In feral organisms, a number of factors, such as age, sex, reproductive status, diet, disease, and general health conditions, can be confounding variables (Neal, 1980). However, successful quantitative use of MO activity in the field has been demonstrated by using caged organisms (Lindström-Seppä and Oikari, 1990) where factors affecting MO activity can be controlled or monitored during the period of exposure. An alternative means of controlling confounding factors is the use of in vitro systems. In these assays, extracts from environmental samples or SPMDs are tested in bioassays by using cell cultures. An example of such an in vitro model system for MO activity is the H4IIE hepatoma cell bioassay (Tillitt and others, 1991). In this bioassay, environmental contaminant extracts are used to dose the cells. After a period of incubation, ethoxyresorufin-o-deethylase (EROD) activity in the cells is measured. The MO response of the H4IIE cells is highly correlated to effects observed in the whole organism (Safe, 1987). Studies have demonstrated the ability of the H4IIE bioassay to be predictive of contaminant responses at higher levels of biological organization, such as egg mortality rates in PCB-exposed populations of fish-eating birds (Tillitt and others, 1992).

Reproductive Parameters

Reproduction is another physiological function that has been shown to be sensitive to contaminant exposure (Thomas, 1990). The complexity of the reproductive process and the confounding influence of behavior, nutritional status, seasonality, and other variables make it difficult to ascertain the effects of contaminants on the reproductive success in feral populations. However, a number of biochemical parameters associated with reproduction have been shown to be useful as indicators of contaminant exposure, including levels of vitellogenin and sex-steroid hormones (Thomas, 1990). Vitellogenin is the major yolk protein precursor in non-mammalian vertebrates. Under the influence of estrogen (van Bohemen and others, 1982), vitellogenin is synthesized in the liver and transported to the ovaries in the blood. Elevated levels of vitellogenin in male organisms have been linked to the presence of environmental contaminants (Folmar and others, 1996). Similarly, levels of sex-steroid hormones (for example, estrogen, testosterone, and precursors) have been shown to be related to reproductive status in fish (Mylonas and others, 1997) and have been shown to be responsive to a variety of environmental contaminants (Thomas, 1990; Folmar and others, 1996).

Histopathology

A wide variety of histopathologic changes in organisms can be used as indicators of contaminant exposure and effects. As with many other biological endpoints, confounding variables at the tissue and cellular levels include other environmental stressors, such as disease, parasitism, and normal seasonal variation (Hinton and others, 1992). However, certain tissues have received considerable attention as indicators of contaminant effects. Liver tissue is a primary target of interest as a result of its role in xenobiotic metabolism. Fatty infiltration, hepatocyte hypertrophy, vacuolation, and other hepatic effects have been related to contaminant exposure (Couch, 1975). Similarly, the kidney has received considerable attention (Meyers and Hendricks, 1985) because of its role as a site of elimination for many environmental contaminants. The gills of aquatic organisms are particularly sensitive to contaminant exposure because they serve as an initial and substantial site of uptake. Responses include epithelial hyperplasia, lamellar fusion, and general necrosis (Meyers and Hendricks, 1985; Jagoe and others, 1987). Finally, gonads (Hinton and others, 1992) and the immune system (Anderson and Zeeman, 1995) have been shown to be sensitive indicators of contaminant effects.

Tissue Analysis

Chemical analysis of contaminant concentrations in biological tissues is widely used as a measure of biological exposure to constituents of concern. Analysis of aquatic organisms' tissues, when used in concert with chemical analysis of the water column and bed sediments, provide a direct measure of the bioavailability of the constituents of concern. When these chemical data are used in conjunction with other biological indicators, effects on individuals and populations of aquatic biota can also be examined. Although measured constituent concentrations in runoff, sediment, and biota would appear to provide a quantitative measure of a cause-and-effect relation for biota, the geochemistry of the receiving waters will affect bioavailability from season to season and site to site (Bricker, 1999), and biological characteristics of the different taxa studied will determine accumulation rates (Crawford and Luoma, 1993). The complexity of the Nation's freshwater environments, as well as differences in surrounding land use, physical and hydrologic features, and variations in flow temperature and water quality from season to season, complicate the use of tissue analysis in a consistent manner on a national or regional scale (U.S. Environmental Protection Agency, 1986). Contaminant concentrations are comparable only within the same species, and for organisms at the same life stage, reproductive condition, size, weight, and sex (Crawford and Luoma, 1993). Also, different constituents are accumulated selectively by different tissues within each organism, so the type of tissue used for analysis is another factor for consideration. Therefore, the consistency of results depends upon a program design that accounts for these chemical, physical, and biological factors.

Many factors must be considered when evaluating use of tissue analysis in studies that are to produce data for potential application in local, regional, or national synthesis studies (Crawford and Luoma, 1993). These factors include: (1) measurable tissue concentrations that vary with environmental concentrations and exposure therein; (2) uptake of constituents that is relatively rapid in comparison to release; (3) tissue concentrations with low variability among individuals collected, to be representative of site conditions at a given time period; (4) availability of organisms that are hardy enough that can withstand contaminant concentrations of interest; (5) organisms that do not commonly travel beyond the immediate travel area; (6) organisms that are abundant and widespread in the study area to withstand repeatable harvest for analysis; (7) organisms that can be collected, and that are large enough to meet sample size requirements; (8) organisms that are easy to find and hardy enough to withstand captivity during controlled laboratory studies; and, (9) a species for which biological and toxicological information is available for comparison. Mollusks, fish, various aquatic invertebrates, and vascular plants have been successfully used in different applications for studies that include tissue analysis, and standard methods for the collection, processing, and analysis of organisms within these groups have been examined in terms of the suitability for a national synthesis of biological, sediment, and water-quality data studies (Crawford and Luoma, 1993).

Semipermeable Membrane Devices

The semipermeable membrane device (SPMD) is an in-situ water-sampling device that mimics the bioconcentration of organic contaminants in lipids of aquatic organisms (Huckins and others, 1993). Although not a biological assessment technique itself, it is a powerful sampling technique for sequestering environmental contaminants for biological assessments. The sampler operates passively and consists of a thin film of neutral lipid enclosed in a flat, semipermeable-membrane tube. Unlike living organisms that metabolize and excrete many toxic organic contaminants, often eliminating the causal link between residue concentration and adverse effects, these time-weighted sampling devices continue to concentrate organic contaminants from water to their maximum partitioning limits (exceeding 1 million fold for certain contaminants). Also, only biologically available contaminants concentrate in the sampler lipid because of the small size of the pores in the polymeric membrane. This selectivity contrasts with nearly all currently used water-monitoring techniques. The compounds taken up by the device can be analyzed by routine chemical analysis or be used as a source of exposure in biological assessment procedures. Data from SPMDs, however, must be calibrated in terms of the different equilibrium concentrations and the different rates of reaching equilibrium concentration for each constituent of interest.

Whole-Organism and Single-Species Techniques

Whole-organism, or single-species, toxicity tests have been widely used to evaluate the effects of environmental contaminants. Mortality, growth, and reproduction are the typical responses measured by toxicity tests. Additionally, whole-organism exposures are often used to obtain the biological samples required for the biochemical, physiological, and histological assessments described above. A summary of historical application of toxicity testing to highway runoff is provided by Smith and Lord (1990). Toxicity-testing procedures have been developed for a wide range of species, including microbes, algae, vascular plants, and aquatic and terrestrial invertebrates and vertebrates. Additionally, tests have been designed that can be conducted on-site or in the laboratory with field-collected samples. The choice of species and life stage to be tested and appropriate routes of exposure are important considerations in whole-organism testing. Species considerations include sensitivity to the contaminants being evaluated, availability of healthy specimens for testing, ease of culture and maintenance, and local importance and relevance to the geographic area being evaluated. Generally, early life stages of organisms are more sensitive to contaminant exposure. The routes of exposure evaluated in toxicity studies may include water, food, air, physical contact, and maternal transfer. The choice of exposure route depends upon the properties and environmental distribution profiles of the contaminants being evaluated. Appropriate environmental samples for assessment may include field-collected water and sediments or contaminant fractions sequestered through sampling procedures, such as the previously described SPMDs. Toxicity testing has many benefits, but it also has some limitations that should be considered as a component of a national or regional water-quality assessment (Elder, 1990). The following descriptions address examples of whole-organism toxicity-testing techniques that have been shown to be useful in evaluating environmental contaminants. Tests of toxicity that are associated with field-collected sediments are most effective when used in concert with other contaminant-evaluation procedures. The Sediment Quality Triad is one such method that combines the power of laboratory sediment-toxicity assessment, field measures of benthic invertebrate community structure, and analytical chemistry to evaluate potentially contaminated sites (Canfield, Kemble, and others, 1994).

Microbial Assays

Microtox® and Mutatox® are microbial assays that use bioluminescent bacteria (*Photobacterium phosphoreum*) to detect the presence of cytotoxic and genotoxic environmental contaminants. The assays can be used with unprocessed water samples or with extracts of various environmental media, including water, sediment, and tissue. They can also be used in conjunction with SPMD extracts. Microtox® is used to evaluate cytotoxicity by quantifying reduction in light output as a result of death of the bacteria. The assay has been shown to be sensitive to a wide range of toxicants (Kaiser and Palabrica, 1991; Jacobs and others, 1993). Mutatox® is similar in concept and procedure, but uses a dark mutant strain of *Photobacterium phosphoreum* to detect the presence of DNA-damaging chemicals. Genotoxicity of a sample is quantified by restoration of light production of bacterial cells upon reverting back to wild-type bacteria. It can be used with a similar suite of environmental media or SPMD extracts. The assay has been shown to detect genotoxicity with over 100 chemicals (Johnson, 1992a,b; Ho and Quinn, 1993). The relative ease and efficiency of the Microtox® and Mutatox® procedures make them ideally suited for screening large numbers of environmental samples.

Algal Assays

Algal growth studies have been used to evaluate the effects of environmental contaminants and nutrient enrichment on aquatic algal communities. The most commonly used species is the green alga *Selenastrum capricornutum.* A variety of responses can be measured, including optical density of exposed cultures, oxygen production and(or) carbon dioxide uptake, cell counts, gravimetric cell mass determinations, and measurement of chlorophyll (American Society for Testing and Materials, 1997e). Increases or decreases in these parameters, compared to control responses, are used to determine effects on algal growth.

Aquatic Invertebrate Assays

Aquatic invertebrates have been widely used to evaluate environmental contaminants that are in receiving waters and aquatic sediments. For evaluation of waterborne contaminants, tests with *Daphnia magna* and *Ceriodaphnia dubia* are most commonly used (American Society for Testing and Materials, 1997b,d). With both species of aquatic invertebrates, assessments of contaminant effects on survival, growth, and reproductive success can be made. Aquatic sediments are often chosen as a medium for toxicity testing because they are recognized as contaminant sinks. Methods for evaluating contaminants that are in sediments have been developed for use with several aquatic invertebrate species, including the amphipod *Hyalella azteca* and the midge *Chironomus tentans* (American Society for Testing and Materials, 1997f). As with the waterborne testing procedures, effects on survival, growth, and reproduction can be measured.

Early Life-Stage Toxicity Studies with Fish

Early developmental stages are often the most sensitive to chemical stressors (McKim, 1977). Toxicity studies can be conducted in which fish are exposed to environmental contaminants in water and(or) food, or by injection of environmental-contaminant extracts. Toxicity studies can be conducted with a wide range of fish species and can provide information on the short-term (acute) and long-term (chronic) toxicity of contaminants (American Society for Testing and Materials, 1997a,c). Egg injection studies are particularly useful for evaluating the effects of contaminants on early developmental stages. The procedure involves injection of contaminants into freshly fertilized eggs and subsequent evaluation of mortality, hatchability, and developmental effects (Walker and others, 1994).

In-Situ Toxicity Assessment

In-situ exposures provide a method for assessing the survival and health of organisms in waters from the geographic area under evaluation. Duration of these tests can extend from 96 hours to 30 days. Early life stages of fish and (or) other organisms are exposed directly to water from the site of interest, using environmental chambers at the site (Finger and Bulak, 1988; Hall and others, 1993). Measurements are made to evaluate effects on survival, growth, and behavior. This type of exposure study is particularly useful for evaluating pollution effects on species that are indigenous to the site of interest. Results from in-situ exposures provide information on the actual response of organisms to mixtures of contaminants as they occur in natural systems. When compared with laboratory toxicity studies with single chemicals, they can provide insight into the additive or synergistic properties of contaminant mixtures. Documentation of effects on survival and development of early life stages of fishes also allows extrapolation to population-level effects, providing valuable information for assessing the role of contaminants on declining populations.

Population and Community Techniques

Measures of contaminant effects at the population and community levels focus on the structural and functional properties of the biotic components of ecosystems. Population and community surveys provide direct measures of aquatic community structure and function. Biological surveys can range from evaluations of single indicator species to evaluations of large proportions of organisms found in an aquatic receiving system. Obviously, both the level of resolution and the associated cost of the evaluation increase with the level of complexity of the survey. Application of biodiversity assessment techniques to transportation projects is not fully developed but may yield valuable information to highway planners, scientists, and engineers involved in addressing environmental concerns (Bardman, 1997). Regional differences in species composition, habitat characteristics, thermal and hydrological regimes, and water-quality problems must be taken into consideration in the design of a nationally consistent ecological assessment program. Fortunately, however, a wide variety of sources of biological population and community information for many areas of the country is readily available from the USGS, the USEPA, the U.S. Fish and Wildlife Service, and many State wildlife and environmental protection agencies (Gurtz, 1994). Structural analysis techniques seek to determine the abundance and distribution of various taxa as indicators of population and community stress. Presence or absence, numerical abundance or biomass, reproductive and recruitment success, and spatial distribution of indicator species are used to determine biotic status (Petersen, 1986; Sheehan and others, 1986). Functional analysis techniques focus more on the ecological processes of ecosystems, such as community respiration, nutrient cycling, decomposition rates, colonization rates, and trophic guild analysis (Cairns and others, 1972; Rapport and others, 1985; Crossey and LaPoint, 1988).

Well-designed studies, using population and community techniques, are a valuable component of water-quality studies (Cuffney and others, 1993a,b).

Population and community techniques relate directly to ambient conditions in receiving waters, incorporate a large variety of exposure pathways, eliminate the need to culture and maintain laboratory test organisms, and incorporate secondary effects that arise from unnatural changes in predator/prey relations. These techniques, however, present a challenge in interpretation of the magnitude of effects caused by changes in water quality with respect to effects caused by different natural and anthropogenic factors that will also change the structure and abundance of different biota in an aquatic system.

Measurements of effects at the higher levels of biological organization are important in terms of clearly demonstrating the ecological relevance of environmental impairment. However, current techniques are not specific to contaminant stress. Other forms of habitat degradation, interspecific competition, and nutrient alteration can cause similar effects at the population and community levels. Therefore, detailed documentation of the characteristics of the local stream habitat is necessary (Meador, Hupp, Cuffney, and Gurtz, 1993). Physical characteristics of the receiving waters, such as the geomorphic channel unit (pool, riffle, or run), riparian vegetation, bank stability, water temperature, stream depth, current velocity, and bed-sediment particle-size distribution, will determine the natural ability of a stream reach to support a given population. Therefore, these factors should be assessed and documented upon site selection, should be measured concurrently with each assessment, and should be similar for control and study sites (Gurtz, 1994). Other natural factors such as extremes of flow, life cycles of aquatic taxa, and the accessibility of in-stream habitats, are important. The USGS National Water-Quality Assessment (NAWQA) Program does annual community assessment work in the summer/fall low-flow period to avoid sampling soon after flood events, to obtain samples of algae, aquatic invertebrates, and fish in a mature development stage, and to access stream sites when smaller streams and rivers can be waded safely (Cuffney and others, 1993a,b; Meador, Cuffney, and Gurtz, 1993; Porter and others, 1993; Gurtz, 1994).

In order to establish cause and effect, it is particularly important to apply population and community techniques in concert with analytical chemistry determinations and other biological measures of contaminant stress that may be more contaminant specific. Water temperature influences the metabolic and reproductive rates of algae, benthic invertebrates, and fish. Aquatic organisms are also sensitive to changes in dissolved oxygen, pH and alkalinity, and other water-quality properties and constituents. Therefore, an understanding of watershed geochemistry is important to interpretation of population and community data.

Different elements of biomonitoring serve separate but complimentary goals when population and community techniques are applied to different key assemblages, including algae, benthic invertebrates, and fish. These different taxonomic groups respond differently to natural or anthropogenic disturbances because of differences in habitat, food, mobility, physiology, and life history; thus, an approach that utilizes more than one assemblage adds information that can be used to develop cause-and-effect relations (Gurtz, 1994). Examples of population and community assessment techniques are described below.

Algal Population and Community Assessments

Algae are an important component of population and community assessments because they have a short life span (days to weeks), they readily exchange constituents with the water column and sediments, and reflect local water quality because they are sedentary (Porter and others, 1993; Gilliom and others, 1995). Algae are operationally defined by physical characteristics of appearance and size, and by the substrate upon which they thrive. Algal populations are typically characterized by the list of taxa present, by interpretation of the community structure, and by the algal biomass per unit area. The taxon-specific physiological requirements or tolerance for defined ranges of water-quality conditions are known for over 3,000 algal species; therefore, population and community data can be a good measure of water quality (Porter and others, 1993). Algal populations can be sampled from natural surfaces, or—for more consistency between sites—from artificial substrates emplaced in a receiving water. Even when the substrates are designed to closely mimic natural surfaces, the population structure may not represent the natural population in the surrounding habitat. This bias, however, may not be a liability when the study objective is to measure the effect of highway-runoff quality on algal populations at a number of sites. An example of protocols for design, sample collection, documentation, and QA/QC for population and community assessments of algae on a regional and national scale is provided by Porter and others (1993).

Aquatic Invertebrate Population and Community Assessments

Aquatic invertebrates are an important component of population and community assessments because these organisms have longer life spans (months to years) than algae, live in close association with streambed sediments, and are relatively sedentary and good indicators of local water quality (Cuffney and others, 1993a,b; Gilliom and others, 1995). Aquatic invertebrates are operationally defined as a diverse group of taxa that live in, on, or near streambed sediments, including aquatic insects, mollusks, crustaceans, and worms. Aquatic invertebrate populations are typically characterized by the list of taxa present, by interpretation of the community structure, by the biomass collected by standard methods within a predefined study area, and by visible deformities in the specimens collected. Aquatic invertebrates exhibit different tolerances to contaminants that are found in sediments and the water column (Hamilton and Saether, 1971; Hare and Carter, 1976; Wiederholm, 1984; Warwick, 1985). Some genera are relatively intolerant, and low-contaminant levels eliminate them from the benthic community, while other genera are more tolerant, and would only be affected or completely disappear at higher contaminant levels. Measures of the presence, absence, and abundance of various taxa can be used as an indicator of aquatic community status (Plafkin and others, 1989). As with fish population assessment, indices have been developed for assessing aquatic habitat quality by the use of aquatic invertebrate community metrics (Hilsenhoff, 1987). Additionally, deformities in chironomid larvae have been shown to be related to the presence of contaminants in aquatic sediments (Hamilton and Saether, 1971; Cushman, 1984; Wiederholm, 1984; Warwick, 1985, 1989). Reported deformities include thickening of the exoskeleton, enlargement and darkening of the head capsule, asymmetric mouth-parts, missing or fused lateral teeth, and deformed antennae. Canfield, Swift, and LaPoint (1994) provide a description of considerations regarding the use of benthic invertebrate assessments for evaluation of contaminated sediments. An example of protocols for design, sample collection, documentation, and QA/QC for population and community assessments of aquatic invertebrates on a regional and national scale is provided by Cuffney and others (1993a,b).

Fish Population and Community Assessments

Fish are an important component of population and community assessments because these organisms have long life spans (years to decades), are of interest to the public, are potentially economically valuable, are highly mobile, and so are indicative of long-term watershed health (Meador, Cuffney, and Gurtz, 1993; Gilliom and others, 1995). Fish exist as a diverse group of species with different preferences for instream habitat. Fish populations are typically characterized by the list of species present, by physical measurements of, and by visible anomalies on, the specimens collected. One of the more widely used methods for evaluating fish community assemblages is the Index of Biotic Integrity (Karr, 1981; Karr and others, 1986). The scientist using the procedure utilizes a number of metrics, including such factors as species composition, trophic composition, and fish abundance and condition, to determine the structural and functional status of the fish community. Although the original index was developed for use in midwestern streams, alternative metrics have been developed for other regions of the country (Miller and others, 1988). An example of protocols for design, sample collection, documentation, and QA/QC for population and community assessments of fish on a regional and national scale is provided by Meador, Cuffney, and Gurtz (1993).

DATA-QUALITY CONSIDERATIONS

Data quality, compatibility, and utility are important considerations in biological assessments of environmental contaminants. Findings of an environmental assessment must also be readily transferable and useful to resource managers and regulators. To meet these objectives, supporting ancillary information must be available that (1) documents the methods and procedures that are used, (2) describes quality-assurance and quality-control procedures that are employed, and

(3) adequately describes the environmental setting that is being evaluated in terms of geographic location, condition, and other confounding variables. Brief discussions of these topics are provided below; more thorough discussions are provided by Meador, Hupp, Cuffney, and Gurtz (1993); Meador, Cuffney, and Gurtz (1993); Gurtz and Muir (1994); and the Intergovernmental Task Force on Monitoring Water Quality (1995).

Documentation of Methods

Biological assessment techniques are continually being developed and refined. New techniques and improvements of existing techniques serve to enhance our understanding of the implications of environmental contaminants. However, this evolution of the science makes it increasingly difficult to compare data over time. This is of particular concern to long-term and broad-scale monitoring and assessment programs that draw upon the expertise of a wide range of scientists. The exclusive use of published and proven procedures would help alleviate this concern, but would impede scientific advancement. Environmental scientists can help resolve this dilemma by thoroughly documenting and describing any new techniques employed and, when practical, by conducting studies designed to compare the results of new and existing methods (ITFM, 1995). This will help to ensure temporal- and spatial-data compatibility and comparability while continuing to allow advancement of the science.

Quality Assurance and Quality Control

In terms of quality assurance and quality control, biological assessments provide a few unique challenges compared to chemical measurement of contaminant residues (USEPA, 1995). The goals are the same: to provide sensitive, reproducible, and transferable data. There are, however, differences in the ways in which certain performance criteria are addressed. The parameters that are typically evaluated as indicators of quality include accuracy, precision, bias, detection limits or performance range, interference, and matrix applicability. In analytical chemistry, these performance parameters can be addressed by the use of internal standards and spiked, blind, and blank samples (Jones, 1999). Directly comparable procedures do not exist, however, for many biological endpoints. Precision and bias can be addressed in the usual manner by subsampling, by repeated measures of an endpoint, and comparison of the results of different techniques. Accuracy, however, is more difficult to determine given the frequent lack of "true" values or applicable standards for biological endpoints. To indirectly address accuracy, environmental scientists draw upon comparisons of results obtained at reference sites, the use of reference toxicants, and an understanding of "normal" ranges of values for biological endpoints. Detection limits and performance ranges are commonly a function of the range of possible values for a biological parameter, rather than a measure of the ability of an instrument or procedure to detect a response. Finally, interference and matrix applicability considerations include variables, such as disease or other factors that can elicit similar biological responses, factors affecting contaminant availability, or other confounding environmental variables.

Description of Environmental Setting

A final consideration for assuring comparability and utility of the results of a biological assessment is an adequate description of the environmental setting for the site that is being evaluated. It is important to provide descriptive (or explanatory) information that precisely defines the geographic location of the sampling effort and that describes pertinent environmental variables that may affect the outcome of the assessment. An important factor to be considered in the design of biological assessments is the size of receiving waters. Important physical and biological characteristics change as small streams develop into large rivers. Therefore, it is important to compare biological characteristics among streams of similar size. Also, such factors as land-use practices in the watershed, the presence or absence of riparian vegetation, streambed substrate, geomorphological features, nutrient levels, and the natural geochemistry of the receiving water may influence the behavior of environmental contaminants and their availability to biota. Additionally, physical and hydrologic habitat characteristics can have a profound influence on the types and quantities of biota that are present. This is particularly important because an acceptable biological assessment technique must be used to discern between natural variability and the effects of anthropogenic influences in order to establish a cause-and-effect relationship. While these variables may seem obvious to the scientist performing the assessment, their documentation is essential to the ultimate users of the information (for example, resource managers, regulators, and the public).

Comparability Issues for a National Synthesis

Contaminants are only one of many possible environmental stressors that can affect the status of biota. The confounding variables identified above are important considerations in any attempt to perform a national synthesis or to build a national data base of contaminant effects. To be useful, the results obtained from a biological assessment must be scientifically comparable (among investigators and laboratories) and geographically transportable (across States or regions). As such, the availability of supporting information, as discussed above, is essential to the process. The isolated results of a toxicity test or a population assessment are of little value without this supporting information.

It would be difficult to rank each of the example techniques discussed in this report in terms of its value to a national assessment. In fact, each has its inherent strengths and weaknesses, and it is through the use of combinations of these techniques to provide multiple lines of evidence that they have their greatest utility. However, some general observations on the inherent strengths of the major categories can be made (table 1). Generally, as one moves from techniques applied at the lower levels of biological organization (biochemical level), to techniques applied at the higher levels (single species and community levels), such factors as chemical specificity and sensitivity tend to decrease. In contrast, responses observed at the higher levels of organization tend to have greater ecological relevance and regulatory utility. This relationship, once again, indicates the importance of using a suite of techniques applied at a variety of levels of biological complexity.

Table 1. Comparative strengths of categories of biological assessment techniques

Category	Relative cost	Relative sensitivity	Chemical sensitivity	Ecological relevance	Regulatory utility
Biochemical, physiological, and histological techniques	Low	High	High	Low	Low
Whole-organism and single-species assay techniques	Medium	Medium	Medium	Medium	High
Population and community techniques	High	Low	Low	High	Medium

BIOLOGICAL EFFECTS OF HIGHWAY-RUNOFF QUALITY: A LITERATURE REVIEW

Relevant journal articles and reports were reviewed as part of this study on potential biological effects from highway runoff. These publications were identified in the National Highway-Runoff Water-Quality Data and Methodology Synthesis (NDAMS) data base as having an emphasis on the biological effects of highways and highway runoff on local ecosystems (Granato, 1997). This review is intended to examine existing information in terms of the factors necessary for assessing biological effects, available biological assessment techniques, and data-quality considerations that may be useful to highway practitioners. This is not an exhaustive review of the available highway-runoff literature, nor is it a survey of the larger body of potentially relevant literature on the biological effects of urban runoff. This review, however, does represent a summary of reports that have a primary emphasis on biological effects of highway pollution that were readily obtainable in a 2-year literature search of much broader scope. Hopefully, the review will also provide information to assess current and future needs of highway practitioners in terms of the effects of highway runoff on local ecosystems.

Of the 44 articles and reports reviewed, 32 were data/interpretive reports, which documented original research, 8 were summary or literature review reports, 2 were abstracts from conference proceeding poster sessions, and 2 were general policy papers (table 2, at end of chapter). Of the 32 data/interpretive reports, 18 were from studies done within the United States, and the remaining 14 were from Canada and Europe. Within the United States, the potential effects of highway-runoff quality were examined on different types of ecosystems in California, Colorado, Florida, Louisiana, Maryland, North Carolina, Ohio, Vermont, Virginia, Washington State, and Wisconsin. Fieldwork, reported by all of these interpretive studies, spanned a 26-year period from 1970 through 1996. About 80 percent of the fieldwork was done before the end of 1985.

Biological studies commonly emphasize different species or taxonomic groups because of the different ways they respond to various environmental stresses. For example, differences in life span, mobility, and ecological niche among algae, aquatic invertebrates, and fish are useful for examining effects of contaminants at different temporal and spatial scales (Gilliom and others, 1995). Among the 32 data/interpretive research reports reviewed, algae were examined in 11; plants, 6; aquatic invertebrates, 16; fish, 9; amphibians, 1; earthworms, 1; and other organisms, 7. Within each group, different species were examined or used as test specimens in the various interpretive reports.

Typically, ecological effects of highway-runoff quality on receiving waters have been predicted using statistical models of runoff-contaminant concentrations and loadings based upon the event mean concentrations of monitored storms (Horner and Mar, 1985; Smith and Lord, 1990; Driscoll and others, 1990; Young and others, 1996). These predictive approaches, which compare modelled loads and concentrations to published regulatory limits, indicate that there should be no measurable effects at sites with annual average daily traffic (ADT) volumes below 30,000 vehicles per day (VPD) (Smith and Lord, 1990; Driscoll and others, 1990; Young and others, 1996). Biological assessments, however, have shown changes in individual organisms and community structures, even at sites with relatively low traffic volumes (table 2).

Although many studies have been done, the full significance of intermittent discharge of highway runoff on the ecology and quality of receiving waters is not well documented (Dupuis, Kaster, and others, 1985; Maltby, Forrow, and others, 1995; Dupuis and others, 1999). It is difficult to assess the effects of highway runoff in a natural setting because increases in ADT are associated with higher levels of background contaminant sources from surrounding land uses (Dupuis, Kobriger, and others, 1985).

Factors for Assessing Biological Effects

Biological effects associated with highway-runoff quality are dependent on the concentrations and availability of the constituents of interest in highway runoff, on the concentrations and availability in receiving waters, and on the long-term storage and availability in soils and sediments in the vicinity of the highway and in receiving waters. Concentrations and availability of constituents in highway runoff depend on the physical and chemical characteristics of the roadway, vehicular sources, precipitation, and deposition from background sources in the study area (Young and others, 1996; Irish and others, 1996). Concentrations and availability of constituents in receiving waters depend on dilution by receiving waters (Dupuis, Kaster, and others, 1985; Horner and Mar, 1985; Driscoll and others, 1990; Cooper and others, 1996), the physical and chemical characteristics of local receiving waters (Driscoll and others, 1990; Bricker, 1999), the magnitude of background sources (Dupuis, Kaster, and others, 1985; Shively, and others 1986; Davis and George, 1987), and biological uptake and processing in the local ecosystem (Birdsall and others, 1986; Baekken, 1994; Maltby, Boxall, and others, 1995; Cooper and others, 1996; Schafer and others, 1998). Field research and resultant highway-runoff quality models indicate that, in general, event mean concentrations of pollutants in runoff and receiving waters are not acutely toxic (Dupuis, Kaster, and others, 1985; Driscoll and others, 1990; Maltby, Forrow, and others, 1995; Dutka and others, 1998). However, studies also indicate that soils and sediments from highway runoff are a reservoir of contaminants that can affect the ecosystems near runoff discharge points

(Portele and others, 1982; Gjessing and others, 1984; Mudre, 1985; Maltby, Forrow, and others, 1995; Boxall and Maltby, 1997).

Highway runoff contains a complex mixture of potentially adverse constituents. These constituents include deicers, nutrients, metals, organic chemicals, sediment, and potentially, herbicides and pesticides. Effects of these different contaminants depend upon study location, environmental setting, and the characteristics of the receiving waters (table 2). Cumulative effects on biological systems from highway-runoff quality include effects of all bioavailable contaminants and any interactions among them.

Deicers were noted as a contaminant of concern in 15 of the studies reviewed (table 2). Several studies specifically mentioned deicers as a potential problem for aquatic ecosystems (Corbett and Manner, 1975; Crowther and Hynes, 1977; Dickman and Gochnauer, 1978; Dupuis, Kaster, and others, 1985). Crowther and Hynes (1977), in a controlled experiment, noted a chronic effect defined as increased drift in streambed organisms in a freshwater trout stream when chloride concentrations exceeded 1,000 milligrams per liter (mg/L). Dickman and Gochnauer (1978) also did a controlled experiment by introducing 1,000 mg/L pure sodium chloride into an unpolluted stream during a 4-week experiment to detect changes in stream microbiota. This study indicated that, when compared to an upstream control station, the abundance and diversity of algae was suppressed by the salt, but bacterial density increased because of suppression of predator organisms. Adams-Kszos and others (1990) noted toxic effects in toxicity tests using bridge runoff when salt concentrations exceeded about 11,000 mg/L. They also noted possible synergistic effects between deicers and metals that caused toxicity in bridge-runoff dilutions. Deicers contain many major and trace elements, and can contribute a large percentage of total solute loads in highway runoff (Harned, 1988; Granato, 1996).

Metals, as environmental contaminants, were mentioned in 32 of the studies reviewed (table 2). In many studies, increased metal concentrations were detected in the tissues of animals and plants exposed to soils and sediments in highway environments (Gish and Christensen, 1973; Corbett and Manner, 1975; Dupuis, Kaster, and others, 1985; Birdsall and others, 1986; Davis and George, 1987; Baekken, 1994; Cooper and others, 1996; Dupuis and others, 1999). Although these studies did not define the toxicity of the metals to these organisms, several studies noted the potential for bioaccumulation of metals higher in the food chain (Gish and Christensen, 1973; Birdsall and others, 1986; Cooper and others, 1996).

The studies reviewed indicated biological accumulation of highway-related metals not typically studied in the United States, including antimony from automobile brakes (Reifenhauser and others, 1995) and the platinum group elements (PGEs) platinum, palladium, and rhodium that are associated with catalytic converters in exhaust systems (Helmers, 1996; Schafer and others, 1998). In addition to these German studies, PGEs have been measured in elevated concentrations in England (Pearce and others, 1997) and in San Diego, California (Hodge and Stallard, 1986). PGEs may be a concern for future highway research because of the widespread use of catalytic converters in automobiles, because PGEs have similar toxicities as copper, chromium, cadmium, nickel, and zinc (Kaiser, 1980), and because PGEs may be available as hydroxide or chloride complexes (Wood, 1991). PGEs, however, are not normally prevalent in aquatic ecosystems, and information about the chemistry and toxicity of these metals is relatively sparse.

Volatile and semivolatile organic compounds (VOCs and SVOCs, respectively) in urban and highway runoff are a major concern because measured concentrations can exceed national drinking water and aquatic life standards and guidelines (Lopes and Dionne, 1998). One or more of these organic compounds normally associated with vehicle exhaust, fuel, lubricants, and(or) asphalt were studied in 19 of the reports that were reviewed (table 2). The majority of highway-runoff investigations, done by the FHWA and the State-highway agencies, analyzed samples for volatile suspended solids (VSS), total organic carbon (TOC), and oil and grease. Studies that were conducted in the 1970’s and early 1980’s, however, did not define individual organic chemicals or the major classes of organics—VOCs, and SVOCs (including polycyclic aromatic hydrocarbons, PAHs)—in highway runoff, receiving waters, or biota (Dupuis, Kaster, and others, 1985; Smith and Lord, 1990; Driscoll and others, 1990). Many later studies of urban and highway runoff from the United States did detect PAHs at concentrations that exceed aquatic health standards (Lopes and Dionne, 1998). Several studies by a British research group found that PAHs were the most toxic of all the highway runoff constituents measured in highway-runoff sediments collected from a British stream

(Boxall and others, 1993; Maltby, Boxall, and others, 1995; Maltby, Forrow, and others, 1995, Boxall and Maltby, 1997). A different European study found tissue enrichment of organic compounds in benthic invertebrates and fish that was up to five times higher than tissue concentrations at background sites (Baekken, 1994). A recent study in California (Cooper and others, 1996), however, did not detect PAHs in road runoff, receiving waters, and the tissue of aquatic biota at the detection limits of 5 parts per billion for the water samples and 2 parts per million for the tissue samples.

Sediment (solid material that has been transported from its place of origin by erosion) is viewed as a major nonpoint-source contaminant throughout the United States (Davenport and others, 1991). Sediment is considered a problematic contaminant because it physically disrupts aquatic habitats and acts as a transport mechanism for other pollutants in aquatic ecosystems (Waters, 1995). Suspended solids and sediment were examined as a potential contaminant in 5 of the studies reviewed, and sediment was examined as a matrix for transport, storage, and release of other potential contaminants in 17 of the studies reviewed (table 2). In one study, effects of sediment from highway construction along a high mountain stream reduced the abundance and diversity of aquatic biota at four of seven sites (Cline and others, 1982). The effects varied from site to site depending on the local depositional environment and hydrologic effects, such as the periodic scouring action of high stream flows at some sites in this high-gradient stream. In many studies, sediments were mentioned as a potential reservoir for metals (van Hassel and others, 1980; Wanielista and others, 1982; Shively and others, 1986) and for organic contaminants (Gjessing and others, 1984; Boxall and others, 1993; Lopes and Dionne, 1998). Ney and van Hassel (1983), concluded that highway-runoff sediments were a source of pollutants to biota in Virginia streams because fish species associated with sediments had higher metal body burdens than species associated with the water column.

Other constituents in highway runoff (table 2) that may adversely affect aquatic life include major ions (in six of the studies reviewed), oxygen demand and oxygen deficit (five studies), nutrients (seven studies), and herbicides/pesticides (four studies). Although major ions (and many trace elements and metals) are natural components of natural waters and necessary nutrients for aquatic organisms (Hem, 1992), a change in the chemical signature of the receiving waters can affect the local aquatic community (Bricker, 1999). For example, Corbett and Manner (1975) noted a change from calcium-carbonate type to sodium chloride-type waters in some receiving streams in Ohio. In another study, the release of sulphate in highway runoff changed nutrient dynamics and caused eutrophication in a small Vermont lake by scavenging the iron that had removed phosphate from the aquatic system (Morgan and others, 1984). Oxygen demand from point sources and urban areas dominated the biological changes in a study that included highway runoff as one source (Davis and George, 1987). The inhibitory effects of highway-runoff constituents seemed to attenuate biological oxygen demand in some laboratory experiments (Portele and others, 1982; Dupuis, Kaster, and others, 1985). However, both stimulatory and inhibitory effects of highway runoff have been recorded in the literature (Winters and Gidley, 1980; Dupuis, Kaster, and others, 1985; Dutka and others, 1998). Highway runoff supplies nutrients to receiving waters, but the effect of these nutrients may be attenuated by metals and other contaminants in stormwater (Grizzard and others, 1980). Potential problems with herbicides and pesticides were discussed in several studies, but these studies concluded that proper management and timing in the application of chemicals to the right-of-way should reduce or eliminate adverse effects (Kobriger and others, 1984; Kramme and Brosnan, 1985; Shively and others, 1986).

Biological Assessment Techniques

The biological assessment techniques recorded in the highway-runoff research included histopathological techniques in the form of tissue analysis of biological samples collected, bioassays in the form of field and laboratory toxicity tests, population and community assessments, and behavioral studies. Of the 44 reports reviewed, 19 reported results of tissue analysis (table 2). The toxicity of soil sediment or runoff was assessed in 25 different reports. Plants, algae, aquatic invertebrates, and fish of different species were used as test subjects in the different toxicity tests. Community assessments were an integral part of about 16 of the studies reviewed. The drift of benthic species in the stream environment was assessed in two separate studies. Biological studies were supported by chemical analysis of soil water or sediment in about 35 of the studies reviewed.

Use of tissue analysis is prevalent in the literature relating to highway-runoff quality. In many studies, tissue analysis indicates that contaminants in sediments and soils near the highway environment can be mobilized within the food chain (table 2). Several studies have detected uptake of contaminants into plant tissues, and in some cases, changes in the physical form and apparent health of plants at sites where sediment and soil had elevated levels of contaminants in the highway environment (Wanielista and others, 1982; Dupuis, Kaster, and others, 1985; McFarland and O'Reilly, 1992; Reifenhauser and others, 1995; Schafer and others, 1998). Gish and Christensen (1973) demonstrated potentially toxic concentrations of metals in earthworms collected from soils near highways. This may indicate the availability of these metals in soils or sediments that could be eroded by runoff during large storms. Ney and van Hassel (1983) noted that the amount of metal uptake depended upon fish species, the specific affinities of the different tissues within a fish, and site characteristics controlling the availability of metals in the local environment. Birdsall and others (1986) found that tissue concentrations of lead in tadpoles varied with differences in ADT among 20 sites in Maryland and Virginia. Generally, concentrations of different highway-runoff constituents in tissue samples collected from aquatic communities were elevated near highway outfalls when compared to background concentrations in the same species (van Hassel and others, 1980; Dupuis, Kaster, and others, 1985; Baekken, 1994; Maltby, Forrow, and others, 1995; Cooper and others, 1996).

Generally, bioassays of highway runoff do not indicate acute toxicity for aquatic life. In a number of algal assays, Winters and Gidley (1980) found both stimulatory and inhibitory effects. They attributed the inhibition to higher metal concentrations in those samples. Wanielista and others (1982), however, detected only stimulatory effects in algal assays. When Portele and others (1982) conducted assays on algae, zooplankton, and rainbow-trout-fish fry, they found that soluble contaminants affected the algae and zooplankton and that suspended solids affected the trout fry. In assays with heterotrophic microorganisms, algae, and salmon eggs, Gjessing and others (1984) did not detect acute toxicity in runoff from a two-lane Norwegian highway. Dupuis, Kaster, and others (1985) did field and(or) laboratory toxicity tests on a number of species, including a number of micro- and macroinvertebrates, algae, and fathead minnow. The field bioassays were done at three sites—two in rural Wisconsin and one in a rural watershed in North Carolina—with ADT counts below the predicted 30,000 VPD biological effect threshold. These sites were chosen to examine the effects of highway runoff without significant background contaminant loads (Dupuis, Kaster, and others, 1985). Dupuis, Kaster, and others (1985) tested undiluted highway runoff from melting snow near a rural highway with low traffic volume (7,400 VPD) and highway runoff from a busy urban freeway (120,000 VPD). Many of these laboratory bioassays, however, were done with filtered runoff, or with runoff that was slowly circulated from reservoir tanks in which sediments had settled. These tests did produce some sluggish behavior in the fish, but no measurable acute toxicity. High mortality in the invertebrates was accompanied by high mortality in control groups, so there was no clear indication of highway-runoff toxicity (Dupuis, Kaster, and others, 1985). The algal bioassays done by Dupuis, Kaster, and others (1985) included a number of treatments with different nutrients and the metal chelating agent EDTA. These tests did not indicate the toxicity of runoff but did indicate an inhibitory effect caused by the metals in solution. A series of reports from a study in England did not demonstrate acute toxicity of runoff or receiving waters, but did determine that PAHs in highway sediments could be toxic to benthic organisms exposed to these contaminants (Boxall and others, 1993; Maltby, Boxall, and others, 1995; Boxall and Maltby, 1997). In a review of different studies on the toxicities of different deicers, including sodium chloride and calcium magnesium acetate (CMA), McFarland and O'Reilly (1992) noted some toxic effects on plants, invertebrates, and freshwater fish at very high deicer concentrations but lesser effects at concentrations expected in receiving waters. Adams-Kszos and others (1990) indicated that bridge runoff was toxic to sunfish when deicing chemical concentrations were high. Dutka and others (1998) used several different standardized bioassay methods on bridge runoff from several storms in Ontario, Canada. None of the tests produced acute toxicity, but different tests indicated genotoxicity for different storms. Because of the differing results from storm to storm and from test to test, Dutka and others (1998) concluded that a battery of tests was necessary to characterize the toxicity of runoff at highway sites.

Population and community techniques generally indicated local differences between control sites and study sites near highway-runoff discharge points.

Corbett and Manner (1975) found that when compared to control sites, areas affected by highway runoff had fewer sensitive species of aquatic plants and animals. Dickman and Gochnauer (1978) documented changes in stream microbiota that were caused by sodium chloride in a controlled experiment in an otherwise unpolluted stream. Cline and others (1982) documented reductions in density, abundance, diversity, and taxonomic structure at four of seven sites that were caused by sediment from highway-construction activities. Wanielista and others (1982) demonstrated that areas affected by bridge drains had fewer species than control areas. Dussart (1984), however, found that areas affected by road runoff had higher productivity of algal and filamentous organisms. Dupuis, Kaster, and others (1985) reported ambiguous results at low traffic sites. In this study, some sites receiving highway runoff showed no changes in abundance or diversity, but other sites, sometimes along the same highway, did show effects from the highway runoff. Mudre (1985) also reported some effects, but had ambiguous results on a new highway with low traffic volumes (ADTs of about 6,000 to 15,000 VPD). It was also demonstrated that the availability of pollutants at these sites was controlled by streamflow, organic carbon content of sediments, and the overland flow distance between the road and the stream (Mudre and Ney, 1986). Davis and George (1987) found that effects from urban runoff overshadowed the effects of highway runoff at several stations along a river with a rural-to-urban gradient in land use. Baekken (1994) discovered that the diversity and abundance of species were lower near a highway outfall than at background sites, but these effects were localized around the individual discharge points. Maltby, Forrow, and others (1995) documented loss of sensitive species and changes in the relative abundance of other species at four of seven sites downstream of a British highway. Cooper and others (1996) did not detect changes in fish and most invertebrates, but did note reductions in stonefly populations in some sites downstream of the highway. In highway-runoff studies, some of the more pronounced effects were apparent among benthic-invertebrate populations. This may be because benthic invertebrates have close associations with streambed sediments (Cuffney and others, 1993a,b), and different species have different and characteristic sensitivities to minor changes in water quality (Kennen, 1998; Newton and others, 1998). In the highway studies, however, differences in population and community structure may also have been partially attributable to other explanatory variables that caused changes between control and study sites (Smith and Kaster, 1983; Cooper and others, 1996).

Data-Quality Considerations

Careful study design and thorough data-quality documentation are considered necessary to overcome the large variabilities in time and space, as well as the large uncertainties that are inherent in studies of aquatic biology. For individual studies to be considered valid, current, and technically defensible (to meet the information needs of the highway community), it is necessary to document (1) methods, (2) quality assurance and quality control (QA/QC) information, (3) a thorough description of the environmental setting, and (4) effects of seasonality (Granato and others, 1998). It is also necessary to standardize protocols for implementing and documenting these four factors to combine existing data, or to design and implement a new data-collection program for regional and(or) national synthesis that will meet information needs and data-quality objectives (DQOs). For example, in a literature review designed to assess potential effects of contaminants from bridges, Dupuis and others (1999) noted that several studies did not provide sufficient documentation to support definitive conclusions for their National Cooperative Research Program study. To implement a regional and(or) national synthesis, it is also important to study enough sites to characterize the various cause-and-effect relationships that may be prevalent in different environmental settings.

Detailed documentation of study methods is necessary to assess existing data sets to ensure that the data reported in different studies are comparable and meet DQOs for a regional or national synthesis (Granato and others, 1998). Methods of sample and data collection, analysis, and interpretation were at least partially documented in 34 of the 44 reports reviewed (table 2). It is difficult, however, to sufficiently document methods with the detail necessary for complete repeatability of experimental results; detailed documentation can be voluminous. For example, Dupuis, Kaster, and others (1985) used 406 pages of text to describe sites, methods, and results for studies at two streams and one lake. This report also was supplemented with a 238-page report that described the methods used and the comparability among accepted methods (Dupuis, Kreutzberger, and others, 1985). Use of national protocols, therefore, may lead to consistent local, regional, and national data sets and will reduce the amount of documentation required in each report by establishing accepted methods at the national level.

Published protocols are useful in that they establish standard methods, document these methods, and provide economy in the presentation of study results. For example, USGS's National Water-Quality Assessment (NAWQA) Program has established standard methods for virtually every aspect of its biological assessment components, including site characterization (Meador, Hupp, Cuffney, and Gurtz 1993; Fitzpatrick and others, 1998), tissue analysis (Crawford and Luoma, 1993; Nowell and Resek, 1994; Hoffman, 1996), and community assessment techniques (Cuffney and others, 1993a,b; Meador, Cuffney, and Gurtz, 1993; Porter and others, 1993). Required methods and resultant protocols should be driven by program objectives; however, method documentation, adequate methods comparison, systematic data-base structures, and collaborative efforts among agencies collecting environmental data will open up many opportunities for use of existing and intensive biological assessment data bases (Gurtz and Muir, 1994; ITFM, 1995). For example, the State of New Jersey has a network of more than 700 stream sites used for macroinvertebrate community assessment that are distributed among different land-use categories in the six physiographic regions of the State (Kennen, 1998). This data set includes a number of minimally disturbed areas in each physiographic region that can be used as regional reference/control sites.

Documented methods are an important part of necessary quality-assurance programs, and quality-control documentation ensures that methods meet data-quality objectives. Therefore, both quality assurance and quality control (QA/QC) are important components of study design and documentation (Jones, 1999). Compared to performance standards for chemical laboratories, objective statements of method accuracies for biological field methods are not quantitative (ITFM, 1995). QA/QC factors typically reported for chemical studies such as precision, bias, performance ranges, interferences, and method detection limits, however, can be defined in the context of biological assessment methods if methods and protocols are well established and method comparability studies are properly documented. For example, Lenz and Miller (1996) compared five different aquatic-invertebrate sample-collection methods at six sites in Wisconsin and found that the equipment and methods used affect the number of and the relative abundance of different species collected.

Most of the highway studies with a biological component incorporated some form of QA/QC documentation because of the variability of biological systems; thus, the need for documented experimental controls is recognized. There was some mention of quality-assurance and quality-control measures in all but 12 of the 44 reports reviewed. Documentation of replicate samples was included in 21 of the reports reviewed (table 2). Use of control sites, or experimental control samples was mentioned in 16 of the studies reviewed. Use of experimental standards was documented in six studies. Other forms of QA/QC were documented in 11 studies. For biological studies, a critical component of the QA/QC and documentation process is proper selection of and complete characterization of the study sites.

In studies of the biological effects of highway-runoff quality, detailed descriptions of the environmental setting are necessary to interpret and standardize results. In most studies, the site characteristics were described as confounding factors that influenced study results. Cline and others (1982) identified site-hydraulic factors as the controlling variables that determined the effects of sediment on biota in a high-gradient mountain stream. In a study of benthic invertebrates, Smith and Kaster (1983) found that differences in streamflow and the composition of stream substrate could overshadow effects of runoff on population characteristics at sites receiving runoff from highways with low traffic volume (ADTs less than 10,000 VPD). In another study, tissue lead content in tadpoles increased with increasing ADT on different highways among 20 sites in Maryland and Virginia (Birdsall and others, 1986). In this study, however, analysis of the differences between sites indicated that seasonality, microtopography (erosive or depositional environments), the residence time and episodic flushing of water and sediments, and differences in site sediment characteristics introduced variability in the relation between ADT and lead concentrations in tadpoles. The site characteristics of topography (stream gradient), flow velocity, sediment organic matter, and the overland flow distance from the pavement to the stream controlled the availability of highway-runoff related metals in sediment at six stream sites near a new highway in Virginia (Mudre and Ney, 1986).

Descriptions of the study-site characteristics were inadequate for use in a quantitative national synthesis for most of the studies reviewed because this information must be assessed using constant methods and documented in consistent formats from site to site for regional or national interpretation. Dupuis, Kaster, and others (1985) fully documented the highway characteristics that they thought would be explanatory variables controlling the quality of storm-water runoff. These characteristics include traffic volume, highway type, number of lanes, existence of curbs, pavement material (concrete or asphalt), and the percent of paved and nonpaved area contributing to the highway-runoff drainage system. Dupuis, Kaster, and others (1985) also characterized many of the physical hydrologic features of the study sites, including historical average annual precipitation, precipitation and stream flow during the study period, watershed area, stream gradient, watershed land use, and other potential sources of point and nonpoint pollution that are commonly recognized as explanatory variables for biological studies. Many of the site characteristics necessary to compare results among sites, however, were not sufficiently documented in this or the other 44 highway-runoff reports reviewed.

To examine the effects of highway-runoff water-quality runoff on biological systems at different sites, it is necessary to document many site characteristics that can be used to relate habitat to physical, chemical, and biological factors. Factors not characterized by most highway studies include elevation, sinuosity (topographic channel pattern), active channel width (the stream width at bank-full discharge), channel conditions and features (such as runs, riffles, and pools), bank stability, water-management features, instream fish cover, canopy cover, and detailed descriptions of the dominant substrate (boulders, cobbles, gravel, sand, silt, and(or) mud). Detailed diagrammatic mapping of stream features is also considered necessary for interpreting results of bioassessment studies (Meador, Hupp, Cuffney, and Gurtz, 1993; ITFM, 1995; Fitzpatrick and others, 1998; Newton and others, 1998). To facilitate a national synthesis, other factors are also considered important, such as site ecoregion, location in latitude and longitude, classification in a nationally recognized system of stream-order number, watershed identification (such as the USGS hydrologic unit code), watershed soils, surficial and bedrock geology, physiography, potential vegetation, and upstream wetlands (Fitzpatrick and others, 1998). Fortunately, methods for site assessment and characterization are well documented and much of the large-scale information is available in existing geographic information systems if the latitude and longitude of a site is known (Meador, Hupp, Cuffney, and Gurtz, 1993; ITFM, 1995; Fitzpatrick and others, 1998; Newton and others, 1998). The USGS national bridge scour data base, with information about 27,000 bridge sites in 12 states, is also a good source of stream-site data, including local land use, stream width, surface profile, vegetation, bed and bank material, channel profile, depth, erosional environment, and location information (G.W. Parker, USGS, oral comun., 1999).

It is necessary to have sufficient and consistent data from enough different sites to characterize explanatory variables to interpret biological and water-quality data on a regional or national scale. Integration of biological and water-quality data is often hindered by lack of consistent data and the small number of sites for which both types of data are available (Kennen, 1998). Driscoll and others (1990) developed a highway-runoff quality model using precipitation, average annual streamflow, and total hardness of surface waters from predefined zones within the conterminous United States to predict pollutant loadings and ecological effects from highway-runoff quality at any given site. To determine the number of sites needed to establish a sufficient national data set, it is necessary to examine the problem in terms of the number of regions needed to quantify each of these explanatory variables. To define pollutant loadings, Driscoll and others (1990) used estimates of average concentrations from highway-runoff studies and estimated runoff volumes from 9 rainfall zones defined by average annual storm characteristics, including duration, intensity, volume, and antecedent dry period (which have been revised to 15 rainfall zones by the USEPA, 1992). Driscoll and others (1990) used 18 divisions of average annual streamflow to estimate dilution in receiving waters. These divisions were defined in a geometric progression from 0.05 to 5.00 cubic feet per second per square mile of drainage area, and when applied nationally, these divisions are used to define 30 zones in the conterminous United States. Driscoll and others (1990) estimate the geochemical availability and effect on aquatic organisms by pollutants in receiving waters using 6 divisions of hardness defined in 5 even increments from less than 60 to greater than 240 parts per million as calcium carbonate. This method of geochemical classification yields 24 different hardness zones within the conterminous United States. When these three variables are combined, they produce about 140 distinct zones of precipitation, dilution, and geochemistry within the conterminous United States. To characterize effects on biota, it is also necessary to characterize habitat features. The ecoregion approach is often used for classification of similar habitat features on a national scale, and about 76 different ecoregions are defined as individual zones within the conterminous United States (Omernik, 1995; ITFM, 1995). Superposition of these zones upon the zones of precipitation, dilution, and geochemistry defined, by Driscoll and others (1990), would greatly increase the number of distinct zones to be studied, and would still define site characteristics in a rather coarse manner.

Ecological systems are subject to variability in time, as well as to variability in space. Effects of seasonality were discussed in 16 of the 44 studies reviewed (table 2). There are two distinct approaches to the problem of seasonality. One approach is to control for seasonality by collecting all samples within prescribed seasonal conditions. This approach assumes that the biological community, if studied under similar conditions from year to year, will integrate adverse effects throughout the year. Investigations using this approach often involve sampling during summer low-flow conditions because aquatic organisms are at a good point in their life cycle for sampling and analysis, and the low flows facilitate sample collection in the streambed (M.R. Meador, USGS oral comun., 1999). Another approach is to attempt a detailed characterization of the effects of runoff during different seasons. For example, examination of the effects of deicing chemicals on aquatic ecosystems would be the driving factor for sampling during the winter in highway-runoff studies; in fact, 12 of the 16 studies that discussed seasonality also addressed deicers as a potential contaminant.

There are also long-term temporal considerations when evaluating effects of highway runoff on biota. Mudre and Ney (1986) demonstrated that the availability of metals (in highway-runoff sediment deposits) was a function of total annual precipitation. During one study in Massachusetts, differences in temperature and precipitation caused loads of deicing chemicals to vary from 50 percent to 200 percent of the median load over a 5-year period (Granato, 1996). Studies should be long enough to document potential effects and(or) interpret data within the context of long-term weather records in the study area (Averett and Schroder, 1994; Granato and others, 1998). Among the 32 data/interpretive reports reviewed, the duration of fieldwork at each site was greater than 1 year in 14 reports, was 1 year or less in 15 reports, and was not documented in 3 reports (table 2).

SUMMARY

Advancements in our understanding of the mechanisms through which contaminants exert their effects have stimulated interest in using biological techniques for environmental pollution assessment and monitoring. Although many biological endpoints have been shown to be responsive to contaminant exposure, relatively few are specific to individual chemicals. No single biological endpoint can fully define the significance of environmental pollution at a given site; each has its particular strength and weakness. Biochemical assays may be most useful for demonstrating direct effects from contaminants; studies with single species may help minimize confounding environmental variables; and population and community assessments may be the most appropriate techniques for estimating the ecological significance of contaminant perturbation. However, when used in conjunction with analytical chemistry and habitat assessment as multiple lines of evidence, biological assessments can help provide the cause-and-effect linkages between environmental pollution and ecological impairment.

A review of 44 reports on the biological effects of highway runoff on local ecosystems reveals several information gaps. The use of different methods from study to study and a general lack of sufficient documentation preclude making quantitative comparisons among different studies using the existing data. Qualitatively, the literature indicates that constituents from highway runoff and from highway-runoff sediments deposited in receiving waters near the highway are found in the tissues of aquatic biota, and that these sources may affect the diversity and productivity of biological communities, even though bioassays would suggest that highway runoff is not often toxic to aquatic biota. To provide the quantitative information needed, it is necessary to obtain information using standard methods, and to document study results in a manner that will be useful for a national or regional synthesis.

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Table 2

Table 2. Documented metadata for reports examining the effects of highway runoff on biota in receiving water

[ADT, average daily traffic; BMP, Best-management practice; D/I, data/interpretive; NA, not applicable; ND, not discussed; P/A, poster/abstract;

Reference	Report type	Dates of data collection	Location/environmental setting
Adams-Kszos and others, 1990	D/I	09/1983–05/1985	New York/Lake Chautauqua, Bridge scupper sampling
Baekken,1994	D/I	1991	Oslo, Norway/2-lane highway, high hardness Norwegian lake
Bardman, 1997	Policy	NA	Continental United States
Birdsall and others, 1986	D/I	07/1982–12/1982	Maryland and Virginia/highway, receiving waters, and control sites
Boxall and others, 1993	P/A	ND	ND/streams affected by highways
Boxall and Maltby, 1997	D/I	10/1993, 01/1994–04/1994	England/streams crossed by M1 motorway
Cline and others, 1982	D/I	1975–77	Rt. 14 Colorado/high mountain stream
Cooper and others, 1996	D/I	03/1995–05/1996	California/streams adjacent to roadways
Corbett and Manner, 1975	R/S	1975 (approx.)	Ohio/roadsides
Crowther and Hynes, 1977	D/I	12/1973–02/1975	Canada, Great Lakes region/rural “trout” stream, urban stream
Davis and George, 1987	D/I	1978–80	England/river on rural-to-urban gradient with sewage, urban, and highway inputs
Dickman and Gochnauer, 1978	D/I	07/1973–10/1973	Quebec, Canada/pristine stream draining humic marsh in a wilderness park
Dupuis, Kaster, and others, 1985	D/I	07/1981–10/1983 (each study done in sequence about 1 year in duration)	Wisconsin, North Carolina/highways in rural stream, lake and piedmont regions
Dupuis and others, 1999	R/S	ND	worldwide studies
Dussart, 1984	D/I	03/1976–04/1976	England/streams by a motorway
Dutka and others, 1998	D/I	ND	Burlington Ontario/highway-bridge runoff
Ellis and others, 1997	R/S	ND	England/receiving waters
Gish and Christensen, 1973	D/I	1970	Maryland and Virginia/highways, small streams and ponds (most near highways)
Gjessing and others, 1984	D/I	1981	Oslo, Norway/2-lane highway (laboratory assessment)
Helmers, 1996	D/I	07/1992–08/1994	Germany/right-of-way of Autobahn A8

PGE, platinum group element; R/S, review/summary; VPD, vehicles per day; ft, foot; mg/L, milligrams per liter; ppm, parts per million; %, percent]

Reference	Chemical analyte(s)	Chemical analysis matrix	Seasonality
Adams-Kszos andothers, 1990	deicers, properties, metals	water	yes
Baekken,1994	whole-effluent toxicity	biota, water	ND
Bardman, 1997	NA	ND	ND
Birdsall and others, 1986	metals	biota, sediment	ND
Boxall and others, 1993	metals, organics	biota, sediment	ND
Boxall and Maltby, 1997	organics	sediment	yes
Cline and others, 1982	total suspended solids	water	ND
Cooper and others, 1996	metals, organics	biota, water	ND
Corbett and Manner, 1975	deicers, majors, metals	water	yes (sodium chloride effects on water quality)
Crowther and Hynes, 1977	deicers	water	yes
Davis and George, 1987	oxygen demand, metals	biota, water	ND
Dickman and Gochnauer, 1978	deicers	water	ND
Dupuis, Kaster, and others, 1985	deicers, metals, organic carbon	biota, sediment, water	yes
Dupuis and others, 1999	deicers, metals, organics	biota, sediment, water (dissolved and whole)	ND
Dussart, 1984	NA (several mentioned but never tested)	biota	yes (“study took place at the end of the winter, so the maximum possible impacts of events, such as road salt, would be identifiable.” No comparison study was done in the summer.)
Dutka and others, 1998	whole-effluent toxicity	water	ND
Ellis and others, 1997	deicers, nutrients, metals, solids, organics, herbicides	biota, sediment, soil, water	deicers
Gish and Christensen, 1973	metals	biota, soil	ND
Gjessing and others, 1984	organics, whole-effluent toxicity	suspended solids, water (filtered)	One November snowmelt event included
Helmers, 1996	metals	biota	ND

Table 2. Documented metadata for reports examining the effects of highway runoff on biota in receiving water—*Continued*

Reference	Report type	Dates of data collection	Location/environmental setting
Horner and Mar, 1985	R/S	1977–82	Washington State/various highways
Karouna-Renier and Sparling, 1997	D/I	06/1994	Maryland/retention ponds collecting stormwater from various land uses including 3 highway sites
Kobriger and others, 1984	R/S	NA	ND/wetlands
Kramme and Brosnan, 1985	D/I	07/1984–11/1984	Ohio/rural highway, grassy right-of way (I-71), semirural highway (I-90), rural, 2-lane road
Madigosky and others, 1991	D/I	05/1989–06/1989	Louisiana/Roadside ditches in rural areas
Maltby, Boxall, and others, 1995	D/I	ND	England/stream near M1 motorway
Maltby, Forrow, and others, 1995	D/I	10/1990–07/1991, 04/1993	England/streams crossed by M1 motorway
McFarland and O'Reilly, 1992	R/S	ND	ND/various field and laboratory studies
McHardy and George, 1985	D/I	01/1977–05/1979	England/river on rural-to- urban gradient with sewage, urban, and highway inputs
McNeill and Olley, 1998	D/I	03/1995–05/1996	Southwest Scotland, highway outfalls on small rural streams crossed by the A74 motorway
Moore and Butler, 1994	R/S	ND	ND
Morgan and others, 1984	D/I	02/1981–12/1982	Vermont/lake surrounded by forest and limited residential land use
Mudre, 1985	D/I	1981–83	Virginia/6 streams with sites upstream, at the bridge, and downstream of a new highway (I-295)
Ney and van Hassel, 1983	D/I	04/1978–02/1979	Virginia/downstream of highway bridge
Portele and others, 1982	D/I	1980–81	Seattle, Washington/highways
Reifenhauser and others, 1995	P/A	ND	Germany/highways and roadways
Schafer and others, 1998	D/I	ND	Germany/plants grown in greenhouse in soils collected from roadside
Shively and others, 1986	D/I	01/1984–08/1985	Virginia/stream near highway, as well as urban area
Smith and Kaster, 1983	D/I	06/1980–06/1981	South Wisconsin/State Route-15, rural stream
Smith, 1976	R/S	ND	world-wide/roadside ecosystems (within 300 ft of the roadway)
Thrasher, 1983	Policy	NA	Continental United States/wetlands
van Hassel and others, 1980	D/I	04, 07, 11/1978 and 02/1979	Southwest Virginia/montain region

Reference	Chemical analyte(s)	Chemical analysis matrix	Seasonality
Horner and Mar, 1985	organics, oxygen demand, metals	water	ND
Karouna-Renier and Sparling, 1997	majors, metals, organics and properties	sediment, pond water	ND
Kobriger and others, 1984	deicers, metals, nutrients, organics, pesticides	biota, sediment, water	deicers
Kramme and Brosnan, 1985	herbicides, organics, properties	water (whole)	ND
Madigosky and others, 1991	metals	tissue	ND
Maltby, Boxall, and others, 1995	metals, organics	biota, sediment	ND
Maltby, Forrow, and others, 1995	metals, organics	bed sediment, runoff	Yes
McFarland and O’Reilly, 1992	deicers, oxygen demand, metals	soil, water	ND
McHardy and George, 1985	metals	tissue, water	ND
McNeill and Olley, 1998	deicers, metals, organics, sediment	water	deicers
Moore and Butler, 1994	metals, nutrients, organics, total suspended solids	water	ND
Morgan and others, 1984	deicers, majors, metals, nutrients	atmospheric deposition, sediment cores, water	yes (limited)
Mudre, 1985	metals	biota, sediment	ND
Ney and van Hassel, 1983	metals, properties	biota	ND
Portele and others, 1982	oxygen demand, metals, nutrients	biota, street sweepings, water	ND
Reifenhauser and others, 1995	metals	biota	ND
Schafer and others, 1998	metals	biota (plants), soil	NA
Shively and others, 1986	deicers, metals, nutrients, organics, pesticides	sediment, water	yes (discussed per parameter)
Smith and Kaster, 1983	deicers, metals, properties	biota, sediment, water	yes
Smith, 1976	metals	atmosphere, biota, soil	ND
Thrasher, 1983	NA	NA	ND
van Hassel and others, 1980	metals	biota, sediment, water	yes

Table 2. Documented metadata for reports examining the effects of highway runoff on biota in receiving water—*Continued*

Reference	Report type	Dates of data collection	Location/environmental setting
Wanielista and others, 1982	D/I	05/1981–05/1982	Central Florida/bridges over streams
Winters and Gidley, 1980	D/I	1976–77	California/roadways over streams and cut-slope runof

Reference	Biota studied	Method	Document method
Adams-Kszos and others, 1990	fish	toxicity testing	yes
Baekken,1994	benthic invertebrates, bivalves, fish	community assessment, tissue analysis	yes
Bardman, 1997	land (terrestrial) species	community assessments	ND
Birdsall and others, 1986	tadpoles	tissue analysis	yes
Boxall and others, 1993	benthic invertebrates	toxicity testing (using sediment and sediment extracts)	ND
Boxall and Maltby, 1997	benthic invertebrates	toxicity testing	yes
Cline and others, 1982	benthic algae, lichen, benthic invertebrates, moss	community assessment	yes
Cooper and others, 1996	benthic invertebrates, fish	tissue analysis	yes
Corbett and Manner, 1975	benthic fauna and vegetation	community assessment	ND
Crowther and Hynes, 1977	benthic invertebrates	toxicity testing, field and lab assessment of drift	yes
Davis and George, 1987	benthic invertebrates, plant tissue	community assessment, tissue analysis	yes

Reference	Chemical analyte(s)	Chemical analysis matrix	Seasonality
Wanielista and others, 1982	deicers, majors, metals, nutrients, organics	biota, soil, water	ND
Winters and Gidley, 1980	deicers, majors, metals, nutrients, organics	water	study took place in the winters of 1976 and 1977

Reference	Quality assurance	Comments
Adams-Kszos and others, 1990	reagent control	Found that a 50% dilution of bridge runoff was toxic to sunfish, especially for winter samples with salt concentrations greater than 11,000 mg/L.
Baekken,1994	controls, replicates	Tissue analysis and community assessment indicated chronic effects adjacent to highway runoff outfall.
Bardman, 1997	ND	Described methods to assess potential effects of bisecting habitats with transportation corridors.
Birdsall and others, 1986	replicates	Lead concentration in frogs is correlated with traffic density and sediment concentrations. Concentrations in frogs are high enough to affect predators.
Boxall and others, 1993	controls	Sediments from a site down gradient of a highway are toxic to the benthic invertebrate *Gammarus pulex*.
Boxall and Maltby, 1997	replicates	PAHs are the major toxins in sediment extracts from sites affected by highway runoff. Did spikes to determine that pyrene accounted for approx. 45% of total toxicity (fluoranthene, 16%; phenanthrene, 3.5%)
Cline and others, 1982	reference sites, replicates	Benthic communities and microinvertebrates were affected by sediment from construction, reducing the density, abundance and diversity, but high flows in this high gradient stream removed sediment deposits and therefore, limited damage spatially and temporally.
Cooper and others, 1996	replicates, clean containers, container blanks, field and trip blanks, field reagent spike	The water quality of the stream, and analysis of tissues indicated that the ecosystem was not affected by runoff from repaved asphalt/concrete pavement surfaces.
Corbett and Manner, 1975	control site	Sensitive species of benthic fauna or vegetation were not found at the highway site.
Crowther and Hynes, 1977	controls, replicates	Chloride pulses greater than or equal to 1,000 mg/L seemed to be the threshold to cause increased drift of species in the field. Static concentrations of 2,500 mg/L produced about 20% mortality in the laboratory.
Davis and George, 1987	replicates	Analysis of plant and animal tissue related to the chemistry of river water and subtle enough to relate to low-level secondary metal impacts.

Table 2. Documented metadata for reports examining the effects of highway runoff on biota in receiving water—*Continued*

Reference	Biota studied	Method	Document method
Dickman and Gochnauer, 1978	algae, bacteria, other microbiota	community assessment on artificial substrate	yes
Dupuis, Kaster, and others, 1985	algae, fish, benthic invertebrates	community assessment, field toxicity, lab toxicity, tissue analysis, drift	extensive
Dupuis and others, 1999	aquatic invertebrates, fish, plants	community assessment, field toxicity, lab toxicity, tissue analysis	ND
Dussart, 1984	algae	community assessment	yes
Dutka and others, 1998	assorted species	a battery of toxicity tests, full strength and concentrated runoff	ND
Ellis and others, 1997	aquatic invertebrates	community assessment, tissue analysis	ND
Gish and Christensen, 1973	earthworms	tissue analysis	yes
Gjessing and others, 1984	algae, heterotrophic microorganisms (bacteria, fungi, protozoa), fish	acute toxicity tests (full strength and several dilutions)	yes
Helmers, 1996	plants	tissue analysis	yes
Horner and Mar, 1985	NA	compare estimated concentrations to regulated standards	ND
Karouna-Renier and Sparling, 1997	aquatic invertebrates	toxicity test	yes
Kobriger and others, 1984	numerous wetland species	NA	NA

Reference	Quality assurance	Comments
Dickman and Gochnauer, 1978	control sites, replicates, standard methods, intermethod comparison	Did controlled experiment in an unpolluted stream. Introduced pure sodium chloride at 1,000 ppm for 4 weeks. Salt reduced abundance and diversity of algae. Bacterial density was enhanced by suppression of predator organisms.
Dupuis, Kaster, and others, 1985	experimental controls, dry and wet weather sampling, replicates, compared	Did not demonstrate acute toxicity of highway runoff. Did observe some effects but not conclusively. Observed effects limited to outfall locations.
Dupuis and others, 1999	ND	Questions traditional long-term continuous exposure methods for toxicity tests. Notes that site specific criteria (based on local geochemistry) may improve evaluation of water-quality criteria. Noted that several of the reports reviewed did not contain sufficient documentation to evaluate results.
Dussart, 1984	replicates	Motorway runoff can affect algal flora, but further analysis is needed to identify the form of the effect.
Dutka and others, 1998	replicates, standard methods	Tested 9 bioassay methods using samples from the beginning and end of different storms. Found different results for different tests within and between storms. Did not detect acute toxicity, but did note some chronic effects (genotoxicity).
Ellis and others, 1997	ND	Referenced several British studies where highway runoff from sites with an ADT greater than 25,000 VPD increased trace-metal and organic chemical body burdens in aquatic invertebrates and reduced species diversity near highway outfalls. Reported immediate acute affects for chemical spills, but delayed chronic effects from instream contaminated sediment.
Gish and Christensen, 1973	controls, replicates	Detected elevated concentrations of metals in worms and soil near highways. Concentrations decreased with distance from the road edge, and decreasing traffic volume. Determined that there was bioconcentration from soil. Concentrations of lead in worms were toxic to predators in food chain.
Gjessing and others, 1984	controls, replicates	Used runoff from a two-lane highway on several species. Toxicity tests using fish eggs were done with highway sediments in a tank of slowly circulating tap water (may be questionable). None of the tests with runoff or sediments demonstrated acute toxicity.
Helmers, 1996	calibration, standards, blanks, replicates	Found aluminum, cerium, lanthanum, neodymium, and zirconium in grass tissues, as well as platinum that was linked to catalytic-converter emissions of vehicles. Over a few years, concentrations were increasing with increasing catalytic-converter use. Antimony and tin were also increasing, but attributable to asbestos-free brake linings.
Horner and Mar, 1985	ND	Method for estimating effects based on regulatory limits and a data base of highway-runoff water-quality values.
Karouna-Renier and Sparling, 1997	controls, replicates, blanks, spikes	Found that pond bottom sediments were not toxic, but test conditions minimized formation of bioavailable forms of constituents in the test chambers.
Kobriger and others, 1984	ND	Feasibility to use wetlands to treat highway runoff.

Table 2. Documented metadata for reports examining the effects of highway runoff on biota in receiving water—*Continued*

Reference	Biota studied	Method	Document method
Kramme and Brosnan, 1985	benthic invertebrates, plants	bioassay/toxicity testing	yes
Madigosky and others, 1991	invertebrates	tissue analysis	yes
Maltby, Boxall, and others, 1995	benthic invertebrates	toxicity identification, evaluation, tissue analysis, lab toxicity tests	yes
Maltby, Forrow, and others, 1995	54 benthic invertebrate taxa, 29 species of aquatic fungi, 20 algal genera	community assessment	yes
McFarland and O'Reilly, 1992	algae, fish, plants	toxicity testing	ND
McHardy and George, 1985	algae	tissue analysis	yes
McNeill and Olley, 1998	benthic invertebrates	community assessment	yes
Moore and Butler, 1994	none	NR	ND
Morgan and others, 1984	algae, fish, phytoplankton, aquatic vegetation	community assessment	yes, some aspects of program limited
Mudre, 1985	benthic invertebrates, fish	community assessment, tissue analysis	yes

Reference	Quality assurance	Comments
Kramme and Brosnan, 1985	blanks, control treatment areas in close proximity experiment controls, standards, spikes	Monitored water-quality impacts of the herbicides 2,4-D and Picloram, and PAHs from road seal-coating material. Each chemical was tested at one urban roadway site. Found that concentrations in runoff were low or undetectable. Neither pesticide affected plant germination rates but the 2,4-D in the runoff from the first postapplication storm did show some chronic effect in growth. Tests with the PAHs, however, did not indicate lethality for the microinvertebrates *Daphnia magna*.
Madigosky and others, 1991	control site	Noted significant increases in the concentrations of lead cadmium and aluminum in the tissues of crayfish collected from roadside ditches in Louisiana when compared to a control site. The elevated concentrations did not seem to affect the crayfish, but were high enough to be a helth hazard to other organisms that use crayfish as a food source.
Maltby, Boxall, and others, 1995	replicates	Stream water mixed with runoff was not toxic but experiments show that aromatic hydrocarbons are accumulated by biota in direct proportion to exposure concentrations. Identified PAHs as the primary toxicant, therefore, population differences among sites in the field studies could be caused by organism's response to sublethal effects.
Maltby, Forrow, and others, 1995	replicates, standards	Demonstrated differences in sediment- and water-quality from upstream to downstream and resultant loss of pollution-sensitive taxa of macroinvertebrates and difference in relative abundance of others. Hydraulics and sediment deposition caused by potential highway runoff may affect communities.
McFarland and O'Reilly, 1992	ND	Did not find calcium magnesium acetate (CMA) to be particularly toxic.
McHardy and George, 1985	control site, replicates	In comparison to stream water, algae accumulated metals at all sites with significant positive correlations for cadmium and zinc. Metal concentrations generally increased along the rural to urban gradient with elevated metals near outfalls of sewage treatment plants, as well as highways, and other nonpoint sources.
McNeill and Olley, 1998	control sites	At many sites, "normal" highway runoff did not have a substantial effect on downstream biota along this new highway with grassy swale BMPs. However, problems with fine sediment and small routine spills from auto accidents were noted as problems.
Moore and Butler, 1994	ND	There are limited data describing the effects of highway runoff on receiving water bodies. Additionally, there is a lack of data describing water quality and the resultant aquatic impacts.
Morgan and others, 1984	ND	Phosphorus loading in a lake is controlled by sedimentation and internal loading. The construction of I-91 in the watershed has caused increased sulfate loading which has promoted internal phosphorus recycling.
Mudre, 1985	control sites, replicates, spikes	Detected elevated concentrations in tissues and some shifts in community structures at sites along a relatively low-volume highway (ADT: 6,000–15,000 VPD). Found substantial site-to-site variability that was caused by interrelated physical and chemical characteristics of these otherwise pristine stream sites.

Table 2. Documented metadata for reports examining the effects of highway runoff on biota in receiving water—*Continued*

Reference	Biota studied	Method	Document method
Ney and van Hassel, 1983	fish (6 species)	tissue analysis	yes
Portele and others, 1982	algae, fish, zooplankton	bioassays/toxicity	yes
Reifenhauser and others, 1995	plants	tissue analysis	yes, but not detailed
Schafer and others, 1998	plants	tissue analysis	yes
Shively and others, 1986	benthics (many species and taxa)	community assessment	yes (water and sediment), no (benthic assessment)
Smith and Kaster, 1983	benthic invertebrates	community assessment	yes
Smith, 1976	insects, plants, worms	tissue analysis	ND
Thrasher, 1983	ND	“ecological impact assessment”	ND
van Hassel and others, 1980	benthic invertebrates, fish	tissue analysis	yes
Wanielista and others, 1982	algae, plants	plant tissue analysis, algal bioassay/toxicity	yes
Winters and Gidley, 1980	algae	bioassay/toxicity testing (in lab)	yes

Reference	Quality assurance	Comments
Ney and van Hassel, 1983	replicates, spikes	Found that fish species associated with sediments had higher metal contents than water-column species, and that different tissues had different affinities for different metals.
Portele and others, 1982	clean containers, field and trip blanks	Soluble fraction of highway runoff adversely affected algae and zooplankton. Suspended solids caused high mortality of rainbow trout.
Reifenhauser and others, 1995	ND	Examined use of grass cultures for localized heavy-metal deposition rates.
Schafer and others, 1998	agricultural-soil controls	Plants in soil affected by highway runoff concentrate heavy metals and PGE.
Shively and others, 1986	yes (no details)	No significant effects on benthos were observed at either site. No significant effects in water-quality parameters were investigated (except iron and lead).
Smith and Kaster, 1983	replicates, control site	Monitored effects of a low-volume highway (ADT —7,000–8,000 VPD). Effects of highway runoff were not distinguishable from effects of habitat characteristics at each site. Need to monitor and document physical stream characteristics, especially substratum and stream current. Differences in measured biological parameters controlled by site characteristics.
Smith, 1976	ND	Lead in particulate form. Found that concentrations decrease with distance from the road. Lead concentrations increase with traffic volume. Particulate load goes out exhaust into atmosphere and is dispersed into the roadside environment.
Thrasher, 1983	NA	Discusses alternatives to construction on wetlands, avoidance, study, mitigation, and reconstruction.
van Hassel and others, 1980	replicates	Tissue concentrations of source metals increased with increasing traffic density. Stream water was not highly contaminated but sediments were. (Sites ranged from an ADT of 50–15,000 VPD).
Wanielista and others, 1982	replicates, standards, reagent controls	Lead levels were much higher in plants collected at bridge sites than control sites. Bridge areas were dominated by fewer species than controls. Stormwater runoff can become toxic to receiving water bodies when mixed in high concentrations.
Winters and Gidley, 1980	replicates	Heavy metals inhibited growth. Elevated levels of nutrients stimulated growth.

Chapter 9. Methodology and Significance of Studies of Atmospheric Deposition in Highway Runoff

By JOHN A. COLMAN, KAREN C. RICE, and TIMOTHY C. WILLOUGHBY

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Methodology and Significance of Studies of Atmospheric Deposition in Highway Runoff

By John A. Colman, Karen C. Rice, *and* Timothy C. Willoughby

Abstract

Atmospheric deposition and the processes that are involved in causing and altering atmospheric deposition in relation to highway surfaces and runoff were evaluated nationwide. Wet deposition is more easily monitored than dry deposition, and data on wet deposition are available for major elements and water properties (constituents affecting acid deposition) from the inter-agency National Atmospheric Deposition Program/National Trends Network (NADP/NTN). Many trace constituents (metals and organic compounds) of interest in highway runoff loads, however, are not included in the NADP/NTN. Dry deposition, which constitutes a large part of total atmospheric deposition for many constituents in highway runoff loads, is difficult to monitor accurately. Dry-deposition rates are not widely available.

Many of the highway-runoff investigations that have addressed atmospheric-deposition sources have had flawed investigative designs or problems with methodology. Some results may be incorrect because of reliance on time-aggregated data collected during a period of changing atmospheric emissions. None of the investigations used methods that could accurately quantify the part of highway runoff load that can be attributed to ambient atmospheric deposition. Lack of information about accurate ambient deposition rates and runoff loads was part of the problem. Samples collected to compute the rates and loads were collected without clean-sampling methods or sampler protocols, and without quality-assurance procedures that could validate the data. Mass-budget calculations comparing deposition and runoff did not consider loss of deposited material during on-highway processing. Loss of deposited particles from highway travel lanes could be large, as has been determined in labeled particle studies, because of resuspension caused by turbulence from passing traffic. Although a cause of resuspension of large particles, traffic turbulence may increase the rate of deposition for small particles and gases by impaction, especially during precipitation periods.

Ultimately, traffic and road maintenance may be determined to be the source of many constituents measured in highway runoff previously attributed to ambient atmospheric deposition. An investigative design using tracers of ambient deposition that are not present in highway traffic sources could determine conclusively what fraction of highway runoff load is contributed by ambient atmospheric deposition.

INTRODUCTION

The atmosphere is the pathway by which inorganic and organic compounds are transported from sources of air pollution to receptors on the ground. These compounds can be deposited locally around sources, when associated with large particles, or in areas far removed from the source, when associated with small particles or in vapor state (Majewski and Capel, 1995). Highway-travel surfaces are large, well-drained impervious areas whose efficiency as collectors of atmospheric deposition depends on the extent of traffic-induced particle resuspension. Deposited material that is not resuspended likely will enter highway runoff.

In addition to receiving constituents from the atmosphere, highways, and highway traffic contribute constituents to the atmosphere. Motor vehicles are recognized as a major source of pollutant emissions to the atmosphere and have a substantial effect on air and water quality (Moe and others, 1982; Ellis and others, 1987, and references therein). Vehicle emissions of gaseous oxides of nitrogen (N), carbon monoxide, trace metals, and organic compounds contribute substantially to the atmosphere (Harrison and Johnston, 1985). Whereas gaseous pollutants emitted from vehicles are rapidly and widely dispersed into the atmosphere, leaving no permanent record in the vicinity of the road, a portion of particulate emissions from vehicles is deposited locally, resulting in contamination of roadside vegetation, soils, surface waters (Harrison and Johnston, 1985; Ward, 1990), and in some cases, ground water. In addition, particulates can derive from the vehicle itself, such as from wear of brake linings, motorized parts, and tires (Shaheen and Boyd, 1975; Ward, 1990).

With the exception of eroded material from road cuts and road berms, most materials delivered to the road surface, and, therefore, subject to appearance in highway runoff, could be considered to be from ambient atmospheric deposition, from traffic, or from both sources. Yet, attempts to simulate loads of runoff constituents based on these causative factors have had little success (Driscoll and others, 1990a). The lack of simulation success limits attempts to mitigate causes of contamination from highway runoff or to estimate constituent loads in highway runoff from new construction. Unanswered are key questions such as whether variation in ambient deposition, from national or urban-to-rural gradients, are important to highway runoff quality in comparison to vehicle-related sources; and the relative importance of highway as compared with other impervious surfaces (usually present in the urban environment) in determining runoff loads to receiving waters.

Complicating factors for modeling simulations may include complex on-highway processes, such as particle resuspension and deposition through turbulence impaction. Other difficulties are changes with time and among sampling programs in deposition-sampler construction materials, sampling procedures, and documentation of sample quality assurance. A final complicating factor is the substantial changes in atmospheric pollution loads that may have occurred during the data-collection period. Emissions of many types of airborne pollution have decreased since the passage of the Federal Clean Air Acts, beginning in 1970 (USEPA, 1999).

The U.S. Geological Survey (USGS) investigates all aspects of the hydrologic cycle including investigations on atmospheric deposition to highway surfaces in relation to constituent loads in runoff. The USGS maintains the database for the National Atmospheric Deposition Program (NADP). These activities account for the interest of the USGS in the topies reviewed in this chapter. The purpose of this report is to describe atmospheric deposition as it relates to highway runoff. Tools and techniques are reviewed, including data-quality assurance procedures that commonly are used for the assessment of atmospheric deposition when determining the occurrence, source, and load of constituents in highway runoff. In addition, this report describes sources of atmospheric-deposition data, reviews articles that discuss atmospheric sources to highway runoff (100 reports are listed in table form), and outlines possible strategies for continuing research within the context of information needed to simulate highway-runoff quality consistently on a regional or national basis.

FORMS OF DEPOSITION AND POST-DEPOSITIONAL TRANSPORT

Atmospheric deposition is defined as the solid, liquid, and gaseous materials deposited by atmospheric processes (Bricker and Rice, 1993). Atmospheric deposition can be divided into two categories—deposition that involves precipitation, called wet deposition (rain, sleet, and snow), and deposition that does not involve precipitation, called dry deposition (settleable particulates and aerosols). Removal of contaminants from the atmosphere by fog, mist, and dew can be classified somewhere between wet and dry deposition but is more closely related to dry deposition (Majewski and Capel, 1995); these types of atmospheric deposition are sometimes termed occult deposition (Stensland and others, 1986).

Atmospheric-deposition samples can be collected in buckets as wet deposition, dry deposition, or bulk deposition (where a bucket is left open so that both wet and dry deposition are collected together). Dry deposition also can be evaluated by deposition onto standard surfaces or from deposition models that use concentrations in air as a function of particle size as inputs. The collection-bucket method for ground-based sampling of wet deposition is straightforward (Majewski and Capel, 1995), although the sampler design and means of sample collection can affect the results. In simplest form, bulk and dry-bucket collection of dry deposition also is straightforward. However, observed variability in multiple-sampler deployments and dependency of result on the bucket design or the collection surface has led to more complex collection devices (Lin and others, 1993; USEPA, 1997).

Wet Deposition

The two major processes that introduce atmospheric contaminants to wet deposition are rainout and washout. Rainout is a process that occurs in clouds and causes formation of water droplets on the pollutant by condensation, nucleation, or gas dissolution. The pollutants then are removed from the atmosphere by rainfall. Washout is the process in which falling precipitation scavenges airborne particulates and aerosols between the cloud base and the ground. In general, rainout is a more effective removal mechanism than washout. These processes can occur continuously during wet deposition because most storms produce convective air currents that add large masses of near-surface air to overlying clouds (Schroder and Hedley, 1986). The path of a storm can have a substantial effect on the chemistry of wet deposition delivered by the storm and may be a large source of variability in event-mean concentrations observed in highway-runoff studies (Driscoll and others, 1990a; Gay and Melching, 1995).

In general, much airborne material is removed from the atmosphere in the early stages of a precipitation event, and the rain becomes more dilute as the event proceeds. For computing annual depositional flux and for accurate comparison among sites, volume-weighting of constituents is necessary because of the concentration dependence on event size. Adjusting the concentrations of constituents by the amount of rainfall collected for the precipitation event allows for a fair comparison among sites. Example data collected from 1982 through 1993 at Catoctin Mountain, Maryland (Rice and Bricker, 1996) show that annual concentrations based on a straight average of samples generally are overestimated relative to volume-weighted annual averages (fig. 1). These data demonstrate the necessity of comparing volume-weighted rather than straight-average annual concentrations among sites.

Dry Deposition

Dry deposition provides a substantial mechanism for removing pollutants from the atmosphere and represents a larger deposition flux of many contaminants than does wet deposition (Kobriger, 1984; Harned, 1988). Solids, nutrients, trace metals, and organic compounds may be contributed to highway surfaces by dry deposition from background and pollution sources (Sartor and others, 1972; Gupta and others, 1981). Gupta and others (1981) reported that typical monthly dustfall loads in major cities across the United States ranged from 2,600 to 26,000 kg/km^2.

Atmospheric materials that contribute to dry deposition include settleable particulates, aerosols, gases, and vapors. Dry-deposition rates are dependent on the size, surface area, and mass of the particle (Legge, 1990). The largest airborne particles (greater than 2.5 µm) are derived from natural sources of mechanical abrasion and wind erosion, and are subject to gravitational settling. These particles are removed from the air mostly by dry deposition (Holsen and Noll, 1992). Smaller particles (from 0.1 to 2.5 µm) result from coagulation processes and primary aerosol emission, and are removed from the atmosphere by precipitation scavenging and by dry-particle deposition. The smallest particles found (less than 0.1 µm) are the result of secondary products of air-pollution emission and are removed mostly by particle coagulation (Holsen and Noll, 1992). Deposition of gases is part of dry deposition and occurs by adsorption on vegetation, soil, and other surfaces.

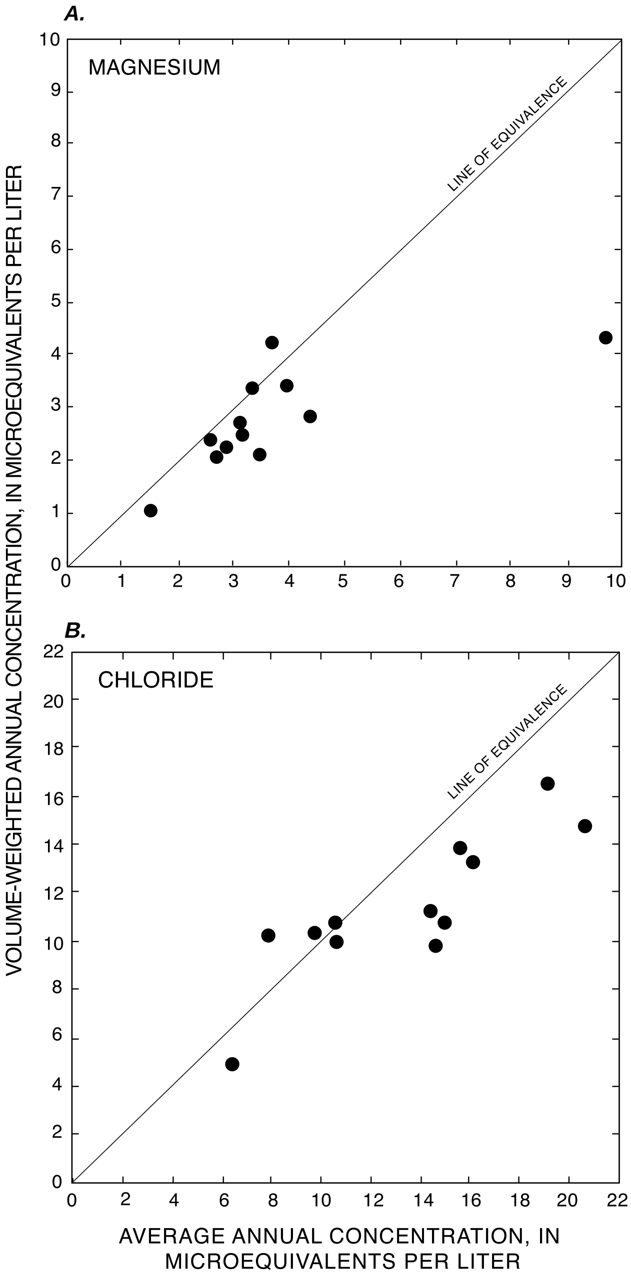

Figure 1. Comparison of average annual concentrations and volume-weighted annual concentrations from wet-deposition samples, 1982 through 1993 at Catoctin Mountain, Maryland, of (*A*) magnesium, and (*B*) chloride (Rice and Bricker, 1996).

The depositional transport of gases is increased by turbulence and roughness of the surface, which can move material through the boundary layer adjacent to deposition surfaces (Hicks and others, 1991). Dry deposition of gases onto highway surfaces has not been formally investigated.

Whereas the measurement of wet deposition by analysis of water collected in an appropriately constructed bucket is relatively straightforward, collection of dry deposition is complex because dry deposition depends on various physical characteristics of the collection surface used. Vandenberg and Knoerr (1985), for instance, measured the following variation for sulfate: 1.1, 3.2 and 5.8 mg $SO_4^{2-}/m^2/d$ for petri plate, interior surface of a bucket, and teflon filter surfaces, respectively. Deposition for N and sulfur (S) chemical species are particularly dependent on the type of surface, because the gas phases, nitric acid (HNO_3) and sulfur dioxide (SO_2), are important components of the total deposition (Hicks and others, 1991; Meyers and others, 1998).

Deposition rates determined by model simulation can be compared with deposition rates measured on a standard surface (Lin and others, 1993). In this report, deposition onto a standard surface refers to a polyvinyl chloride (PVC) plate with a sharply beveled (10 degrees) leading edge, on which are attached Mylar strips covered with a thin layer of Apezion L grease (Lin and others, 1993). The plate is directed into the wind with a wind vane. The device collects dry deposition on the grease-coated strips in a reproducible way with minimal turbulence. Model results have indicated that deposition velocities can be defined for all forms of dry deposition so that deposition can be modeled as a function of constituent concentration in air. For particulates, deposition velocities are functions of air turbulence, collection surface roughness, collection surface stickiness, and settling velocity, which differs by particle size. Particles in air can be separated by size using rotary-impactor samplers for large particles (6.5 to 36.5 µm) and conventional cascade-impactor samplers for small particles (0.43 to 10 µm) (Holsen and Noll, 1992). Cascade-impactor samplers draw air through a series of differently sized jets arranged with sampling plates on which particles of successive size ranges are inertially impacted out of the air stream. For gases, deposition velocities can be modeled as functions of air turbulence and meteorological data (Hicks and others, 1991; Meyers and others, 1998).

Deposition to a standard surface has advantages over deposition to a dry-deposition bucket collector in terms of reproducibility of result and correspondence to total deposition where turbulence is at a minimum. Deposition to a standard surface still may need to be adjusted to apply to highway surfaces to account for on-highway processing because of highway-specific characteristics, such as traffic-induced turbulence and highway surface roughness. These adjustments have not been investigated but likely would depend on particle size of the deposited material. If particle-size data are necessary for an accurate estimate of highway loading, then air monitoring by impactor sampler as well as chemical analysis and estimated deposition velocity of each size fraction would be required.

Most mass-balance budget investigations, whether of highways, or urban or rural catchments, have relied on direct measurements of material collected in bulk or dust buckets to estimate atmospheric dry deposition. In perhaps the most exhaustive mass-balance investigation of a catchment, at Hubbard Brook, New Hampshire, deposition samples were collected in bulk collectors. Investigators at Hubbard Brook (Likens and Bormann, 1995) state that, although bulk collectors are “not very efficient at quantifying the deposition of very fine particles—smaller than 1µm—bulk collector results for calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), and chloride (Cl) (dominated, presumably, by wet deposition and dry deposition of particles greater than 1µm), are fairly accurate.” Bulk measurements of deposition for N and S, which have appreciable gas-phase deposition components, were adjusted upwards in the Hubbard Brook budgets (Likens and Bormann, 1995). If bulk collectors are assumed to measure large particle flux correctly, they may be suitable for estimating constituent fluxes whose dry deposition is dominated by large-particle flux.

Saltation and Resuspension

In the geologic context, saltation refers to sediment transport in which particles are moved forward by bouncing along a surface, such as sand grains being pushed up a dune by the wind. In the highway context, saltation refers to deposition that bounces (as from a road salt application) or is splashed (particularly by moving traffic) and can result in material being moved off the road. Thus, saltation is a type of post-depositional transport. Vehicle spray has been shown to reintroduce contaminants to the atmosphere during periods of wet deposition (Irish and others, 1996) and clearly affects amounts of total precipitation and associated concentrations of constituents that are measured in runoff. Highway saltation measurements have been made with a collector that is slotted on the side to measure material that arrives at the collection location by way of a horizontal particle flight path (Harned, 1988; Kobriger and Geinopolos, 1984). Quality-assurance procedures for these saltation collectors, however, have not been documented. A blank could be measured by turning the collector away from the highway to determine how much of the total sample collected could have been from other than horizontal transport of resuspended material from the highway. Without associated quality-assurance measures, the saltation collectors only confirm that horizontal transport does occur, rather than providing a value for a budget term in the highway mass balance.

Resuspension also can be a sediment transport process, but it refers to finer particles that can be supported by the upward currents in turbulent eddies and moved greater distances than the sand-sized particles. Jones and Tinker (1984) found that the amounts of contaminants entrained by resuspension of wet deposition depend on traffic density, duration of the rainfall, wind speed, and wind direction. Likewise, dry deposition on highways can be reintroduced into the atmosphere and transported to different locations by wind and anthropogenic activities, such as construction and automobile turbulence (Nicholson and Branson, 1990). Moe and others (1982) suggest that resuspended dust from roadways is preventing many cities from achieving national ambient air-quality standards for total-suspended particulates.

In a test with fluorescent marked particles, more than 70 percent of 12-µm silica particles were removed from the highway surface by four passes of a passenger vehicle at 40 miles per hour (Nicholson and Branson, 1990; fig. 2). Because kinetic energy increases with the square of velocity, a still greater percentage of particles would be removed by mixed traffic (cars and trucks) at more usual highway speeds of 60 to 70 miles per hour. Particle removal by vehicle turbulence was determined to be a function of particle size. Experiments were done with 4.2-, 9.5-, 12-, and 20-µm particles; only about 40 percent of particles were removed at 40 miles per hour when particle size was 4.2 µm (fig. 2).

The resuspension results emphasize the complex effect that particle size may have on particle-associated pollutants. Dry deposition of gases and particles might be increased by vehicle turbulence, but resuspension by turbulence would differentially affect particles according to size. Redeposition of the resuspended large particles likely would occur before long transport, so polluntants associated in large particles could be swept from the traveled highway surface but be redeposited in substantial amounts nearby.

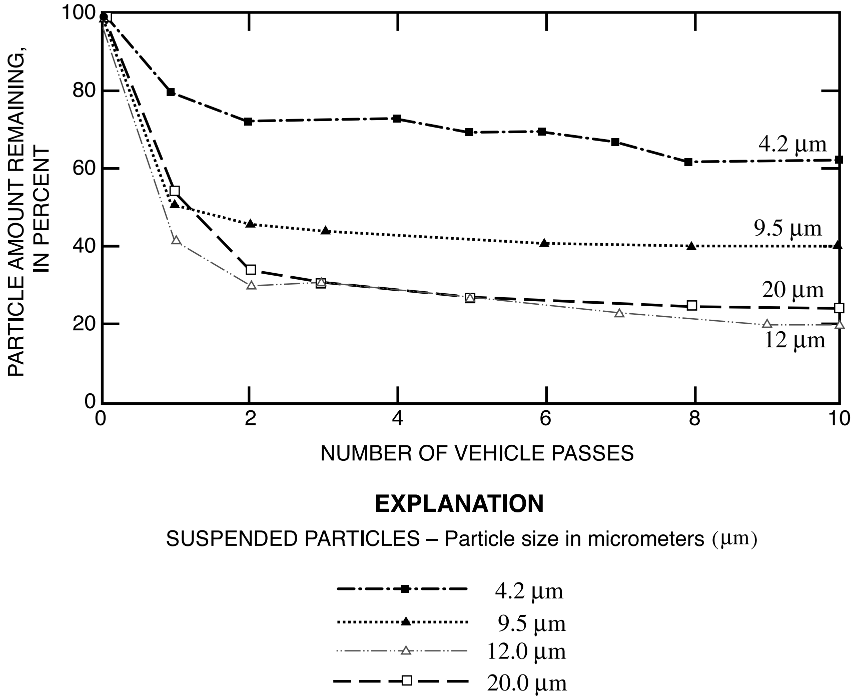

Figure 2. The resuspension of particles marked with fluorescent dye by turbulence from a medium-size vehicle traveling at 40 miles per hour, averaged for three separate experiments (Nicholson and Branson, 1990).

DATA FROM EXISTING MONITORING PROGRAMS

Atmospheric deposition has been studied intensively in the United States over the last 20 years, especially with regard to those constituents connected with acid deposition. Recently (1996) measurement of wet deposition of mercury (Hg) has begun to receive the same attention as the acid constituents, and wet deposition of other trace metals has been measured at some sites. Many of the scientific, technical, and logistic issues involved in creating a national network to characterize concentrations and loadings of pollutants from atmospheric deposition have been examined. The sources of information given here provide information on deposition of major elements, Hg, and precipitation, as well as conditions of meteorology and climate on a regional and national scale, as may be useful to highway-runoff investigations.

Wet deposition. The National Atmospheric Deposition Program (NADP), designed as a long-term program for chemical analysis of precipitation, was started in the United States in 1978 (Cowling, 1982). By late 1981, 93 sampling stations across the Nation had been established and were operational (Cowling, 1982). Now combined with the National Trends Network (NTN), the NADP/NTN cooperates with a variety of Federal, State, and private entities and currently operates more than 200 wet-deposition sampling sites spanning the continental United States, Alaska, Puerto Rico, and the Virgin Islands.

The NADP/NTN uses well-defined field methods and an extensive quality-assurance program to generate valid, defensible, and comparable results. The purpose of the network is to collect data on the chemistry of precipitation for monitoring geographical and temporal long-term trends. The precipitation at each station is collected weekly, and if it is of sufficient volume, analyzed for pH, conductivity, and the ions calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), potassium (K^{+}), ammonia (NH_3) and ammonium (NH_4^{+}), chloride (Cl^{-}), nitrate (NO_3^{-}), and sulfate (SO_4^{2-}). Data that can be obtained from the NADP/NTN are available on the Internet (NADP, 1998a). NADP/NTN data include weekly and daily precipitation chemistry; monthly, seasonal, and annual precipitation-weighted mean concentrations; annual and seasonal deposition totals; daily precipitation totals; and isopleth maps of constituent concentrations in precipitation and deposition rate [figs. 9*A*-*F* (at back of report); NADP, 2000a]. Data available from the NADP/NTN may be useful in establishing background wet-deposition constituent loadings for highway runoff studies.

The Atmospheric Integrated Research Monitoring Network (AIRMoN) is a subnetwork of the NADP/NTN run by the National Oceanographic and Atmospheric Administration (NOAA). In the AIRMoN program, wet-deposition samples are collected daily at a network of nine sites. Data are used for studying precipitation chemistry trends with a greater temporal resolution than the NADP/NTN (NADP, 1998b).

The NADP Mercury Deposition Network (NADP/MDN) is another subset monitoring program that measures Hg in precipitation. The program has been adding stations since startup in 1996, and currently (2000) includes more than 40 sites, most of which are in the eastern United States. Samples are collected weekly and collection and analysis are covered by a strong quality-assurance program. Results available through the Internet include annual volume-weighted concentrations and annual deposition (NADP, 2000b) plotted on a national map without isopleths (for example, fig. 3).

Dry deposition. Data from two dry-deposition measurement programs are available through the Internet. These programs are exclusively focussed on the problem of ozone and acid deposition. The goal of these two programs is to model dry deposition using measurements from reasonably non-complex collection of N and S chemical forms in atmospheric and meteorological data. The programs are the Atmospheric Integrated Research Monitoring Network (AIRMoN-dry program) run by NOAA Air Resources Laboratory (NOAA, 2000) and the Clean Air Status and Trends Network (CASTNET) run by the U.S. Environmental Protection Agency (USEPA) (USEPA, 2000a). Thirteen sites are available with dry-deposition estimates for SO_2, HNO_3, NO_3^{-}, and SO_4^{2-}. Because dry deposition of the measured constituents depends on deposition surface and local meteorological conditions, dry-deposition data users are cautioned against extrapolating to other conditions and locations (USEPA, 2000a).

Bulk deposition. The longest continuous record of precipitation chemistry in the United States is from the Hubbard Brook Experimental Forest in New Hampshire. Data have been collected at the Hubbard Brook site since 1963 and are discussed by Likens and Bormann (1995). Measurements have been limited to the concentrations of major ions and nutrients and water-quality properties such as pH. Estimates are made to correct bulk S and N deposition rates because of dry deposition of their gas phases, which are underestimated by the bulk collectors, as discussed previously.

Air pollution data. Although not directly a measure of deposition, air-quality information could be related to deposition. The USEPA's Toxic Release Inventory is a valuable source of information regarding the use, manufacture, treatment, transportation, or release of selected toxic chemicals into the environment. The Toxic Release Inventory can assist in locating point sources that might be affecting the atmospheric-deposition chemistry in an area (USEPA, 1998a). The States and cities collect data on air quality in a program administered by the USEPA (2000b). The data, which concern smog-producing constituents, NO_2, SO_2, O_3, and CO, particulates (PM_{10}) and lead (Pb), can be retrieved by monitoring site or by region (USEPA, 2000c).

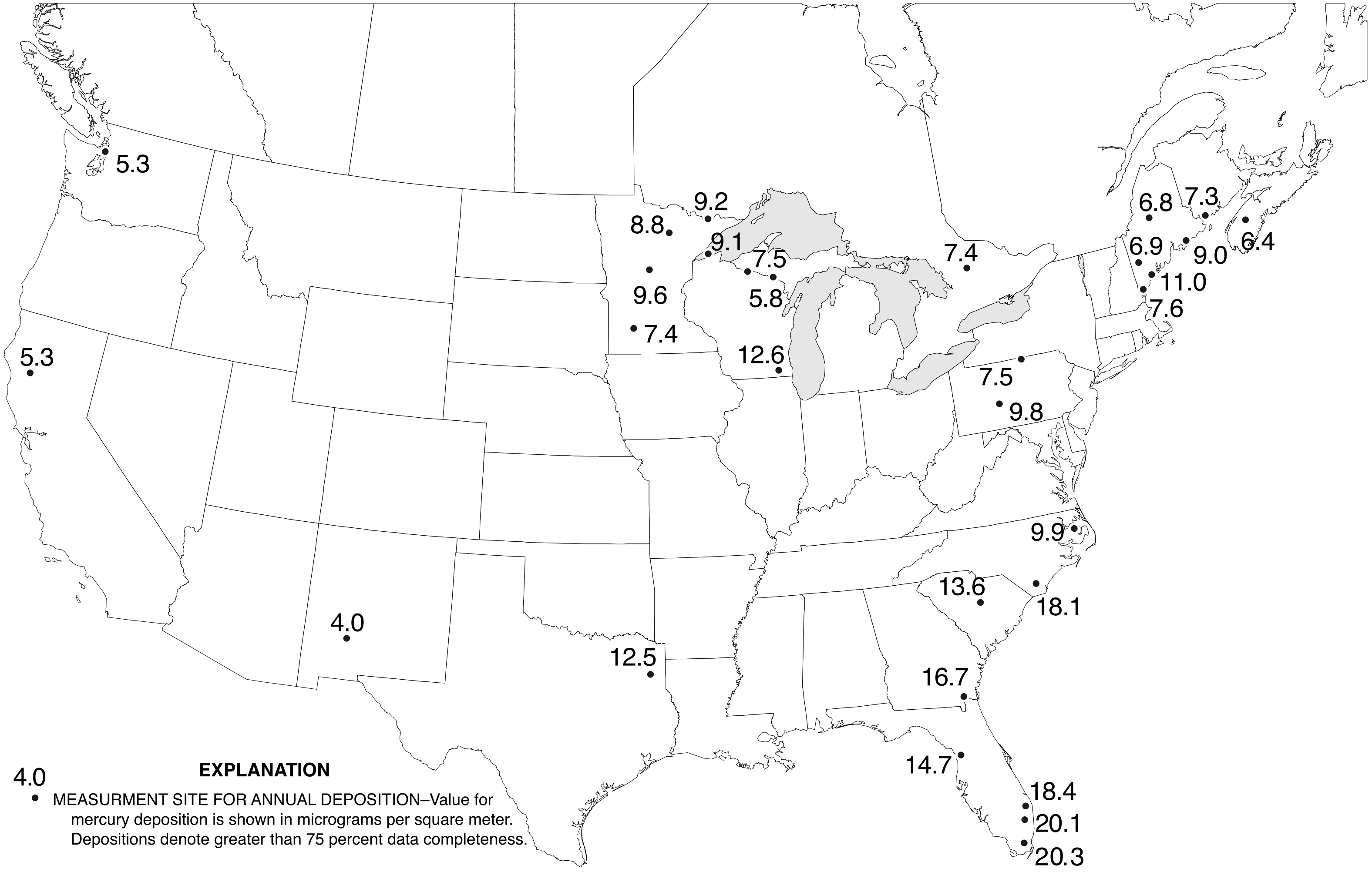

Figure 3. Annual wet-deposition rates of mercury during 1998 in the United States based on National Atmospheric Deposition Program/Mercury Deposition Network data (NADP, 2000c).

Meteorologic data. NOAA collects information concerning meteorological and climatological conditions throughout the United States. This information can be obtained from NOAA through their Regional Climate Centers. Information that may be useful in atmospheric-deposition studies includes daily and monthly high and low temperatures, precipitation amounts, wind speed and direction, and humidity (NOAA, 1998).

In summary, the available national network data are excellent for wet deposition and for acid-deposition constituents, but include only the one atypical trace metal, Hg. The dry-deposition data are focussed exclusively on acid-deposition constituents and are made available with a warning about use away from the local collection conditions.

MAJOR INORGANIC CONSTITUENTS AND WATER-QUALITY PROPERTIES

The major inorganic constituents and water-quality properties of atmospheric deposition are reviewed in this section. N and P species, often classified separately as “nutrients” in investigations of water, are included because of their relatively high atmospheric deposition.

Sources, Importance, and Chemistry

Table 1. Common major inorganic constituents of highway runoff and their primary sources

[From Kobriger, 1984]

Constituent	Primary sources
Particulates	Pavement wear
Bromide	Automobile exhaust
Calcium	Deicing agents
Chloride	Deicing agents
Magnesium	Deicing agents
Nitrogen	Atmospheric deposition and roadside fertilizer application
Phosphorus	Atmospheric deposition and roadside fertilizer application
Sodium	Deicing agents
Sulfate	Roadway beds, fuel, deicing agents, atmospheric deposition

Common major inorganic constituents of highway runoff and their primary sources (Kobriger, 1984) are shown in table 1. Of the nine constituents, sources for four, bromide (Br^-), N, P, S, are listed as atmospheric or partly atmospheric. In some locations, however, suspended solids likely could be added to the atmospheric source list, as could Ca^{2+}, Mg^{2+}, Na^+, and possibly Cl^- in warm areas, where these constituents are not applied in deicing salts.

Sediment transport is a major concern in highway runoff and certainly one source is atmospheric dust. Gupta and others (1981) reported (based on dust-bucket results) that typical monthly dustfall loads in major cities across the United States ranged from 86 to 860 mg/m^2/d. Lin and others (1993) used modeled impactor-sampler data and deposition to a standard-plate collector to determine that total-particulate deposition at a Chicago, Illinois, site varied between 90 and 270 mg/m^2/d, with 99.94 percent in the greater-than-2.5-µm fraction. Deposition of the greater-than-2.5-µm fraction is controlled by gravitational settling and may be subject to resuspension by traffic turbulence. A recent investigation comparing two sizes of road particulate matter (PM) concluded that the smaller $PM_{2.5}$ fraction, reflective of auto exhaust, exceeded the larger PM_{10} fraction, which is reflective of dustfall, at both urban and rural sites (Lamoree and Turner, 1999).

Major elements generally are not toxic and may be of less interest in highway-runoff investigations than are trace metals, many of which are toxic. Na, however, is important in drinking-water supplies because of its effect on the human circulatory system. Several highway-runoff projects have attempted to determine the extent to which Na contaminates aquifers and reservoirs near highways (Granato, 1996; Waldron, 1998). Also, the water-quality properties pH and specific conductance can affect chemical reactivity of atmospheric deposition on the highway surface (Bricker, 1999). Atmospheric deposition usually is acidic, particularly in the eastern United States (Rice and Bricker, 1992; Bricker, 1999), which could enhance the geochemical mobility of many highway contaminants. In contrast to typical trace-metal speciation in surface waters, a large percentage of trace metals in highway runoff (more than 50 percent) may be dissolved (Breault and Granato, 2000).

Character of Deposition Data

High-quality deposition data are available in greater quantity for the major constituents than for any other group because major inorganic constituents and water-quality properties (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, NH_3, Cl^{-}, NO_3^{-}, SO_4^{2-}, pH, and specific conductance) commonly are chosen for measurement in acid-deposition studies. Although accounting for only part of total deposition, the wet-deposition maps that are produced by the NADP/NTN enable observations about variability and relative deposition rates across the country. The degree of variability in the NADP/NTN wet deposition is small enough that data from the more-than-200 National collection sites can be contoured. In many areas, a reasonable approximation of the wet-deposition rate at a location between measured sites could be made by linear interpolation. Thus, highway mass-balance investigations could use the NADP data for a quality-assurance comparison check on ambient wet-deposition data collected on highway research sites. Because both wet and dry deposition originate from constituents in the atmosphere, wet deposition indicates, to a degree, the potential for constituent loads from dry and total deposition.

The deposition data maps indicate that there are lower deposition rates (order of magnitude less) for most of the major constituents in the west than in the midwest and eastern part of the country. There appears to be an eastern shift to deposition of constituents associated with combustion, such as SO_4^{2-}, (fig. 9*A*) and NO_3^{-} (fig. 9*B*) compared with those dominated by continental dust, such as Ca^{2+}, (fig. 9*C*) and those associated with agriculture, specifically the application of NH_3 in fertilizer (fig. 9*D*). Na^{+} (fig. 9*E*) and Cl^{-} (fig. 9*F*) deposition rates are uniformly low across the country except in coastal regions where sea spray increases rates.

Trends analysis of the wet acid-deposition data indicate that acid deposition has decreased nationwide between 1980 and 1991 (Baier and Cohn, 1993). Statistically significant downward trends in SO_4^{2-} deposition occurred at 26 of 33 stations examined and at 3 stations for NO_3^{-}. Significant upward trends in pH were observed at nine stations, and a significant downward trend was observed at one station.

The dry-deposition networks (AIRMoN-dry and CASTNET) address only N, S, and ozone. At sites where both wet and dry deposition are measured, contributions from the two sources can be compared. Generally, the dry-deposition rates are much greater than the wet-deposition rates, and dry deposition of the gas forms (HNO_3, and SO_2) are substantial (10 times the particulate forms).

Reliable dry-deposition data for the other major elements are scarce. Ca dry deposition (7.1 $mg/m^2/d$) measured June through October 1991 in Chicago by standard surface deposition and by model simulation (Lin and others, 1993) was completely dominated by large-sized particles and more than 10 times the wet deposition measured by NADP in 1998 in the same area (0.69 $mg/m^2/d$). Measurements of dry deposition of six crustal elements—aluminum (Al), Ca, iron (Fe), Mg, silicon (Si), and titanium (Ti)—to a standard surface during July 1991 at three locations around southern Lake Michigan (at Chicago, on Lake Michigan, and at South Haven) varied in proportion to Ca deposition rates of 6.4, 1.5, and 3.0 $mg/m^2/d$, respectively (Holsen and others, 1993). This variation likely relates to prevailing wind direction and to relative proximity to a crustal source among the three sites.

Bulk collectors would represent a potential source of dry-deposition data if, as assumed by Likens and Bormann (1995), bulk collector results for Ca, Mg, Na, K, and Cl are accurate. An estimate of dry deposition could be made by comparison of their results with NADP wet deposition for northern New Hampshire. Replicates of bulk-collection results are variable, however (Kobriger and Geinopolos, 1984), so that the difference statistic, which represents dry deposition, likely would be inaccurate.

Phosphorus is not reported by NADP because concentrations in wet deposition generally are too low to be measured accurately. But dry deposition of phosphorus may be substantial and thus important in highway runoff that enters surface waters (Dudley and others, 1997). Analysis of year-long data collected in association with a lake budget in Walden Pond, Concord, Massachusetts, indicated that phosphorus deposition was dominated strongly by dry deposition (Colman and Friesz, 2001). Wet deposition was 0.010 $mg/m^2/d$, and dry deposition, measured in a bucket with water to simulate the lake-collector surface, was 0.14 mg/m^2/d. The seasonal pattern of dry deposition indicated that pollen was a major component of the phosphorus load.

Uses in Highway-Runoff Investigations

Cl^- and Na^+ are important major ions in the highway runoff context because of their use in road-salt applications and because of potential health effects of Na^+ in water supplies. Ambient Cl^- and Na^+ deposition enter into road-salt runoff investigations as part of background loads. The NADP deposition maps (figs. 9*E*,*F*) show that Cl^- in precipitation (less than 1 mg/L) never approaches the concentrations of Cl^- in runoff associated with deicing in the north (100s to 1,000s of mg/L, Driscoll and others, 1990b). This result is the case even in northern near-marine areas (Massachusetts, Maine, Oregon, and Washington), where sea salt is incorporated into precipitation (Gay and Melching, 1995). If the wet-deposition rates are increased by a factor of 10 to account for dry deposition, resulting total deposition is still much less (10 times) in runoff at sites where road salt was applied.

The major elements may have a particular use in assessing how the highway processes of saltation and resuspension affect transport of ambient deposition to highway runoff. The major elements are more likely to be conservative in their chemistry and to be derived from ambient atmospheric deposition (rather than from engine and vehicle wear) than the trace metals. In addition, their measurements are less subject to quality-assurance problems during collection and analysis. Na^+ and Cl^- might be used in warm areas where deicing agents are not used. Generally anions do not adsorb to solids, so the negatively charged chloride ion would be conservative during event-associated transport. Comparison of the Cl^- runoff rate with Cl^- deposition rate might indicate, for example, the net effect between the processes of loss from resuspension and that of increase because of turbulence impaction on the highway.

Although the major-element sources and chemistry are relatively simple, some considerations indicate that these likely tracers might give misleading results if the highway site is not carefully chosen. For example, concentrations may be greatly affected by bank erosion and soil brought onto highways on tires and vehicle underbodies because aluminum (Al), Ca, Fe, Mg, manganese (Mn), and Si and suspended solids can be large components of these materials. Highway surfaces themselves can erode and contribute major ions, especially Mg and Ca, from concrete surfaces.

TRACE METALS AND CYANIDE

Trace metals and cyanide are reviewed in this section. Trace metals are deposited on highways from vehicles and the atmosphere. Cyanide is present in highway deicing salts.

Sources, Importance, and Chemistry

Trace metals and cyanide are important contaminants in highway runoff and may have substantial sources in ambient as well as vehicle-related atmospheric deposition. Trace metals are emitted to the atmosphere by both natural and anthropogenic sources. Natural processes, such as volcanic emissions and weathering of earth-surface materials (soils and bedrock), can contribute particulate-bound trace metals to the atmosphere. Anthropogenic activities are recognized as sources of trace metals to the atmosphere and include combustion of municipal solid waste (Campbell, 1976; Germani and Zoller, 1994), combustion of fossil fuels in coal- and oil-fired power plants (Campbell, 1976), releases from metal smelters (Crecelius and others, 1975; Ragaini and others, 1977), automobile emissions (Shaheen and Boyd, 1975; Ondov and others, 1982), and a large number of industrial stack emissions. Chemical analysis has indicated that fuels and exhaust contain many metals in measurable quantities, including Al, Ca, cobalt (Co), Fe, K, lithium (Li), Mg, Mn, Na, platinum (Pt), antimony (Sb), strontium (Sr), Ti, and V, in addition to the commonly studied trace metals cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), Pb, and zinc (Zn) (Hildemann and others, 1991; Hee, 1994). Vehicular emission of trace metals is well recognized as a source of contaminants to the roadside environment (Harrison and Johnston, 1985). Common trace metals in highway runoff and their primary sources are shown in table 2.

Table 2. Common trace constituents in highway runoff and their primary sources

[From Kobriger, 1984]

Constituent	Primary sources
Cadmium	Tire wear and insecticide application
Chromium	Metal plating, moving engine parts, and break-lining wear
Copper	Metal plating, bearing and bushing wear, moving engine parts, break-lining wear, and fungicide and insecticide application
Iron	Autobody rust, moving engine parts, and steel highway structures
Lead	Automobile emission, tire wear, lubricating oil and grease, and break wear
Manganese	Moving engine parts
Nickel	Automobile emission, lubricating oil, metal plating, bushing wear, brake-lining wear, and asphalt paving
Zinc	Tire wear, motor oil, and grease
Cyanide	Deicing agents

By comparison with deposition rates of the major elements, the size of the atmospheric-deposition source for the trace metals is less well known. These metals are present in trace amounts in earth crustal materials, but vehicles have large percentages of these elements in their components, even pure sources such as copper wiring, cadmium plating, chromium trim, and substantial presence in gasoline. Although trace metals detected in highway runoff likely come from vehicles, quantifying that source by difference between deposition and runoff is difficult. Low concentrations (microgram per liter level) in deposition and runoff mean the load difference between the two is inaccurate unless great care is taken with precision in sampling methods (Breault and Granato, 2000).

Deicing agents such as rock salt (NaCl), calcium chloride ($CaCl_2$), and sand mixtures can contain impurities such as trace metals and cyanide, which is used as an anticaking agent. Measurable concentrations of Cd, Cr, Cu, Pb, Ni, Zn, and cyanide were detected in samples of deicing salts (Kobriger, 1984; Granato, 1996). Cd, Cu, Fe, Pb, Ni, Zn, and cyanide were found in deicing agents and sand mixtures that were used in Efland, N.C. (Harned, 1988).

The trace metals are important because of their toxicity in aquatic systems. In highway runoff, much of the trace-metal load may be in bioavailable, dissolved form (Bricker, 1999). Even the nondissolved load, however, which accumulates in sediment deposits on stream and lake beds, can be bioactive and is associated with tumors in fish and sediment toxicity (Buckler and Granato, 1999; Rice 1999). The chemistry of trace metals can be complex. In the aerobic aquatic environment, trace metals generally oxidize to cations and may become sorbed to solid phases or precipitate as metal oxides. The interaction between trace metals and organic materials is substantial and may lead to increased trace-metal mobility (Breault and others, 1996).

Character of Deposition Data

With the exception of wet deposition of Hg, deposition data for the trace metals is not available from a national network; therefore, information on rates and variability of trace-metal deposition data is much harder to assess than for the major elements. Another problem with gathering trace-metal deposition data is data quality for trace-metal concentrations, which typically are in the low or sub microgram-per-liter range in wet deposition (Vermette and others, 1995; Willoughby, 1995), or for Hg, in the low nanogram-per-liter range (NADP, 2000b).

Careful selection of collector construction materials and of protocols for cleaning, sample handling, and sample processing is necessary to avoid sample contamination of the trace metals. During the past 25 years, problems of contamination of trace-metal samples during sampling have been recognized. Contamination of Pb samples in oceanography studies was one of the first contamination problems to be recognized. Correction of the contamination problems resulted in estimates of seawater Pb concentrations orders of magnitude less than those previously measured (Patterson and Settle, 1976).

Similar downward adjustments in trace-metal concentration may be necessary for atmospheric-deposition estimates. Trace-constituent data on atmospheric deposition separated according to early studies (1987 and prior) without, and later studies (1993 and later) with, quality-assurance procedures are shown in table 3. The wet-deposition rates for trace metals in earlier studies (Chicago data of Lazrus and others, 1970) are much higher than in later investigations (Vermette and others, 1995; Willoughby, 1995), which may reflect changes in sampling, especially in sampler materials and in sample handling, since the earlier investigations. Changes in actual deposition rates, however, can not be ruled out as a cause for the much higher early deposition rates.

Table 3. Atmospheric deposition rates, for constituents of concern in highway runoff, measured by dry-, wet-, and bulk-deposition collectors and by dry deposition onto a standard grease-covered plate

[All rates are in milligrams per square meter per day. --, no data]

Constituent	Early investigations without quality assurance					Recent investigations with quality assurance			
	Dry deposition	Wet deposition	Bulk collector	Comments	Reference	Dry deposition to standard plate	Wet deposition	Comments	Reference
					TRACE METALS				
Cadmium	--	--	0.0031	--	Hedges, 1987	0.0050	--	South Haven, Mich.	Holsen and others, 1993
			.0243	near rural highway	Harrison and Johnston, 1985	--	0.0002	Gary, Ind.	Willoughby, 1995
			.0014	far from rural highway	Harrison and Johnston, 1985	--	.0005	1 m precipitation assumed, average 3 sites	Vermette and others, 1995
	--	--	--	--	--	.0055	--	South Lake Michigan	Zufall and others, 1998
Copper	--	--	--	--	--	--	.0029	Gary, Ind.	Willoughby, 1995
		0.1800		Chicago, Ill.	Lazrus and others, 1970	--	.0027	1 m precipitation assumed, average 3 sites	Vermette and others, 1995
			.2143	near rural highway	Harrison and Johnston, 1985	.0600	--	Chicago, Ill.	Paode and others, 1998
			.0214	far from rural highway	Harrison and Johnston, 1985	.0100	--	South Lake Michigan	Paode and others, 1998
Chromium	--	--	--	--	--	--	.0115	Gary, Ind.	Willoughby, 1995
Nickel	--	.0267	--	Chicago, Ill.	Lazrus and others, 1970	.1270	--	Chicago, Ill.	Lin and others, 1993
						.0100	--	Lake Michigan	Holsen and others, 1993

Table 3. Atmospheric deposition rates, for constituents of concern in highway runoff, measured by dry-, wet-, and bulk-deposition collectors and by dry deposition onto a standard grease-covered plate—*Continued*

Constituent	Early investigations without quality assurance					Recent investigations with quality assurance			
	Dry deposition	Wet deposition	Bulk collector	Comments	Reference	Dry deposition to standard plate	Wet deposition	Comments	Reference
				TRACE METALS—*Continued*					
Lead	--	--	--	--	--	--	0.0029	Gary, Ind.	Willoughby, 1995
	--	0.4600	--	Chicago, Ill.	Lazrus and others, 1970	0.0700	--	Chicago, Ill.	Paode and others, 1998
	--	--	1.6857	near rural highway	Harrison and Johnston, 1985	.0030	--	South Lake Michigan	Paode and others, 1999
	--	--	.0714	far from rural highway	Harrison and Johnston, 1985	--	.0060	1 m precipitation Assumed; average 3 sites	Vermette and others, 1995
Zinc	--	1.6533	--	Chicago, Ill.	Lazrus and others, 1970	--	.0066	Gary, Ind.	Willoughby, 1995
	2.8493	--	--	--	Barret and others, 1994				
				ORGANIC COMPOUNDS					
PCBs	--	--	--	--	--	0.0028 to .0097	--	Chicago, Ill.	Holsen and others, 1991
						--	0.0026	1 m precipitation assumed; 50 km north of Minneapolis, Minn.	Franz and others, 1991
Total PAHs	--	--	--	--	--	--	.0528	1 m precipitation assumed; 50 km north of Minneapolis, Minn.	Franz and others, 1991
1,2,4,Trichloro-benzene	--	--	--	--	--	--	.0088	1 m precipitation assumed; 50 km north of Minneapolis, Minn.	Franz and others, 1991

Part of the more recent trace-metal wet deposition data in table 3 were from a NADP pilot investigation of trace metals in precipitation (Vermette and others, 1995). The original data were volume-weighted concentrations for six metals in three sites (Illinois, Colorado, and Tennessee). Manganese varied the most among sites by a factor of 5. Cd and Cu varied by only 20 and 34 percent, respectively, but deposition rates for these constituents were very low. The deposition data in table 3 from this investigation were based on these volume-weighted concentrations and assumed annual rainfall of 100 cm (less would apply in Colorado; Smieszek and Granato, 2000). Other wet-deposition rates for trace metals from Gary, Indiana (near Chicago), are available in table 3 (Willoughby, 1995). These rates were measured with appropriate quality-assurance protocol in the heavily industrial Chicago area and may be considered to indicate high rates of wet deposition reliably. Note that even these methods might not prevent contamination for very low-concentration contaminants like Hg. The estimated maximum deposition rate was 0.00018 mg/m^2/d, which is three times the maximum rate measured in the 1998 MDN program (NADP, 2000b).

Ambient wet-deposition rates are better known for Hg than other trace metals because of the MDN national Hg deposition network of some 40 sites with excellent quality-assurance procedures. The network data indicate that ambient wet deposition of Hg ranges from 0.00001 mg/m^2/d in Arizona to 0.00006 mg/m^2/d in South Florida (fig. 3). These low Hg wet-deposition rates may represent less than half of total Hg deposition. Much of the two most common forms of Hg in the atmosphere, Hg^0 and Hg^{2+}, is transported to the earth through dry deposition (Lin and Pehkonen, 1999).

As is the case for the major elements, trace-metal deposition may be dominated by dry deposition. In the case of Pb, for instance, dry-deposition measurements made from June to October 1991 were 0.13 mg/m^2/d in Chicago (Lin and others, 1993), whereas a Chicago-area average wet-deposition measurement in 1992–93 (Willoughby, 1995) was 0.0029 mg/m^2/d, 45 times less.

Pb is an example of an element whose release into the environment has changed because of environmental laws restricting its use, especially in gasoline (Callender and Rice, 2000; Callender and Van Metre, 1997). Average Pb concentrations in air (from 160 sites nationwide) decreased dramatically during 1978–88 (fig. 4, USEPA, 1998b). The comparisons in the preceding paragraph, however, concern years (1992–93), during which Pb concentrations in the atmosphere were relatively stable.

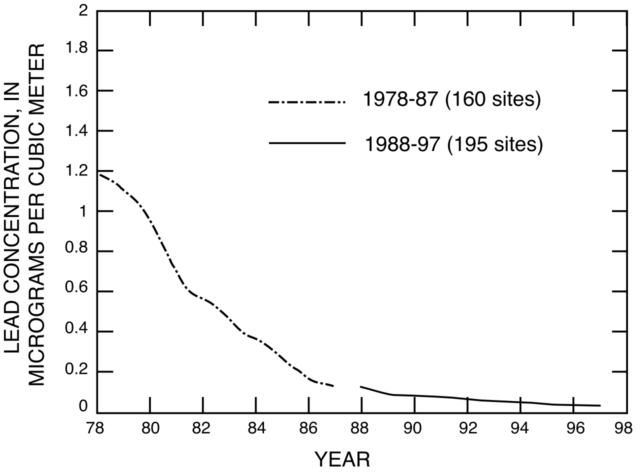

Figure 4. Long-term trend in ambient atmospheric lead concentration in the United States (U.S. Environmental Protection Agency, 1998b).

Dry-deposition rates depend on particle size. Lin and others (1993) determined that although Pb concentrations were higher on smaller particles than on larger particles, particle flux for Pb was dominated by dry deposition of large-sized particles because deposition velocities for the large-size particles were much greater than deposition velocities for small-size particles. Investigation of dry deposition over Lake Michigan indicated that these relations may be seasonal. Zufall and others (1998) determined that deposition was dominated by large-sized particles (greater than 8 µm) during July 1994 but was dominated by smaller particles (4–8 µm) during January 1995.

Dry-deposition rates can vary dramatically from urban to rural areas and can be extremely low in rural areas. An investigation of deposition of three trace metals (Cu, Pb, and Zn) onto a standard surface in environments around Chicago (Paode and others, 1998) indicated that dry fluxes for all metals were greatest in Chicago, less in coastal South Haven, Michigan, and least over the water in Lake Michigan between Chicago and South Haven. Highest dry-deposition rates were 0.17 and 0.6 mg/m^2/d, for Cu and Zn, respectively; low rates were 0.003 and 0.005 mg/m^2/d, for Pb and Cd, respectively (table 3).

Finally, the extremely high trace-metal deposition rates associated with smelter operations should be noted. A recent investigation of dry deposition downwind from a Zn-Pb smelter in Australia, using some quality-assurance procedures such as duplicate deployment, sample spikes, blanks, and reference materials, determined median rates of 19, 22, 12, 0.61, 0.40, and 0.052 mg/m^2/d for Pb, Zn, Fe, Cu, As, and Cd, respectively (van Alphen, 1999).

Uses in Highway-Runoff Investigations

Toxicity of the trace metals is the principal reason for investigating their deposition to highway surfaces. The wear of vehicle metal parts and tires is an important potential source of trace metals, and elevated concentrations (above background levels) of trace metals are measured in highway runoff. Trace metals, including isotopes, also may be investigated to help determine the relative contribution of ambient and vehicle sources to highway runoff. For these kinds of investigations, trace elements must be present in ambient-deposition sources, but not present in vehicle-related sources.

ORGANIC COMPOUNDS

Deposition of organic compounds is reviewed in this section. Organic compounds in deposition originate from vehicle and industrial sources.

Sources, Importance, and Chemistry

Vehicle emissions are a well-documented source of volatile, semivolatile, and other organic compounds to the atmosphere (Harrison and Johnston, 1985; Westerholm and others, 1988; Gardner and others, 1995). Organic compounds are common constituents in highway runoff (Lopes and Dionne, 1998). Volatile organic compounds tend to partition from the particulate and aqueous phases to the gaseous phase. Semivolatile organic compounds generally partition toward the particulate and aqueous phases. Semivolatile organic compounds, therefore, usually are deposited near the highway (Harrison and Johnston, 1985).

Polycyclic aromatic hydrocarbons (PAHs), which are semivolatile organic compounds, and their derivatives are among the organic compounds of most concern because of their effects on human health (Harrison and Johnston, 1985). Harrison and Johnston (1985) determined that vehicle-generated PAHs were deposited primarily within 15 m of the highway. Elevated PAH concentrations (above background levels) at distances greater than 30 m from a highway usually were measured in winter and early spring, coinciding with the combustion of fossil fuels for domestic heating (Harrison and Johnston, 1985). Methyl *tert*-butyl ether (MTBE) is a volatile organic compound made from methanol and used as a gasoline additive to improve air quality in urban areas. The compound can have adverse human health effects, however (Squillace and others, 1995). The amount of MTBE released from motor vehicles is unknown but could be an important source of MTBE to the environment (Squillace and others, 1995).

Organic-compound pesticides have been recognized as potential air pollutants since 1946 (Daines, 1952). Before the 1960s, atmospheric deposition of pesticides generally was thought to be a local problem caused by spray drift (Majewski and Capel, 1995). Long-range movement of pesticides was thought to be minimal because their volatility and solubility in water are low. The detection of DDT (dichloro-diphenyl-trichloroethane) and other organochlorine compounds in fish and mammals in the Arctic and Antarctic proved that pesticides can be transported over long distances (Cade and others, 1968). Almost all pesticides investigated have been detected in air, rain, snow, or fog in the United States at various times of the year (Majewski and Capel, 1995). Pesticides, especially herbicides, can be applied to or near roadways. Harned (1988) measured elevated levels of the herbicide 2,4-D [(2,4-dichlorophenoxy)acetic acid] in a stream near a highway about 2 weeks after the herbicide was applied to weeds along the roadway.

Character of Deposition Data

Concentrations of organic pollutants in precipitation were measured in 1986 by Franz and others, (1991) at a site 50 km north of Minneapolis, Minn. If precipitation were 100 cm per year, polychlorinated biphenyl (PCB), phenanthrene, and *p,p′*dichloro-diphenyl-dichloroethylene (*p,p′*-DDE) wet-deposition rates would be 0.0026, 0.0086, and 0.00073 mg/m^2/yr, respectively. Results for other polyaromatic hydrocarbons (PAHs) and chlorinated compounds are in table 3.

The amount of PCB dry deposition to a standard surface has been investigated in Chicago. The estimated PCB flux varied between 0.0028 and 0.0097 $mg/m^2/d$, which was up to three orders of magnitude greater than that estimated to fall in nonurban areas (Holsen and others, 1991). Unlike the trace metals, these PCB dry-deposition values do not differ greatly from those for wet deposition.

Uses in Highway-Runoff Investigations

Excluding those organic compounds with roadway uses, such as the herbicide 2,4-D, investigations of some of the contaminant compounds might be useful for elucidating the on-highway processes that determine how much of what is measured as ambient deposition in collectors falls onto highways and moves into highway runoff. Although vehicle fluids and exhausts are sources of organic compounds to the atmosphere, some of the pesticides and PCBs are unlikely to be of vehicle origin. Unlike the major elements or the trace metals, these manmade compounds are not found in nature and their molecular structures are specific enough not to occur except through intentional synthesis. Manufacture and use of PCBs have been prohibited for over 25 years so that they are no longer part of vehicle materials or fluids. PCBs get into the atmosphere mostly in vapor form and may adhere to distinctly different particles and follow different atmospheric-transport processes than do the major elements or the trace metals.

REVIEW OF ARTICLES ON ATMOSPHERIC SOURCES FOR HIGHWAY RUNOFF

Atmospheric deposition has been a subject of many highway publications (table 5, at back of report). These include studies in which collectors were deployed transverse to the highway to determine the effect of traffic on atmospheric deposition and traffic-related processes of saltation and resuspension. In the highway-runoff context, however, atmospheric deposition is of interest chiefly as a source for constituents in runoff. Many highway-runoff studies result in questions about, or are designed to determine, which part of highway runoff comes from ambient atmospheric deposition and which comes from traffic. These sources may covary because both traffic volume and ambient atmospheric deposition increase across the gradient from rural to urban land use.

Comparison of Traffic-Related and Ambient Atmospheric-Deposition Sources

Whether vehicles or ambient atmospheric deposition is the dominant source of runoff constituents is an important topic not yet resolved for many constituents measured in highway runoff. If traffic sources dominate, runoff loads would be similar for all highways, or proportional to traffic volume. If traffic contribution were small, runoff loads would depend on local atmospheric deposition, which can differ greatly along the gradient from rural to urban land use, particularly for dry deposition. For some constituents, both ambient atmospheric deposition and traffic sources may make large contributions, or their relative contributions might depend on land use. For instance, ambient air may be a problem for a given constituent in urban areas or near a smelter, but usually not in rural areas.

Deposition Rates and Highway Proximity

One way to determine the relative importance of traffic-related and ambient atmospheric-deposition sources is through examination of deposition rates at sites at different distances from the highway. Deposition fluxes of Cd, Cu, and Pb were determined to be highly elevated (6, 13, 33 times, respectively) in bulk samplers within 20 to 40 m of a highway in England in comparison with background levels measured 40 to 220 m from the highway (fig. 5) (Harrison and Johnston, 1985). Deposition rates for PAHs, which are a combustion product of fossil fuels, would be expected to decrease with distance from highways. The Harrison and Johnston (1985) investigation in England found that PAH deposition increased as the distances of measurement sites from their investigated highway decreased; otherwise, the highway had clean air blowing in off the Atlantic Ocean. Harrison and Johnston (1985) concluded that roadway-derived PAH was deposited primarily within 25 m of the road and was 100 times greater than background levels. The highest deposition rate recorded was 0.0010 $mg/m^2/d$. PAHs

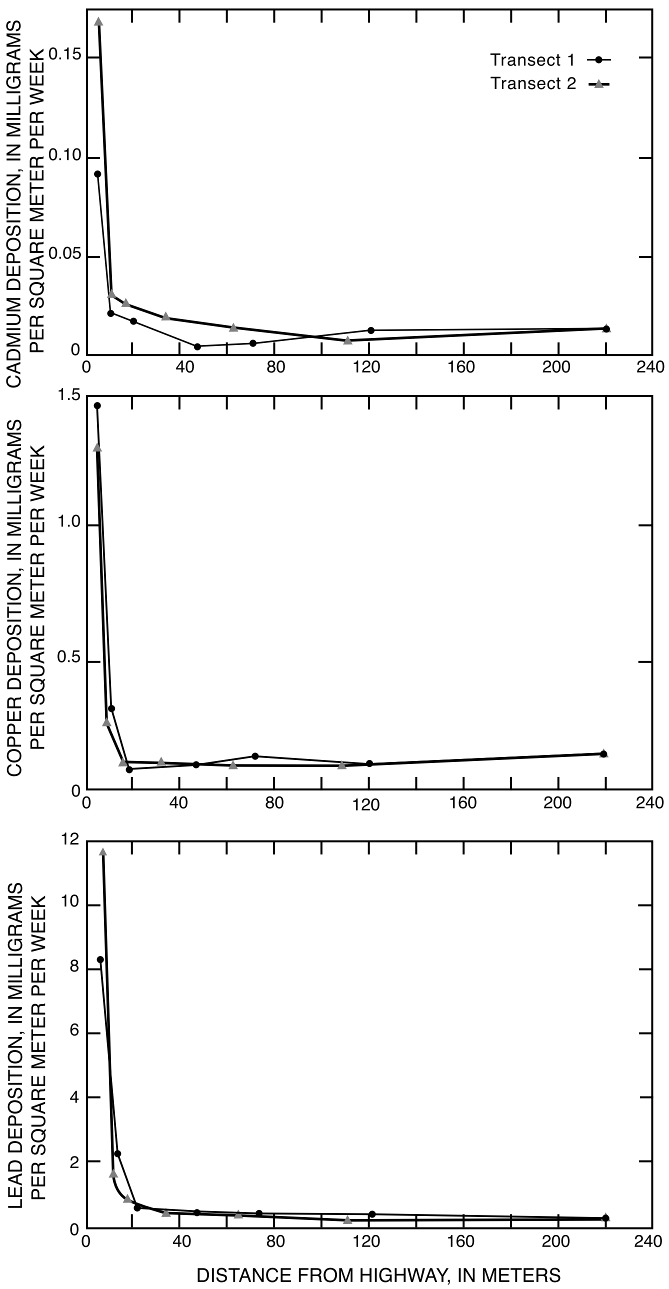

Figure 5. Average bulk deposition rate of trace metals for the period from October 14, 1981, to June 15, 1983, along two transects with distance from a rural highway in England (Harrison and Johnston, 1985).

are produced by non-vehicle sources of fossil-fuel burning as well, and the rate of deposition from urban air can be higher than the rural, near-highway rate (Harrison and Johnston, 1985).

Similar decreases (as PAH) in concentrations of trace metal as the distance from the roadway increases were observed in studies by Hedges and Wren (1987), Warren and Birch (1987), and Hewitt and Rashed (1990). Atmospheric deposition of highway-generated total particulate matter (TPM) and associated constituents onto areas adjacent to roadway surfaces appeared to be related to average daily traffic, wind speed and direction, available surface load, and terrain and landscape features (Kobriger, 1984). Harned (1988) compared dustfall by dry deposition between a site on Interstate 85 in North Carolina and a site about 0.5 mi from the highway. Land use at the highway site was 100 percent transportation and utilities. Land use at the background site was predominantly mixed forest, cropland, pasture, and open space. Samples collected in dust buckets at the highway site were compared with samples collected in a wet-dry collector at the background site. By adding the wet and dry fractions collected at the background site, Harned (1988) concluded that the proportion of the total loading attributable to background conditions was unexpectedly high, ranging from 42 percent for Zn to 93 percent of the total particulate loading rate determined for the highway site. Because there were no other apparent sources for these constituents in the area, this high proportion of the total dustfall loading rate at the background site suggested that dust from highways can be carried considerable distances. Harned (1988) compared trace-element loadings in bulk-deposition samples collected at the background site with samples collected by dust buckets located near the highway and observed that median loadings computed from the background samples were smaller than loadings computed from highway samples. Harned (1988) also showed, by analyzing samples from soil and from dust buckets arranged perpendicular to the road, that the highway was a source of contaminants in local atmospheric deposition and that concentration levels of all the monitored trace metals decreased as distance from the road increased.

Near-highway transects of soils and deposition are important ways to determine relative importance of highway and atmospherically derived sources. For constituents collected using appropriate methods, deposition measurements may be better because they are not subject to leaching loss, as would be soil concentration measurements. The studies cited showing that deposition rate decreases with increasing distance from the highway indicate that highways are large sources of these contaminants relative to atmospheric deposition. Potential problems with these investigations may be present because measurements are taken from dust buckets or bulk collectors. These methods of collection have uncertain quality-assurance procedures and uncertain collection efficiencies that may depend on turbulence conditions, which could be traffic-related.

Lower background dry deposition (Holsen and others, 1993) and wet-deposition values (Willoughby, 1995) have been measured in investigations with appropriate collector construction and quality-assurance programs in environments more urban than that of the Harrison and Johnston investigation (table 3). Thus, the 33-fold difference for Pb measured by Harrison and Johnston (1985) may be still greater if clean methods had been used to collect the background sample. The effect of uncertain collection efficiency might be to either over or under sample deposition and could, thus, increase or decrease the measured gradient.

Mass Balance

Mass balance is another approach used to separate vehicle and ambient-deposition contributions to highway runoff loads. Direct measurements of vehicle contributions to roadways are difficult to make because ambient and vehicle-related contributions at the roadway cannot be separated. Direct contributions from ambient deposition, however, can be quantified by use of an atmospheric-deposition collector removed a suitable distance from the road. Many investigators have used a mass-balance approach to compute the vehicle deposition by subtracting atmospheric deposition from runoff loads. The method has a major flaw if actual atmospheric deposition to the highways is different from that determined by the collector.

Barrett and others (1995) in their literature review on quantity and control of pollution from highway runoff and construction state that “atmospheric sources contribute a significant amount of the pollutant load in highway runoff.” Cited were (1) Irwin and Losey (1978) with ambient bulk deposition versus runoff values for 15 runoff constituents for a highway bridge in Florida—contributions to bridge runoff from bulk collection ranged from 18 percent for Pb to 38 percent for Cu to 490 percent for Na; (2) Bellinger and others (1982) on precipitation loads to highway runoff for major ions (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, and $SO_4{}^{2-}$), which were actually small, averaging 2 percent, and total solids, which averaged about 10 percent; and (3) Gupta and others (1981) on dustfall, who reported deposition rates ranging from 130 to 900 $mg/m^2/d$ at Federal highway monitoring sites. Barrett and others (1995) state that “if all the dustfall remained on the highway, dustfall load would approximately equal the load in the runoff.”

Working with data from 31 urban catchments across the United States, Ebbert and Wagner (1987) determined percentage of runoff load that came from rainfall for 12 constituents. For example, 40 percent of N, 6 percent of Pb, and 2 percent of suspended solids measured in runoff was from rainfall input. Again, these values assume conservation during transport in the catchment. A complete mass-balance approach was taken by Kobriger and others (1982) for a rural highway site in North Carolina. Atmospheric fallout was 8 percent of the total material loading the highway surface, with vehicle deposition and highway maintenance (including sanding and salting) of 25 and 67 percent, respectively. Vehicular deposition was calculated as the difference between the highway-runoff load, and the salting-sanding and atmospheric load.

Problems may result with the mass-balance approach. Implicit in the mass-difference calculation to compute traffic contribution is the assumption that the atmospheric contribution is transferred to runoff with 100 percent conservation. But a contaminant may precipitate in the drain or catch basin, or be subject to resuspension and deposition off the highway. A large percentage of dry deposition, which composes a large proportion of trace-metal contaminants, apparently would be subject especially to resuspension (as reviewed under “Forms of Deposition and Post-Depositional Transport”). Likely, a large percentage of deposition from both vehicles and ambient atmospheric sources is moved off highways by resuspension, in which case comparisons of measured atmospheric loads with runoff loads leads to incorrect values for traffic loads.

Sample contamination during sample collection and processing could add to uncertainty in the mass-balance calculation. Much of the deposition data has been collected with methods that are known to cause contamination problems at the concentrations that might be expected in the samplers (Patterson and Settle, 1976; Windom and others, 1991). When samples for precipitation have been collected with clean techniques, concentrations have been lower than those without the clean-techniques procedures (table 3).

In another mass-balance approach to determining sources of highway runoff, the assumption has been made that ambient atmospheric loadings are the difference between highway runoff loadings measured in urban and rural settings. Various investigators have implied that ambient-atmospheric inputs can be important even for those pollutants (trace metals) that would appear to be dominated by traffic. Driscoll and others (1990a) reported that the most important factor that affects the types and amounts of contaminants contributed to highway runoff is the surrounding land use. Constituent loadings in areas where the dominant land use is industrial have been reported to be substantially greater than in areas where the dominant land use is residential or commercial (Gupta and others, 1981; Schroder and others, 1989; Driscoll and others, 1990a). Results from highway runoff studies conducted in the early 1980s indicate that total particulate matter measured in bulk deposition collected at urban sites contained approximately four times greater loadings than total particulate matter collected at rural sites. Similarly, trace-element bulk deposition was greater at background urban sites than at background rural sites (Dannecker and Stechmann, 1990; Smith and Lord, 1990). Complicating this approach are traffic and atmospheric sources, both of which are less in rural areas than in urban areas.

Regression Models of Federal Highway Administration Data

Another means of attributing runoff constituents to sources is through regression equations. A fundamental mass-balance consideration in atmospheric sources to highway runoff concerns the precipitation/runoff water balance. Regressions of water balances of precipitation and by the Federal Highway Administration (Driscoll and others, 1990a) indicate that about 80 percent of the water that falls onto impervious sections of highways runs off. The relation relates runoff from a given surface area to precipitation on the surface area as a function of percent of surface area that is impervious and given as

$$\text{Runoff} = \text{Precipitation}\ [0.007\ (\text{Percent impervious surface area}) + 0.1]\ .$$

Of the 20 percent lost from impervious surfaces, presumably some water evaporates and some splashes off the highway. These processes, of unknown relative magnitude, would act with contrasting effects on wet-deposition constituents. Evaporation would concentrate nonvolatile constituents in the water, resulting in no constituent loss in runoff, whereas splash loss removes both water and constituents in the water from runoff.

Regressions of data from 10 years of investigation supported by the Federal Highway Administration (Driscoll and others, 1990a) indicated that simple models that simulate trace-metal pollutant concentrations in runoff were not possible. Event mean concentration (EMC) of each of the monitored constituents during a storm were regressed first against storm size and then against average daily traffic level (ADT). Lack of correlation against storm or runoff volume was taken to “eliminate any concern for possible bias because of differences in the size of monitored storms at different investigation sites.” Initially, the analysis indicated that EMC was less for rural sites compared to urban sites for each of the pollutants monitored. ADT also was less at the rural sites and actually was used to distinguish between rural (less than 30,000 vehicles per day) and urban (greater than 30,000 vehicles per day) classifications. Subsequent regression of EMC and ADT was applied only to higher ADT-level urban data. Most of the latter regressions resulted in low degrees of correlation. Some of the regressions, such as for phosphate and nitrate EMC, had negative slopes leading to the counterintuitive results that more traffic results in less pollution. An exception was the regression result for Zn. With one outlier removed, the Zn correlation was positive with an r^2 of 0.70. The outlier, with an EMC almost three times the next highest value, was associated with a site downwind from a Zn smelter.

Driscoll and others (1990a) concluded that the explanatory variable database (that is ADT) was not sufficiently large for regression analysis to develop general relations that could be used to simulate pollutant loads in highway runoff. The data for the urban regressions came from some 24 highway sites throughout the continental United States. Given the degree of climate variation across the country, an argument for insufficient explanatory variables sounds plausible. Driscoll and others suggested explanatory variables should include climate variables, atmospheric deposition and removals, highway-site situations, operational situations, and surrounding land-use characteristics. The investigation emphasized that the “runoff quality differed significantly between highways in urban areas versus those in rural areas.” Traffic densities are markedly different between these two categories of surrounding land use, but the lack of a clear correlation of trace-metal EMC with ADT within each grouping led to the conclusion that the general atmospheric-quality differences between urban and rural areas were the most important effect. Cited also was an investigation in Germany that concluded ADT is not a dominant factor and that the characteristics of the surrounding area are a more important effect (Stotz, 1987).

Other causes of the lack of a correlation should be considered, especially that of questionable data. No amount of explanatory variables from an expanded data-collection program will improve the regressions between trace-metal concentrations and ADT if the runoff data are biased or not of comparable quality. For instance, variability in the Hg runoff data was extreme. EMC Hg values at the urban sites ranged from 1 to 1,500 ng/L. This variation was too large for vehicles to be the sole cause, because ADT varied only by a factor of three. Variation that occurs nationally in atmospheric deposition of Hg also is small. As measured by the MDN, wet-deposition Hg varies across the country by only a factor of two. Hg is difficult to sample even in relatively high-concentration environments because of sample contamination during the sampling and sample processing (Bloom, 1995). Unless extraordinary sampling methods are used, such as described by Colman and Breault (2000), much higher concentrations of Hg would be attributed to runoff than actually are present. Extraordinary trace-metal sampling methods, including strict quality-assurance procedures and sampling using a clean hands-dirty hands protocol, were not used in the highway-data collection.

Even without quality-assurance procedures, the EMC/ADT regression indicated Zn concentration in runoff was related to traffic volume. Zn is a component of tires and should provide a strong traffic-related signal in runoff. Also, Zn is the trace metal generally measured at highest concentration in runoff investigations. Zn sampling was subject to the same lack of quality assurance and clean technique as the other uncorrelated trace metals. Perhaps the Zn signal is strong enough in runoff sampling to be observed despite contributions from possible contamination.

Lack of quality assurance would obscure an EMC/ADT correlation actually present. Alternatively, concentrations in runoff actually may not be correlated to traffic volume. Factors contributing to a lack of correlation for trace metals might be that traffic is both a source of trace metals and of turbulence that potentially moves the metals off the road surface onto adjacent areas. The turbulence causes resuspension that can substantially remove large-sized particles. The large-size particles are not transported far before being redeposited, as reviewed above. Thus, an active highway surface with no pollutant particles may be bounded by an enriched zone on the breakdown lane and (or) berm. This potential transport mechanism has been confirmed by various studies indicating that highways with curbs, which restrict horizontal transport of resuspended particulates, have higher pollutant loads in runoff than noncurbed sections of highway (Gupta and others, 1981; Kobriger and Geinopolos, 1984; Driscoll and others, 1990a). If included in the area drained, substantial runoff load could be generated by the adjacent off-road area. Data available in the investigation by Driscoll and others were not controlled for amount of the adjacent off-road area being drained. With high deposition rates expected in the off-road areas, the variable inclusion could greatly alter the correlation between traffic and runoff loads.

One final consideration concerns aggregation of data collected over long time periods. Emissions to the atmosphere of some constituents have changed in response to emissions control programs of the USEPA (USEPA, 1998b). There have been substantial changes in emissions of the criteria pollutants from vehicle exhausts during the past 27 years (fig. 6) (USEPA, 1999).

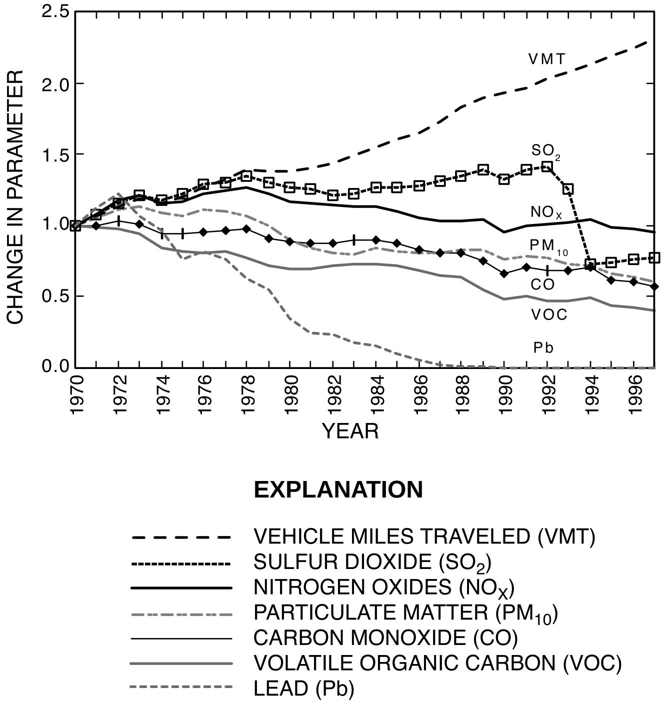

Figure 6. Change in criteria pollutant emissions from vehicles compared to vehicle travel, 1970–97 in the United States (USEPA, 1999).

On-Highway Processing

In general, little is known about on-highway processing of deposited materials. Greater knowledge of this area likely would lead to better simulations of constituent loads in highway runoff.

Two important on-highway processes, saltation and resuspension, were reviewed under “Forms of Deposition and Post-Depositional Transport.” These processes relate to one prevalent on-highway processing theory: the number of dry days between large storms events (the antecedent dry period) can have a major effect on airborne particulates that build up on roadways. Associated with this theory are the concepts that light to moderate precipitation events of low intensity or intense rains of short duration do not clean the roadway completely, and that airborne particulate amounts increase at relatively constant rates for pollutants such as Pb, Br, and Ca (Moe and others, 1982). This buildup process, however, may be more associated with impervious surfaces in urban catchments than with active roadways. Resuspension of material deposited by traffic could greatly alter the effect of storm interval on runoff loads from travel lanes compared to nontravel lanes or other impervious surfaces. Investigations of runoff from travel lanes of a highway in Boston, Mass. (K.P. Smith, USGS, written commun., 2000), indicate no association of runoff of total-solids load with interval between storms. Results of the Boston investigation indicated that most material moves when there is heavy precipitation and soil adjacent to the highway erodes onto the impervious, drained, travel lane. (There are no breakdown lanes between the soil and the travel lanes at the site.)

The effect of turbulence on redistribution of highway sediment was described in Kobriger and Geinopolos (1984). As determined from sweeping and flushing studies, solids tend to accumulate in the break down and median lanes. Kobriger and Geinopolos (1984) conclude that runoff loadings come from these nontravel lanes rather than from travel lanes. The importance of on-highway processing was recognized by at least one investigator who has divided highway-runoff constituents into three categories: (1) constituents, such as suspended solids, that are affected by conditions during dry periods and that may be mitigated by dry-period activities; (2) constituents that are affected mostly by conditions during rainfall events and that may be mitigated only by use of runoff controls; and (3) constituents that are affected equally by dry and wet conditions (Irish and others, 1996).

The duration of a storm may interact with traffic turbulence and the deposition process of washout to affect highway-runoff quality substantially. In a Seattle, Washington investigation, constituent loads in highway runoff could be simulated by average traffic volume measured during the course of a rain event (Chui and others, 1982). Loads appeared to be more a function of kinetic energy provided by the moving vehicles than of rainfall. Washout by vehicle turbulence during wet weather might be particularly effective at trapping some of the gases exhausted from car tail pipes. Otherwise, as noted by Harrison and Johnston (1985), various major compounds that are present in vehicle exhaust, including oxides of nitrogen and carbon monoxide, are gases that rapidly and widely disperse, leaving no permanent record near the road.

Quality Assurance

Several of the investigative approaches described in this report would be compromised if concentrations measured at the low end of the concentration range were not accurate. If rates are being computed, a small absolute difference in concentration can lead to a large relative difference in deposition rate and in conclusions resulting from the application of the rate. The highway-runoff investigations completed in the 1970s and 1980s do not appear to have been conducted using clean methods to collect precipitation data or highway-runoff data. For example, no mention is made in the documentation regarding use of Teflon in sampler construction, cleaning of samplers before deployment, clean rooms or benches where samplers and samples are processed, or precautions used to transport samplers after cleaning. Nor is any verification generally given on sample integrity by reference to analysis of equipment blanks, trip blanks, standard reference materials, sample spikes or blind sample analysis, all usual quality-assurance procedures (Jones, 1999).

One quality-assurance procedure, use of multiple bulk samplers at a site to determine precision, was applied at a Milwaukee, Wisconsin, site in work reported by Kobriger and others (1982). Groups of three samplers placed 0, 5, 15, 30, and 300 m from the highway were used to compute relative error (standard deviation divided by mean) for the measurements collected at each distance from the highway. The relative errors ranged from 2 to 93 percent. Mean relative error was about 20 percent. These results and other measures of quality assurance would be useful in future investigations to assess sources of variation in runoff data and to establish the quality and comparability of data collected at different sites.

STRATEGIES AND METHODS FOR FUTURE INVESTIGATIONS

Future investigation designs for atmospheric-deposition contributions to highway runoff should consider that currently little is known conclusively about the atmospheric source or how deposited material is transported from the highway to runoff. As discussed in the section “Review of Articles on Atmospheric Sources for Highway Runoff,” uncertainties include measurements of atmospheric-deposition rates, especially in the highway investigation context, because virtually all wet and dry data have been collected with minimal quality-assurance procedures, and all dry data have been collected using bulk or dry-bucket samplers. In addition, the runoff database from projects sponsored by the Federal Highway Administration likely is not accurate for Hg and perhaps other trace metals because of lack of clean-sampling methods and application of quality-control procedures.

Even the correspondence between accurate dry-deposition rates, such as determined from deposition to standard surfaces, and net deposition to the highway that would be available for runoff is an area of uncertainty. Unlike most pavement surfaces, highway travel surfaces underlie a high-energy, turbulent environment because of traffic-induced air turbulence. The effect of air turbulence on highway-deposited materials generally is not considered in investigations of sources of highway runoff. Potential redistribution of particles by moving vehicles complicates determination of the part of a given constituent measured in highway runoff that can be attributed to atmospheric deposition. In summary, on-highway processes that affect deposited material are poorly understood; these processes include effects from resuspension and evaporation. This poor understanding, in turn, has prevented accurate determinations of ambient atmospheric-deposition contributions to highway runoff loads in mass-balance calculations.

Given the effect that vehicles have on air quality in general, and on contributions to highway surfaces from vehicle wear, the contribution from vehicles to highway-runoff loads is likely to dominate over ambient atmospheric deposition for many pollutant constituents. For those constituents in runoff predominantly from vehicle sources, the details of ambient atmospheric deposition and processing may not be important, and investigations could be narrowed to vehicle-related sources. Much of what follows are strategies and techniques to determine whether ambient deposition sources are important for given constituents and to separate out the ambient deposition contribution to highway-runoff loads.

Particle Size and Sources

The potential importance of particle size for deposition and on-highway processing of deposited materials, and thus for connections between sources of deposition and highway runoff, already has been emphasized in this report. Multiple conceptual models for particle-dependent processing are possible. For some constituents, large-size particles that are subject to resuspension may dominate deposition. For other constituents, small particles that are removed by traffic turbulence or a combination of turbulence and precipitation may dominate. At present, it is not known which of these or other particle-dependent conceptual models may be dominant or acting in combination for each constituent.

Because of the complexity of processes operating on the highway surface, verification of a conceptual model may be difficult. Alternatively, tracers associated with one particle size or loading source could be used to indicate the net effects of on-highway processing of deposited materials.

Investigative Design

An initial investigative strategy could be to work out net highway processing for ambient-deposition constituents as a function of domination by large or small-sized particles. The fraction of total deposition of a constituent that is recovered in runoff could be related to the particle size that dominates deposition of the constituent, where total deposition is measured as the sum of wet deposition and dry deposition onto a standard surface removed from direct influence of the highway. Constituents would need to be chosen that were not contributed by highway maintenance procedures (including deicing) or vehicles. The data on relative deposition rates as a function of particle size would need to be obtained from literature values or modeled on the basis of deposition velocities, and site data on particle size and constituent concentration.

Once percent recovery as a function of particle size is known for constituents present only in ambient deposition, runoff loads from ambient deposition could be computed for other constituents with multiple (including vehicle) sources, such as Zn or Cu, from the equation

$$F_{rl} = (X_d Y_l)/(Y_d X_l),$$

where

F_{rl}	is	fraction of constituent X in the runoff load attributable to ambient deposition;
X_d (mg/m^2/d)	is	the ambient deposition rate of constituent X measured by wet deposition and standard surface collectors,
X_l (mg/m^2/d)	is	the load of constituent X in runoff from the highway;
Y_d (mg/m^2/d)	is	the deposition rate of ambient sole-source element measured by wet deposition and standard-surface collectors; and
Y_l (mg/m^2/d)	is	the load of ambient sole-source constituent in runoff from the highway.

Investigations of this type possibly could eliminate contributions of many constituents from ambient atmospheric deposition from further consideration. If, for example, more than 90 percent of a constituent in highway runoff is from nonambient deposition sources, further investigation of the ambient source may not be warranted, even in an urban environment.

Tracers of Atmospheric Deposition

Determination of the ambient-deposition fraction of runoff requires measurements of deposition and runoff of elements that are present in atmospheric deposition but not in vehicle or road-maintenance sources. Various isotopic tracers of atmospheric deposition (Pb-210 and Be-7) have been used in erosion and runoff investigations as a means to distinguish among sediment sources (Schroeder, 1995; Baskaran and others, 1993). Neither isotope would be likely to originate from nonatmospheric sources. Pb-emission sources to the atmosphere in the Straits of Dover have been identified using isotopic-ratio signatures (^{206}Pb/^{207}Pb, Deboudt and others, 1999). To use this ratio in tracing ambient deposition, knowledge of ^{206}Pb/^{207}Pb in highway or vehicle sources would be necessary.

Possible tracers in addition to the isotopes are the rare earth elements, major elements, or organic constituents such as pollen, or PCBs, which are not associated with traffic sources. The rare earth elements (such as the crustal element scandium) might act as good tracers of particles that dominate trace-metal ambient deposition. The presence of these elements in traffic sources has not yet been studied. Cost-effective analysis of their concentrations can be made using inductively coupled plasma-atomic emission spectroscopy (Fishman, 1993). Utility of a tracer would depend on local conditions. Use of the major elements, Na, Cl, Ca, K, would be appropriate only for road locations where deicing salt was not applied.

Appropriate Network for Data Collection

The general lack of accurate deposition information may indicate a need for a new investigative program to generate correct deposition data sets, especially for trace contaminants, measured across the country. The Federal highway system extends nationally, and deposition is likely to vary nationally, so only a national deposition program could provide the atmospheric source data needed. Until ambient deposition has been clearly established as a major source of pollutants in highway runoff, however, a national program modeled, for example, on the NADP network may not be warranted. An initial network that would determine whether constituents were important in ambient deposition should be installed at highway sites investigated so that deposition and runoff can be compared as directly as possible.

Site Selection for Sampler Placement

Collection-site criteria established by the NADP for wet acidic deposition, as determined from the National Trends Network Site Operation Manual (National Atmospheric Deposition Program, 2000c), are appropriate for sites established to measure deposition to highways. These criteria include the requirement that sites be clear in all directions of any obstruction that extends upward more than 30 degrees from the horizon. Vegetation should be representative of the area and distance from atmospheric emission sources should be considered. Data-collection sites should be in the same direction with respect to prevailing winds from sources as are the highway sections in the investigations.

Duration and Frequency of Data Collection

In general, the duration of atmospheric-deposition studies conducted at a site should be a minimum of 1 year to detect seasonal variations in concentrations of the constituents of interest. For example, concentrations of pesticides in rain and air frequently are elevated (above background levels) during the warm-temperature months, which coincide with application times (Majewski and Capel, 1995). Long-term sampling programs (longer than 1 year) are more desirable than short-term programs (less than 1 year) because interpretation of meteorological data for a single year can be misleading (Likens and Bormann, 1995). Long-term trends in deposition of specific constituents and the effects of climatic variations can be identified only in long-term data sets. Volume-weighted major-ion concentrations varied by as much as a factor of eight (for Na) among various major ions monitored in wet deposition at Catoctin Mountain, Maryland, for 9 years (Rice and Bricker, 1996, table 4). What may appear to be a seasonal pattern in a short-term data set may be insignificant in a long-term data set. Likewise, a seasonal effect may be minimized in the short-term data set and prove to be significant during a longer time period. Long-term data sets for a highway that has undergone an increase in traffic density also would be useful to determine the effect of the increased highway-runoff loads.

The sampling interval, which is the time between activation of the atmospheric-deposition sampler and retrieval of the sample, needs to be documented for all studies. Wet-deposition samples can be collected on an event basis, or, more commonly, at daily or weekly sampling intervals. Few studies have been conducted with sampling intervals longer than 1 week because of quality-control concerns (Likens and Bormann, 1995). Collection of dry-deposition samples requires short sampling intervals to reduce the amount of debris, such as leaves or bird droppings, that enters the collector.

Table 4. Annual volume-weighted mean concentrations of chemical constituents in precipitation collected from the U.S. Geological Survey precipitation-collection station at Catoctin Mountain, Maryland, 1982–91

[From Rice and others, 1993. All values in microequivalents per liter, except where noted]

Year	Precipitation (inches)	Calcium	Magnesium	Sodium	Potassium	Chloride	Nitrate	Sulfate
1982	32.86	8.51	2.10	9.95	2.68	11.20	23.51	45.30
1983	54.76	11.86	3.40	7.88	1.02	16.48	23.04	51.19
1984	56.65	13.17	2.39	11.01	1.88	10.35	21.68	58.79
1985	40.41	6.92	3.37	8.90	3.51	10.25	19.07	43.18
1986	36.72	10.73	2.22	6.01	1.85	10.80	24.64	54.78
1987	42.77	8.06	2.12	7.14	2.61	14.77	27.56	60.71
1988	36.28	8.67	2.51	5.24	2.28	9.99	25.30	61.73
1989	40.87	3.51	1.04	1.37	1.35	4.89	20.00	44.00
1990	49.65	7.33	2.71	6.93	2.35	10.75	23.24	49.55
1991	37.70	9.78	4.31	2.28	0.71	9.79	25.39	56.54

Ancillary Data Requirements

Recording the amount of precipitation is mandatory for making comparisons of concentrations of specific constituents nationwide. Types of rain gages include wedge and tube, weighing bucket, and tipping bucket. Other useful ancillary information for atmospheric-deposition studies includes the ambient wind speed and direction (from an anemometer) and the daily temperature fluctuation (from a thermistor). Electronic data loggers (such as the CR10 series of Campbell Scientific Instruments, Inc.) are useful for recording these types of ancillary information as well as digital output from recording rain gages (Church and others, 1999).

Collector Type and Installation

Collector types and installation are described in this section. Collectors of wet and dry deposition are considered.

Wet-Deposition Collectors

Several commercially manufactured wet-deposition collectors are available. Most of these collectors have a large collection area that drains into a bucket or through a funnel into a collection bottle or extraction cartridge (Majewski and Capel, 1995). Wet-deposition collectors are closed during dry periods to exclude dry deposition and open automatically when a sensor detects precipitation. If the collector is left open and is not cleaned just prior to a precipitation event, bulk deposition is collected (Majewski and Capel, 1995). Franz and others (1991) have reviewed the collection efficiencies of commercially available wet-deposition collectors. Modifications to commercially manufactured collectors may be necessary for the collection of specific constituents. For example, modifications were made to a standard Aerochem Metrics Model 301 wet/dry collector for the collection of major ions and trace elements in the heavily industrialized Gary, Indiana, area (fig. 7). Most of these modifications, which include the use of Teflon parts, were made to decrease possible trace-metal contamination of the sample from the sampler (Willoughby, 1995).

For collection of major inorganic ions in precipitation, the polyethylene bucket that comes with standard atmospheric-deposition collectors is sufficient (Robertson and Wilson, 1985). With the low detection limits used for trace metals and organic compounds, however, came the realization that for constituents other than major ions, the materials used to construct the sample container affected the chemistry of the sample. Constituents can sorb or desorb from the sample container. New materials such as Teflon started being used in the late 1970s to circumvent the sample-contamination problem. Teflon is the preferred material for the collection of trace elements (Fogg and Fitzgerald, 1979; Tramontano and others, 1987). Teflon, aluminum, and stainless steel are the preferred construction materials for the collection of pesticides in wet deposition (Majewski and Capel, 1995). These sampler materials are used for the respective constituents because they neither contribute to nor attenuate the constituents in significant amounts. Likewise, the need for clean sampling methods, such as the use of gloves for handling the sample container and the use of ultra-pure acids for the preservation of samples, became necessary as laboratory detection limits were lowered.

Dust Buckets and Bulk Collectors

Dry-deposition measurements are subject to many external effects, of which the principal one is the physical shape and dimensions of the sample collector. The airstream across the opening of the collector is subject to disturbances, and many collectors are not modified to minimize or eliminate these disturbances (Sanderson and others, 1963). Turbulence set up by air currents passing across the collector surfaces may cause resuspending of deposited material. Studies have indicated that dust volumes collected by an array of identical collectors at one site varied by as little as 15 percent (Sanderson and others, 1963). Conversely, dust volumes collected by an array of different types of collectors at a single site differed by as much as 100 percent (Sanderson and others, 1963).

Volumes of material deposited in bulk collectors could have a lack of reproducibility similar to that of the volumes deposited in the dust-bucket collectors. To the extent that constituent deposition is dominated by dry deposition of large particles, bulk collectors may be more appropriate to collect bulk-deposition samples than they would be if smaller particles or gases dominate deposition.

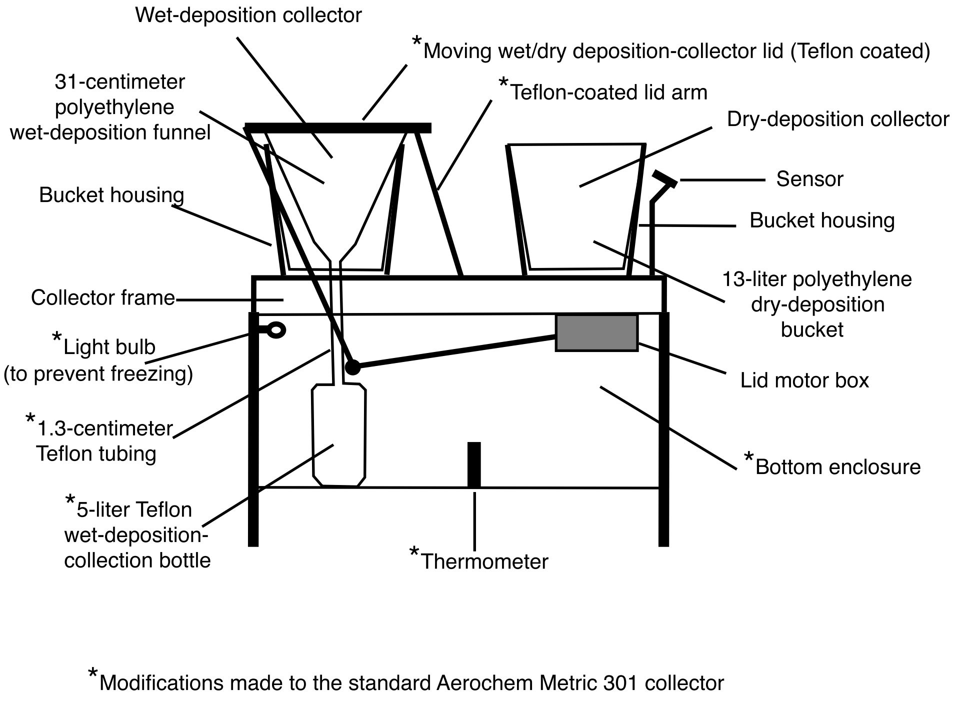

Figure 7. Modified Aerochem Metrics Model 301 wet/dry collector that was used for the collection of trace elements in Gary, Indiana (Willoughby, 1995).

Impactor Samplers and Standard-Surface Collectors

For many of the constituents of interest, accurate assessment of dry deposition would require impactor or standard-surface collectors or both. For example, if particle size is required to assess on-highway processing, impactor samplers must be used to collect samples. Impactors appropriate for the range of particles that are important in atmospheric deposition are described in Lin and others (1993). Rotary impactor samplers are appropriate for large particles (6.5 to 36.5 µm) and conventional cascade impactor samplers for small particles (0.43 to 10 µm). Results from impactor collectors can be compared, using deposition velocities, to deposition rates measured using a standard-surface collector to determine whether modeled and experimentally determined deposition agree. Standard surface refers to a PVC plate with a sharply beveled (10 degrees) leading edge covered by Mylar strips coated with a thin layer of Apezion L grease (Lin and others, 1993). A wind vane directs the beveled edge into the wind. Dry deposition to this surface is a reproducible and accurate measure of deposition in places where surface roughness and turbulence is low. Processing the collectors consists of weighing the grease-coated Mylar film before and after collection, and then extracting the grease from the films for chemical analysis to determine constituent concentration.

Quality Assurance

Any analytical measurement contains a certain amount of error. Error can be introduced when samples are collected, transported, processed, or analyzed. Database errors can be introduced when data are stored on paper or electronically. To minimize all potential errors, atmospheric-deposition networks need a comprehensive, well-documented, quality-assurance plan. Without a quality-assurance plan, the error component of atmospheric-deposition data would be unknown and the usefulness of these data in environmental studies would be diminished. In addition, estimates of overall network data precision provide scientists who investigate precipitation chemistry with confidence in their findings. These estimates also provide a baseline against which to measure the performance of improved collectors and sample-collection procedures (Robertson and Wilson, 1985).

Field-Data Collection

To maintain data quality during collection, a training program for site operators is necessary, and data-collection procedures used by the site operator should be documented. Required documentation includes a description of the routine maintenance of the field equipment (wet or dry collector, rain gage, and other equipment); the procedures used to clean the sampling equipment (Willoughby, 1995); a description of the procedures for approaching the collector to remove the samples—for example, site operators should approach the collector from the downwind side to minimize windblown contaminants from entering the collector (Bigelow, 1982); the protocol for using “clean hands” procedures when working with the sample (Horowitz and others, 1994); and descriptions of procedures for removing the sample from the collector, measuring water-quality properties, and preserving the sample when necessary. During the site visit, the site operator should document the day and time the sample was collected and the time that the new sample-collection container was put in place.

If constituent concentrations or water-quality properties are measured in the field, it is necessary to determine the quality of field measurements. The NADP/NTN has an intersite comparison program to evaluate precision and accuracy of on-site measurements of pH and specific conductance (Willoughby and others, 1991; Nilles and others, 1992). For the intersite comparison program, identical samples with known pH and specific conductance are sent to site operators. Although the site operators know they are participating in an external quality-assurance program, they do not know the actual pH and specific conductance values of the solution. The results from each site operator are compared to all other site operators in the network (Willoughby and others, 1991). Results that are outside the acceptable limits are an indication of equipment problems or the need for additional site-operator training.

Other quality-control samples, such as field blanks, may be necessary at some sites. For example, an investigation of major ions and trace elements in wet deposition near Gary, Ind., used funnel rinses and system blanks to identify possible sources of contamination of the samples (Willoughby, 1995). In the funnel rinse, deionized water that had been adjusted to a pH similar to the wet deposition being collected was poured through the funnel immediately after the equipment was installed in the collector. The funnel rinse was processed by the same method as the wet-deposition samples to quantify possible contamination resulting from cleaning, shipping, and installing the funnel in the collector. The system blank was processed in the same manner as the funnel rinses and the wet-deposition samples, and was collected to evaluate possible contamination resulting from dry periods of 1 week. Acidified, deionized water was passed through the funnel at the end of the 1-week sampling period. The results were compared to the results from the acidified, deionized water-funnel rinses and the wet-deposition samples collected from October 17, 1995, through November 12, 1996, at the Gary Regional Airport (fig. 8). These data indicate that the quality-control steps successfully minimized sampling artifacts and show the difference between sampling artifacts and actual contaminant loadings during this sampling period.

The NADP/NTN also conducts a colocated sampler program. For the colocated sampler program, identical samplers are placed near each other at the same sampling site. Samples from the same precipitation event are collected in each collector and analyzed by the same laboratory using the same analytical methods. The results then are compared, and a variance is computed (Nilles and others, 1992). Peters and Reese (1995) compared results from colocated samplers and found that concentration in wet deposition generally was less variable and had lower concentrations of major inorganic ions and nutrients than did bulk deposition.

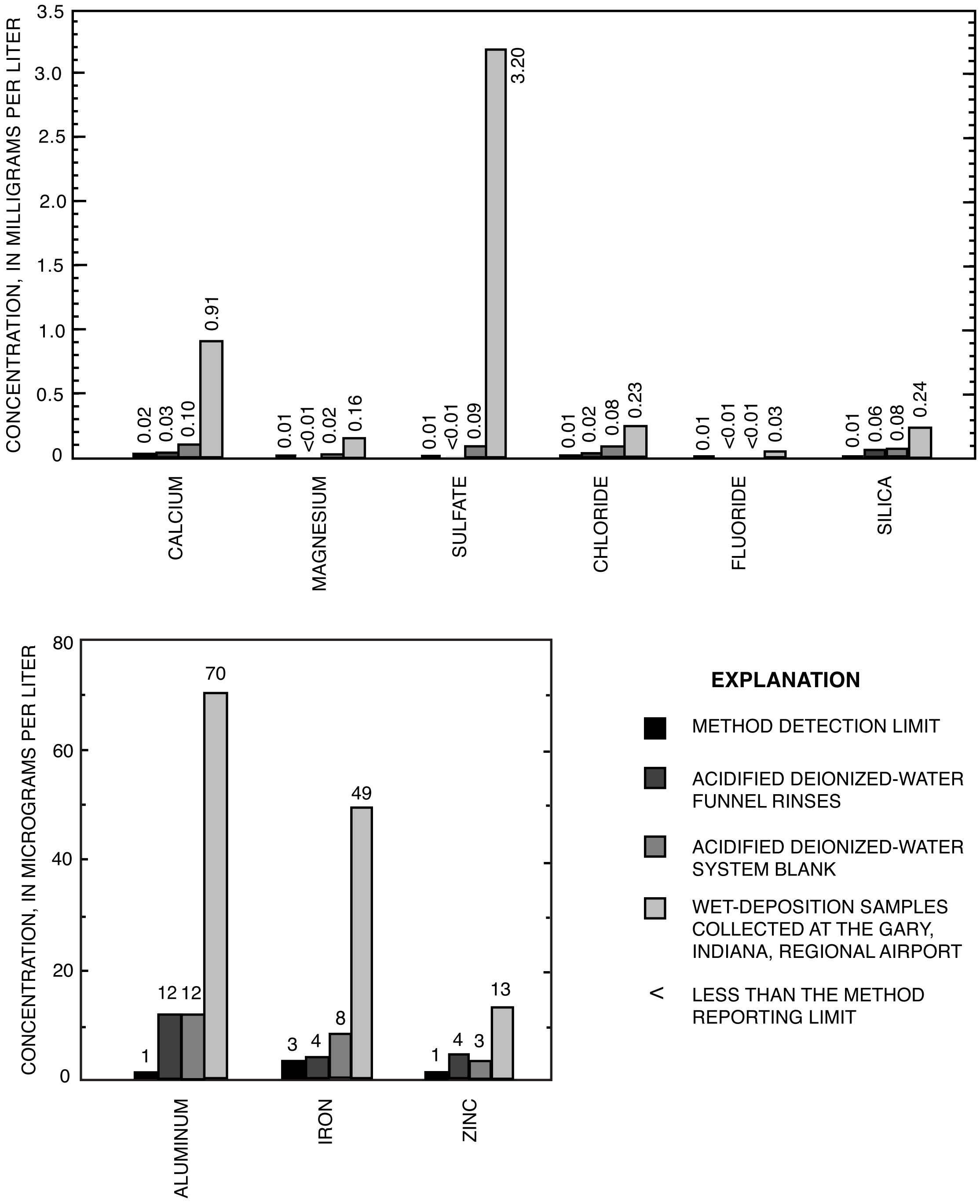

Figure 8. Median concentrations of chemical constituents measured in quality-control samples collected at the Gary, Indiana, Regional Airport from October 17, 1995, to November 12, 1996.

For studies in which contamination in highway runoff and in atmospheric deposition are being investigated, it may be necessary to establish a background site to determine constituent loadings that are not directly related to highway runoff. For background sites, all known emission point sources within a 50-km radius, as well as the constituents being emitted into the atmosphere by these sources and their combined annual emissions, should be recorded. It also is important to document land use and topography near the sampling site. A map of the sampling site should be included with the site-description documentation. For studies conducted near the highway, land use, topography, average daily traffic, and the number of days between storm events should be documented. Examples of sampling-site descriptions used by the NADP/NTN are provided in Robertson and Wojciechowski (1986).

Because the concentrations of atmospheric-deposition constituents generally are low, it is critical that data-collection efforts follow a quality-assurance/quality-control plan to ensure that the sampling program produces data of known quality. Quality-assurance (QA) programs include the precautionary actions used to prevent systematic bias. Examples of QA include using noncontaminating materials and sample containers, cleaning the sampling equipment, preserving samples soon after collection, and shipping samples overnight to the laboratory (Jones, 1999). Quality-control (QC) programs include the steps used to check that QA is effective and to evaluate variability in the data because of random error. Examples of QC include equipment-blank samples to determine if the sampling equipment is clean, replicates to assess sample variance and analytical precision, and samples spiked with analytes to evaluate analyte degradation and recovery (Jones, 1999). For small individual studies, the QA plan usually is described briefly along with investigation results. For large state, regional, or national studies, the QA plan should be published in conjunction with reports that document methods and results of these studies (Jones, 1999).

A technically defensible database used to assess the importance of atmospheric deposition to highway-runoff studies requires consistent national standards for data collection and processing. The Intergovernmental Task Force on Monitoring Water Quality (ITFM) is developing and implementing a national strategic plan to achieve effective collection, interpretation, and presentation of water-quality data and to improve the availability of information for decision making at all government levels and the private sector. The ITFM is composed of 10 Federal agencies, 9 State and interstate agencies, and 1 American Indian tribe. Products of the ITFM include a framework for monitoring programs; selection criteria for environmental indicators; and ecological, chemical, and physical criteria for evaluating water quality according to environmental management objectives (Intergovernmental Task Force on Monitoring Water Quality, 1995).

Laboratory Analysis

Most analytical laboratories have an internal quality-assurance program to evaluate the accuracy, precision, and bias of the measurements and to insure that appropriate protocols and control standards are being implemented. Examples of internal quality assurance include programs for data validation, analysis of method blanks, replicates, standard reference water samples, spike samples, and internal blind sampling.

Validation of sample data involves the comparison of data against acceptable limits, checking ion balances, and reanalysis of the sample, if necessary. Method blanks are prepared in the laboratory as an analyte-free matrix and are carried through the entire sample preparation and analytical procedure to identify contamination from the laboratory during sample preparation and analysis. A replicate sample is an environmental sample that is split into two or more aliquots and submitted to the laboratory for analysis (Bricker, 1999). Analysis of replicate samples provides information about the precision associated with sample handling (after splitting), shipping, storage, and laboratory procedures. Standard reference water samples are produced and certified by the U.S. National Institute of Standards and Technology and are used to assess performance and assess bias for each analysis, and to determine long-term estimates of method variability. A laboratory matrix spike is an environmental sample (that contains a known concentration of one or more of the analytes). The matrix spike is analyzed by the laboratory to assess method performance by recovery of analytes in a particular matrix (Jones, 1999)

Blind-sample programs can be internal or external and are used to quantify the bias caused by random laboratory contamination (Jones, 1999). The NADP/NTN uses an internal blind-sample program to assess the variation of analyte determinations caused by routine on-site and laboratory sample-handling procedures. In the blind-sample program, samples with known concentrations are sent to the analytical laboratory for analysis. The samples are disguised so that the laboratory staff is not aware that the sample is a quality-control sample. Results reported for the sample then are compared to the known concentrations (Willoughby and others, 1991).

In addition to internal laboratory quality assurance, networks should have an external quality-assurance program. The NADP/NTN conducts an interlaboratory comparison program to evaluate bias and analytical precision in measurements made by laboratories that measure atmospheric-deposition samples. For the interlaboratory comparison program, identical samples are sent to participating laboratories. The laboratories analyze the samples using the same procedures used to measure environmental samples. The results from the laboratories are compared, and analytical precision and bias are determined for each laboratory and for all the laboratories as a group (Willoughby and others, 1991).

Establishing, defining, and documenting detection limits is an important part of quality-assurance plans (Jones, 1999). The Minimum Reporting Level (MRL) is the lowest concentration that can be quantified accurately by a given analytical method. The Method Detection Limit (MDL) is the lowest concentration that the method can detect reliably. Investigation objectives define whether the MRL, the MDL, or both will be used and documented. It is difficult to combine and compare results from different studies, or within one investigation, when detection limits are variable or unknown (Majewski and Capel, 1995). Analytical and effective detection limits for many constituents have been improved during the past 5–10 years; therefore, the QA plan, and any data reports produced by an investigation, should document analytical and effective detection limits and any changes in those limits. When constituents are not detected at the MRL, the results from screening at the MDL should be recorded. Because many constituents in atmospheric deposition have relatively low concentrations (low micrograms per liter level), pre-concentration or extraction processes are often used to increase effective detection limits by proportionally increasing the concentration of constituents in the analyte matrix. Therefore, detection limits are often a function of the the available sample size used for the pre-concentration or extraction processes, as well as of the analytical method.

SUMMARY AND CONCLUSIONS

A general national model for simulation of pollutant constituents in highway runoff is not available at present because the processes leading to incorporation of chemical constituents in runoff are not understood, or because the data for modeling the chemical constituents in highway runoff are inadequate. A better understanding of atmospheric-deposition processes and deposition rates is necessary for improving the modeling capability. Little is known about deposition processes and rates that are specific to highway environments. For many of the pollutants that are important in highway runoff, dry deposition in nonhighway environments is greater than wet deposition. This result means that on-highway processing of the particles that make up dry deposition is important in determining the part of deposition that becomes runoff. In an investigation of these processes, labeled particles have been found to be efficiently removed from highway surfaces by traffic. Concentrations of particles in deposition collectors and knowledge of settling indicate that new deposition locations of removed particles would not be very distant from their original settling locations so that there may be a sharp gradient between the “swept clean” travel lanes and adjacent emergency-lane and berm surfaces. But depending on particle size, traffic could either sweep the travel lanes clean or cause more deposition by impacting particles (or gases) on the highway surface.

Runoff loads of many trace metals and organic constituents that are products of combustion would be expected to originate from traffic rather than from ambient deposition. If ambient deposition could be demonstrated to be insignificant compared to traffic sources, then predictive deposition models would be simplified. Many mass-balance budget investigations have indicated, however, that ambient deposition is a substantial part of the runoff load. Comparisons of deposition with runoff loads have been based on the assumption that on-highway transport of deposition is conservative. Because of resuspension from traffic-induced turbulence, however, transport is unlikely to be conservative.

Lack of quality-assurance programs or clean-hands techniques in collecting deposition and runoff samples has contributed to the problem, sometimes in subtle ways. For instance, sharp gradients have been measured in deposition rates of materials in a row of collectors deployed on a transect transverse to highways. The finding that more deposition is measured near the highway than far from the highway indicates that traffic is a major source of deposited materials. Whereas detection of the gradient is an indication that collection methods are appropriate, comparison of the background results of the highway studies with deposition rates measured using clean methods and quality-assurance protocol shows that the former may be 10 times greater than actual background levels.

Programs that investigate atmospheric-deposition sources to highway runoff and which include analysis of tracers of ambient deposition may accomplish two types of objectives: determination of whether ambient deposition is important for pollutant constituents and determination of the character of on-highway processing of atmospheric deposition. Such programs may be logical precusors to any national investigation of atmospheric deposition that might be undertaken in support of highway-runoff projects.

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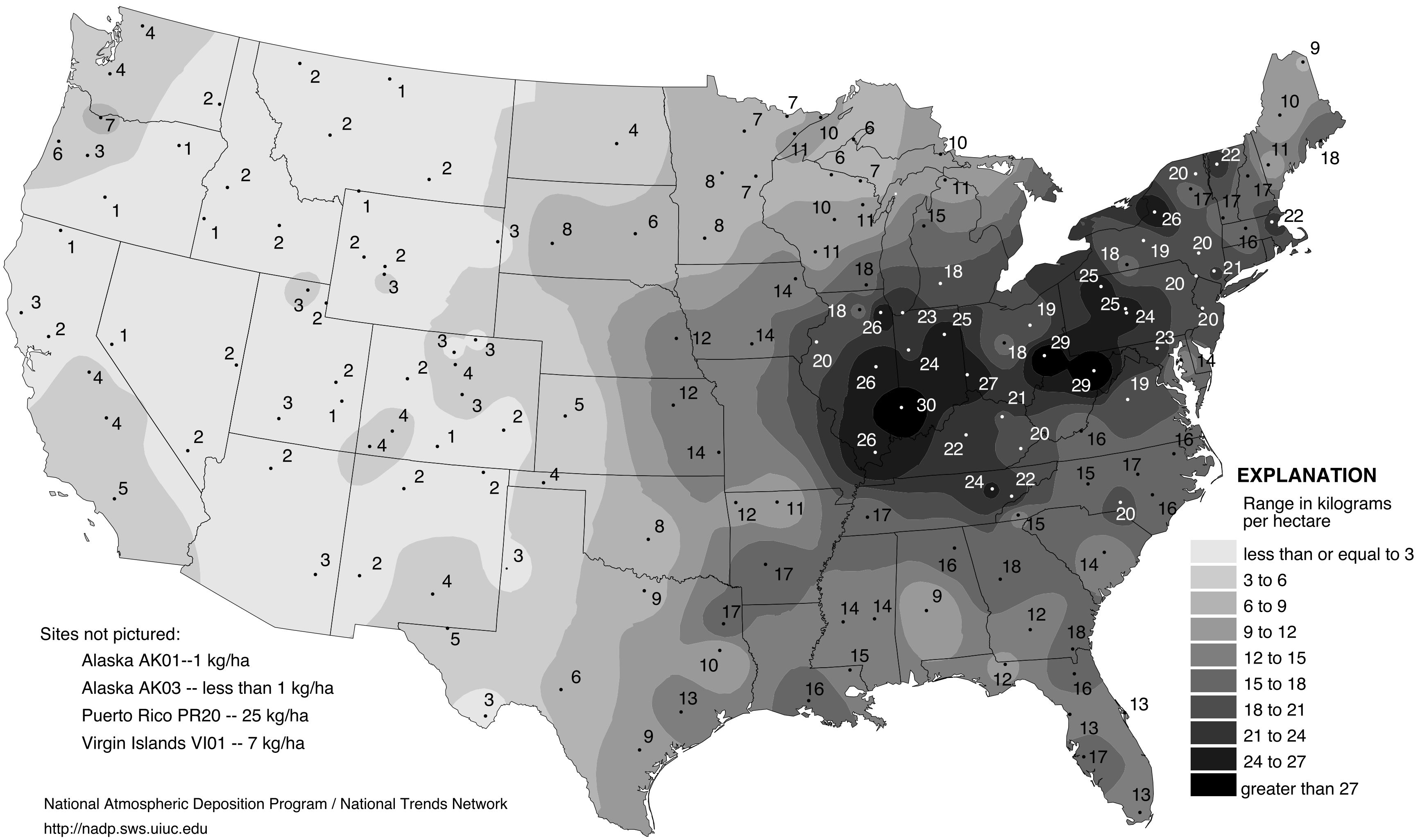
Figure 9

A. **Estimated sulfate ion deposition, 1998 [Kilograms per hectare (kg/ha)]**



Sites not pictured:

Alaska AK01--1 kg/ha

Alaska AK03 -- less than 1 kg/ha

Puerto Rico PR20 -- 25 kg/ha

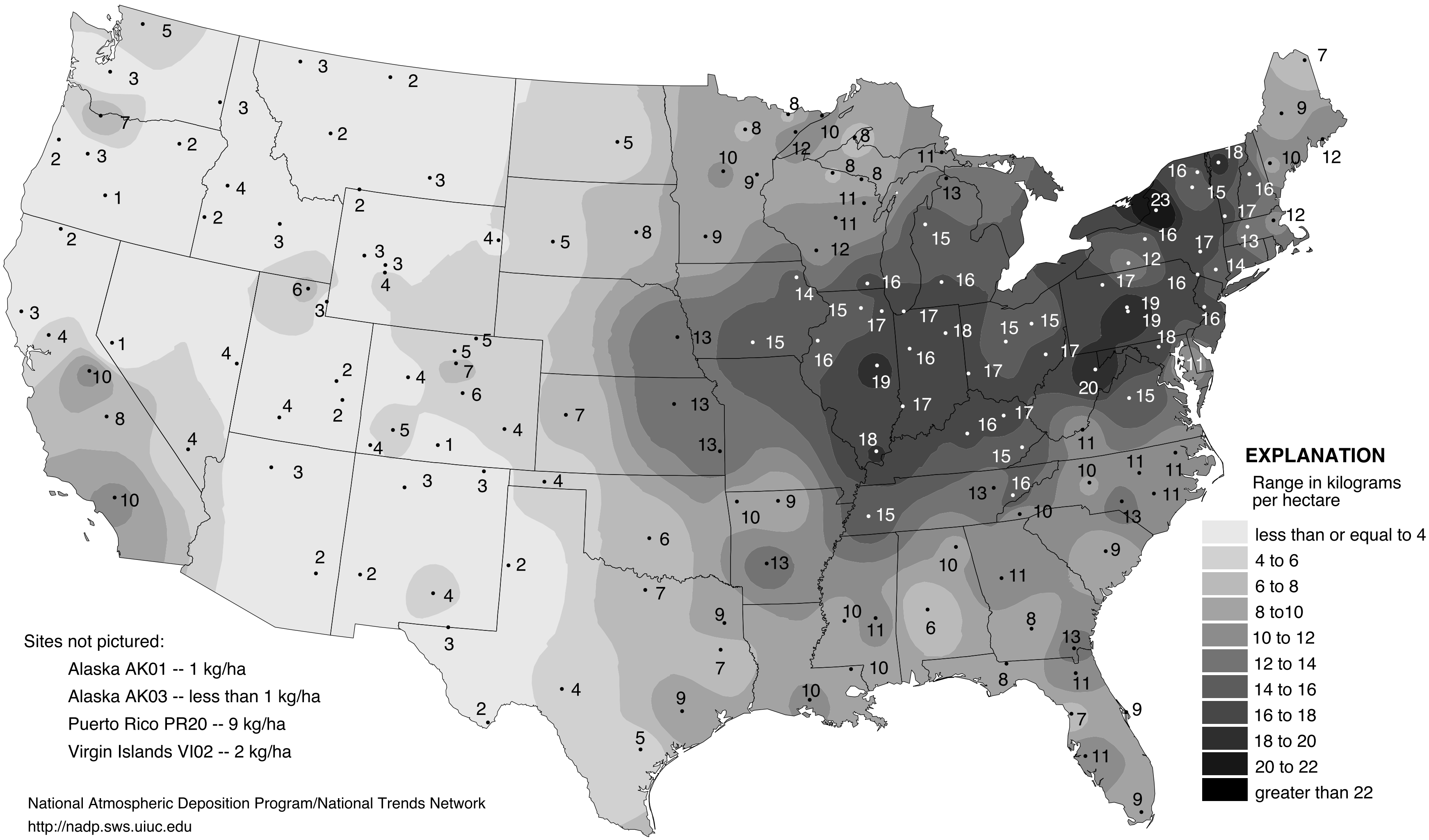
Virgin Islands VI01 -- 7 kg/ha

National Atmospheric Deposition Program / National Trends Network

http://nadp.sws.uiuc.edu

Figure 9. Annual wet-deposition rates mapped for 1998 for the United States based on National Atmospheric Deposition Program / National Trends Network (NADP/NTN) data for (*A*) sulfate, (*B*) nitrate, (*C*) calcium, (*D*) ammonium, (*E*) sodium, and (*F*) chloride.

B. Estimated nitrate ion deposition, 1998 [Kilograms per hectare (kg/ha)]



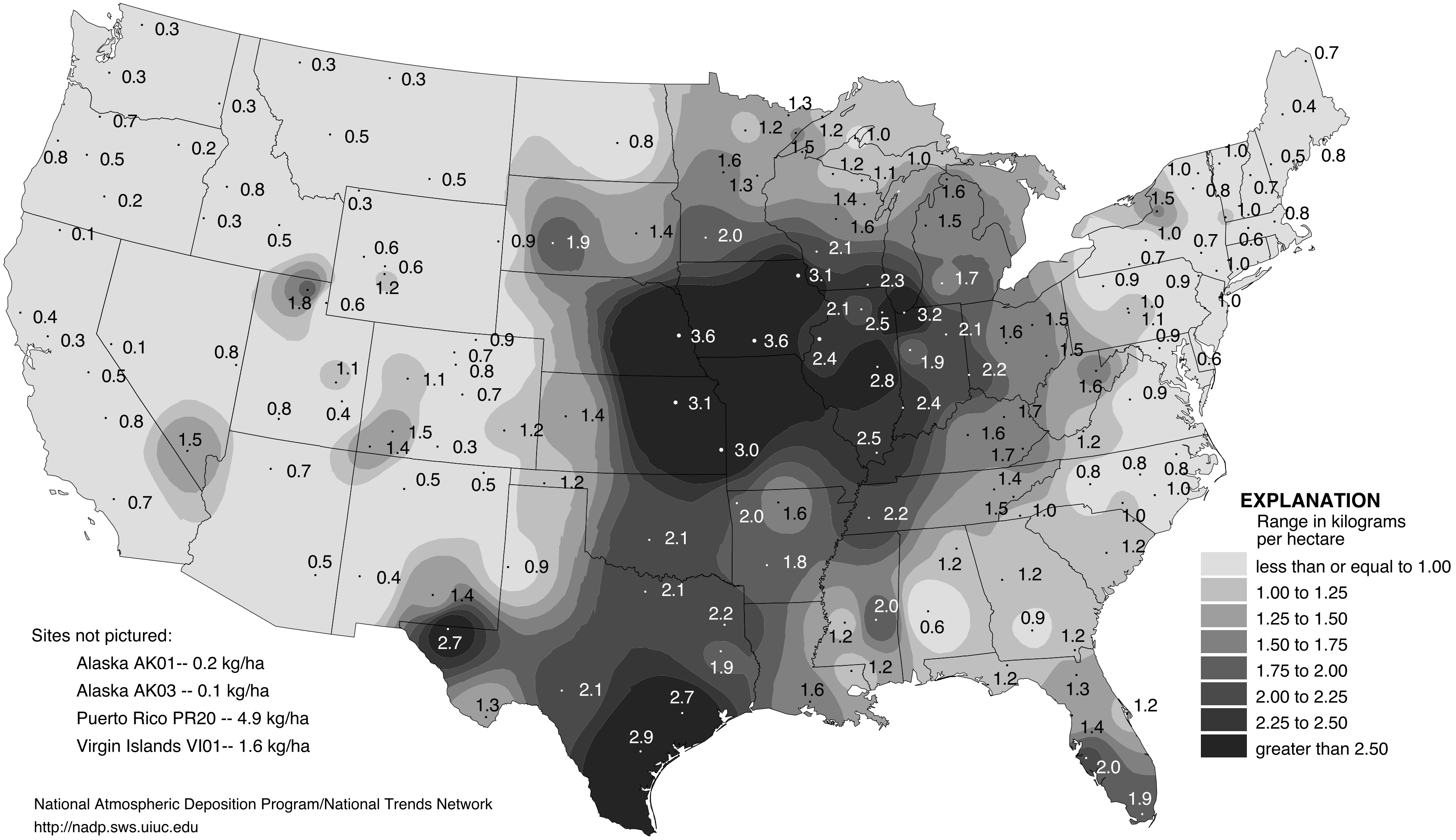
Sites not pictured:

- Alaska AK01 -- 1 kg/ha
- Alaska AK03 -- less than 1 kg/ha
- Puerto Rico PR20 -- 9 kg/ha
- Virgin Islands VI02 -- 2 kg/ha

National Atmospheric Deposition Program/National Trends Network
http://nadp.sws.uiuc.edu

Figure 9. Annual wet-deposition rates mapped for 1998 for the United States based on NADP/NTN data for (*A*) sulfate, (*B*) nitrate, (*C*) calcium, (*D*) ammonium, (*E*) sodium, and (*F*) chloride—*Continued*.

C. Estimated calcium ion deposition, 1998 [Kilograms per hectare (kg/ha)]



Sites not pictured:

- Alaska AK01-- 0.2 kg/ha
- Alaska AK03 -- 0.1 kg/ha
- Puerto Rico PR20 -- 4.9 kg/ha
- Virgin Islands VI01-- 1.6 kg/ha

National Atmospheric Deposition Program/National Trends Network
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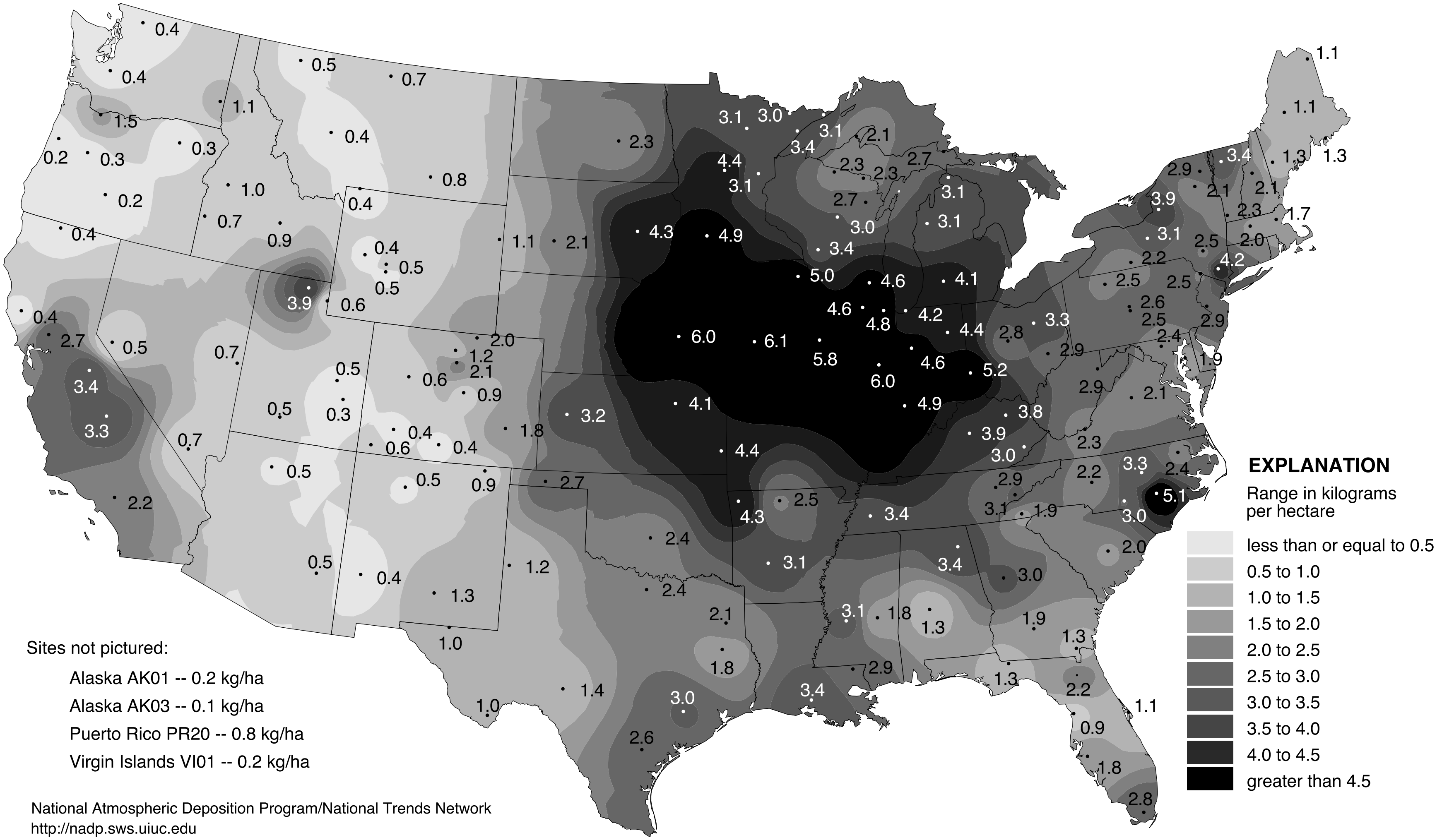
Figure 9. Annual wet-deposition rates mapped for 1998 for the United States based on NADP/NTN data for (*A*) sulfate, (*B*) nitrate, (*C*) calcium, (*D*) ammonium, (*E*) sodium, and (*F*) chloride—*Continued*.

D. Estimated ammonium ion deposition, 1998 [Kilograms per hectare (kg/ha)]



Sites not pictured:

Alaska AK01 -- 0.2 kg/ha
Alaska AK03 -- 0.1 kg/ha
Puerto Rico PR20 -- 0.8 kg/ha
Virgin Islands VI01 -- 0.2 kg/ha

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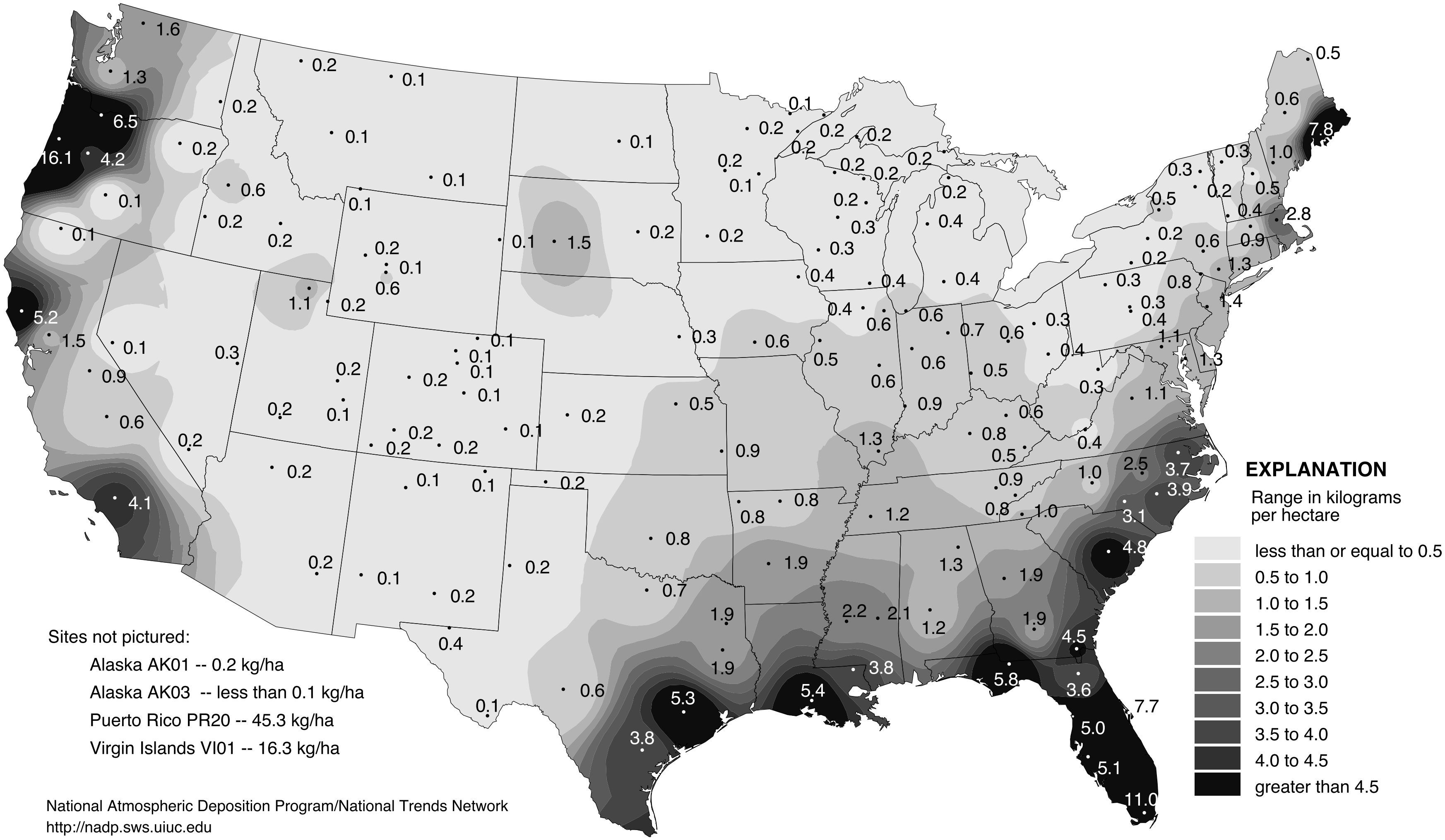
Figure 9. Annual wet-deposition rates mapped for 1998 for the United States based on NADP/NTN data for (*A*) sulfate, (*B*) nitrate, (*C*) calcium, (*D*) ammonium, (*E*) sodium, and (*F*) chloride—*Continued*.

E. Estimated sodium ion deposition, 1998 [Kilograms per hectare (kg/ha)]



Sites not pictured:

Alaska AK01 -- 0.2 kg/ha
Alaska AK03 -- less than 0.1 kg/ha
Puerto Rico PR20 -- 45.3 kg/ha
Virgin Islands VI01 -- 16.3 kg/ha

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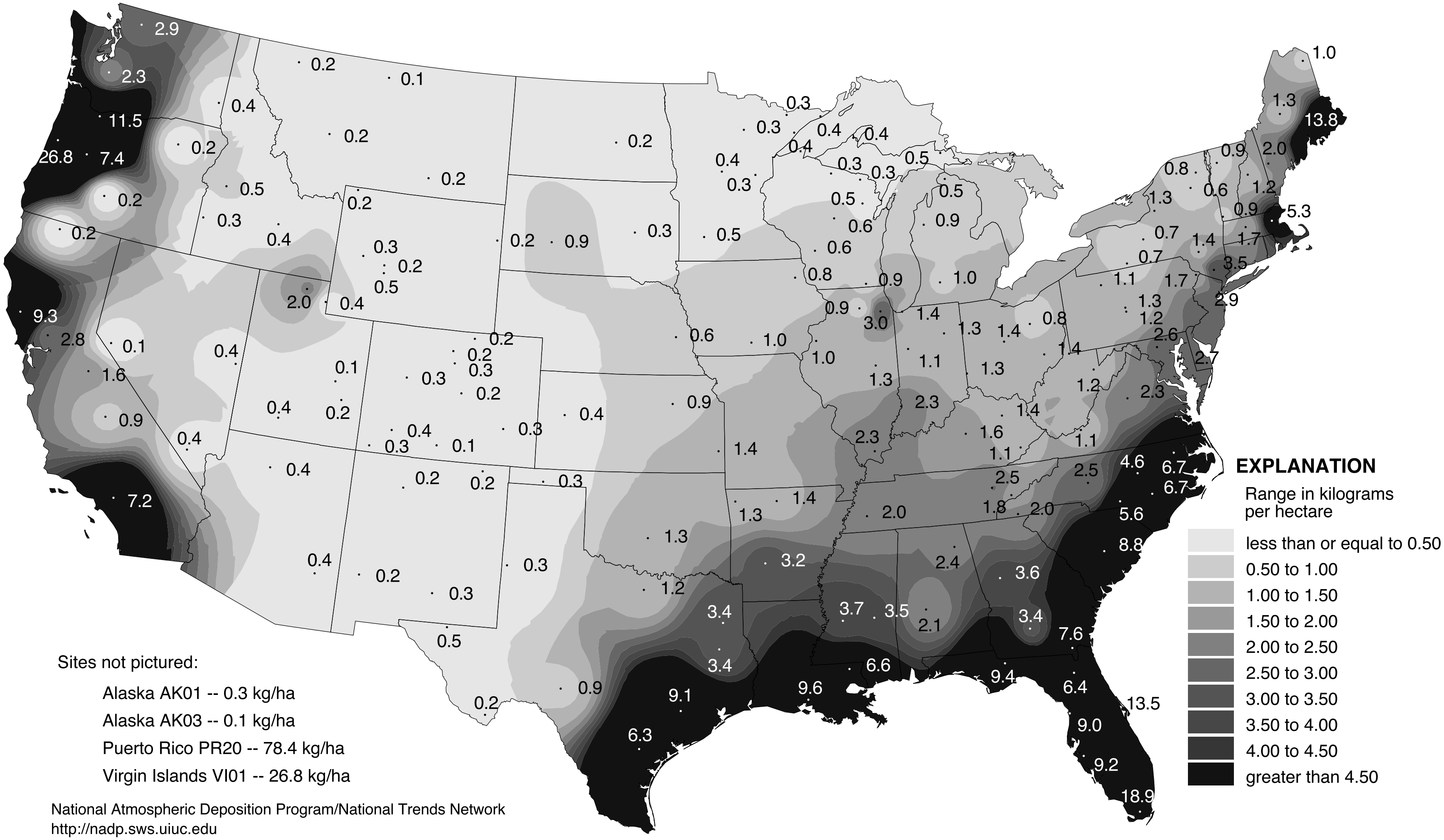
Figure 9. Annual wet-deposition rates mapped for 1998 for the United States based on NADP/NTN data for (*A*) sulfate, (*B*) nitrate, (*C*) calcium, (*D*) ammonium, (*E*) sodium, and (*F*) chloride—*Continued*.

F. **Estimated chloride ion deposition, 1998 [Kilograms per hectare (kg/ha)]**



Sites not pictured:

Alaska AK01 -- 0.3 kg/ha
Alaska AK03 -- 0.1 kg/ha
Puerto Rico PR20 -- 78.4 kg/ha
Virgin Islands VI01 -- 26.8 kg/ha

National Atmospheric Deposition Program/National Trends Network
http://nadp.sws.uiuc.edu

Figure 9. Annual wet-deposition rates mapped for 1998 for the United States based on NADP/NTN data for (*A*) sulfate, (*B*) nitrate, (*C*) calcium, (*D*) ammonium, (*E*) sodium, and (*F*) chloride—*Continued*.

Table 5

Table 5. Reports that address highway-runoff constituent loads and atmospheric deposition sources

[**Report type:** D, data; D/I, data/interpretive; FHWA, Federal Highway Administration; MI, model/interpretive; R/S, Review/Summary. **Investigation type:** ND, not discussed; cm, centimeter; g/m^2/d, gram per square meter per day; L, liter; µm, micrometer; %, percent; >, greater than]

Reference	Report type	Period of sampling	Type of sampling/method	Location/setting	Document method	
					Sample collection	Analytical
Adachi and Kobayashi (1992)	D/I	January–December 1990	Wet deposition/ND	Kobe, Japan/urban	ND	ND
Arimoto (1989)	R/S	ND	Bulk deposition	Great Lakes region/urban and rural	ND	ND
Asman and others (1982)	D/I	January 1978–December 1980	Wet deposition/precipitation collectors	Netherlands/rural	Yes	ND
Ball (1996)	D/I	ND	Dry deposition/vacuum cleaner	Sydney, Australia/urban	Yes	ND
Barkdoll and others (1977)	D/I	ND	Bulk deposition/continuous recorder, dustfall jar	Knoxville, Tenn./urban	Yes	ND
Beech (1980)	D/I	ND	Bulk deposition/collection from swimming pools	Miami, Fla./urban	Yes	Yes
Bidleman (1988)	R/S	ND	Bulk deposition/ND	ND	ND	ND
Bigelow (1982)	M/I	ND	Bulk deposition/wet-dry collector	ND	Yes	Yes
Brinkman (1985)	R/S	ND	ND	ND	ND	ND
Cadle (1985)	D/I	June 25, 1981–June 16, 1982	Bulk deposition/dual-filter method, denuder-difference method, impactors	Warren, Mich./urban	Yes	Yes
Cahill and Seiber (2000)	D/I	July 23–30, 1998; August 23–30, 1998	Water samples/1-L glass bottles	British Columbia, Yukon Territory, Canada, Alaska/urban; Northern California/urban	Yes	Yes
Capel and others (1998)	D/I	March –November 1988; March–April 1990	Wet deposition/wet-only rain sampler	St. Paul, Minn./urban	Yes	Yes
Clarke and Papapanayotou (1987)	D/I	October–December 1985	Vehicle emissions/filters	Leeds, U.K./urban	Yes	Yes
Dannecker and others (1990)	D/I	1986–87	Bulk deposition/wet only sampler, Bergerhoff instrument (dryfall)	Hamburg, Germany/urban	Yes	Yes
Dasch (1985)	D/I	August 1981–June 1982	Bulk deposition/wet-dry collector	Warren, Mich./urban; Lapeer, Mich./rural	Yes	Yes
Deboudt and others (1999)	D/I	March–October 1995	Dry deposition/cascade impactors	Straits of Dover, U.K./urban	Yes	Yes

A, atmospheric; NADP, National Atmospheric Deposition Program; PAHs, Polycyclic aromatic hydrocarbons, R, runoff; PCBs, polychlorinated biphenyl;

Reference	Investigation type	Chemical analyte	QA/QC	Comments
Adachi and Kobayashi (1992)	A	Major inorganic constituents, water-quality properties	ND	Ni^{2+} in rainwater can be used as indicator for air pollution by motor vehicle exhausts.
Arimoto (1989)	A	Trace elements, major inorganic constituents, organic compounds, water-quality properties	ND	Review of the atmospheric deposition of chemical contaminants to the Great Lakes Basin
Asman and others (1982)	A	Major inorganic constituents, organic compounds, water-quality properties	ND	Bird-droppings have an influence on the chemical composition of precipitation samples
Ball (1996)	A	Trace elements, major inorganic constituents	ND	Most of constituent load found to be sorbed onto sediment particles less than 70 µm in size
Barkdoll and others (1977)	A,R	Trace elements, major inorganic constituents, organic compounds, water-quality properties	ND	Discusses the effects of dustfall on urban stormwater quality
Beech (1980)	A	Trace elements, major inorganic constituents, water-quality properties	standard methods	Metal concentrations in swimming pools located along highways not appreciably different than other urban swimming pools.
Bidleman (1988)	A	Organic compounds	ND	Atmospheric processes of semivolatile organic compounds
Bigelow (1982)	A	Major inorganic constituents, organic compounds, water-quality properties	standards	NADP collection site operation manual
Brinkman (1985)	A,R	Trace elements, major inorganic constituents, organic compounds, water-quality properties	ND	Discusses sources and loadings of stormwater pollutants
Cadle (1985)	A	Major inorganic constituents, organic compounds	standards, blanks	Discusses factors affecting the seasonal variation
Cahill and Seiber (2000)	A,R	Organic compounds	blanks	Trifluoroacetate, breakdown product of hydrofluorocarbons and hydrochlorofluorocarbons, found at higher concentrations in surface waters near urban areas
Capel and others (1998)	A	Organic compounds, water-quality properties	standards	Discusses the wet atmospheric deposition of pesticides in Minnesota
Clarke and Papapanayotou (1987)	A	Major inorganic constituents, organic compounds	ND	Traffic-generated carbonaceous aerosols have a major effect on urban air pollution
Dannecker and others (1990)	A,R	Trace elements, organic compounds	ND	Pollutant concentrations in bulk deposition and runoff similar
Dasch (1985)	A	Major inorganic constituents, organic compounds	ND	Dry deposition strongly influenced by affinity of surface for gases and the retention characteristics of the surface for particles
Deboudt and others (1999)	A	Trace elements	blanks	Automobile source minor component of particulate lead in air

Table 5. Reports that address highway-runoff constituent loads and atmospheric deposition sources—*Continued*

Reference	Report type	Period of sampling	Type of sampling/method	Location/setting	Document method	
					Sample collection	Analytical
deLuca (1991)	D/I	ND	Wet deposition/rainfall collector	Porto Alegre, Brazil/urban	Yes	ND
Diamond and others (2000)	D/I	ND	Bulk deposition/Kimwipes	Toronto, Ontario/urban	Yes	Yes
Dossett and Bowersox (1991)	M/I	ND	Bulk deposition/wet-dry collector	ND	ND	ND
Dupuis and Lord (1982)	R/S: FHWA	ND	Various	ND	Yes	Yes
Ebbert and Wagner (1987)	D/I	1977–83	Bulk deposition/rainfall collector, dryfall collector	31 catchments across United States/urban	ND	ND
Ellis and others (1987)	D/I	ND	ND	London region/urban	ND	ND
Endlich and others (1988)	D/I	1978–83	Wet deposition/automatic precipitation sampler, weighing bucket rain gage	Turners Falls, Mass./urban; Fort Wayne, Ind./urban; Lancaster, Kans./urban; Raleigh, N.C./urban; Selma, Ala./urban; Zanesville, Ohio/urban	Yes	Yes
Fisher (1987)	R/S	ND	Highway related emissions	Europe/urban	ND	ND
Franz and others (1991)	D/I	May 8, 1986–October 13, 1986	Wet deposition/automatic wet deposition sampler	Minneapolis, Minn./urban	Yes	Yes
Fraser and others (1999)	D/I	September 8–9, 21, 1993	Vehicle emissions/low-volume particulate matter sampler, high volume dichotomous sampler	Los Angeles, Calif./urban; Long Beach, Los Angeles, Azusa, Claremont, Calif./urban	Yes	Yes
Garnaud and others (1999)	D/I	November 1994–May 1997	Bulk deposition/total deposition collector	Paris/urban	Yes	Yes
Gay and Melching (1995)	D/I	March 1983–April 1985	Wet deposition/precipitation collectors	Princeton, Mass./rural; Truro, Mass./rural	Yes	Yes
Germani and Zoller (1994)	D/I	November–December 1978	Dry deposition/cascade impactors	Alexandria, Va./urban	Yes	Yes
Grosjean (1983)	D/I	August–September 1981; February–March 1982	Air/filter samplers	Los Angeles region/urban	Yes	Yes
Gupta, Agnew, Gruber, and Kreutzberger (1981)	R/S: FHWA	March 1976–September 1977	Bulk deposition/precipitation gauge, dustfall bucket, weirs, flumes, level sensing instruments	Milwaukee, Wisc./urban; Harrisburg, Penn./rural; Nashville, Tenn./urban; Denver, Colo./urban	Yes	Yes
Habibi (1973)	D/I	ND	Vehicle emissions	ND	Yes	Yes
Halverson and others (1984)	D/I	July 1980–June 1981	Wet deposition/automatic precipitation collector	State College, Penn. region/urban	Yes	Yes

Reference	Investi-gation type	Chemical analyte	QA/QC	Comments
deLuca (1991)	A,R	Trace elements, major inorganic constituents, organic compounds, water-quality properties	ND	Ammonia, chlorides, and sulphates from atmospheric deposition affect stormwater quality
Diamond and others (2000)	A	Organic compounds	blanks	Organic film containing semivolatile organic compuonds such as PCBs and PAHs can be seen in oily sheen found on roadways
Dossett and Bowersox (1991)	A	ND	ND	Sample contamination can occur when raindrops splash off of the sampler
Dupuis and Lord (1982)	A	ND	ND	Discusses instrumentation requirements for a comprehensive field-monitoring program
Ebbert and Wagner (1987)	A,R	Trace elements, major inorganic constituents, organic compounds	ND	Study indicates rainfalll is substantial source of some constituents, especially nitrogen species, in storm runoff from urban catchments
Ellis and others (1987)	R	Trace elements, organic compounds, water-quality properties	ND	Metal concentrations in stormwater runoff higher in highway locations than in urban/residential and rural areas
Endlich and others(1988)	A	Trace elements, major inorganic constituents, organic compounds, water-quality properties	ND	Discusses chemical constituents in precipitation
Fisher (1987)	A	Major inorganic constituents	ND	Nitrogen oxides have direct affect on acid deposition
Franz and others (1991)	A	Organic compounds	blanks	All samplers collected at about 95% efficiency when periods of sampler malfunctioning were not considered
Fraser and others (1999)	A	Trace elements, major inorganic constituents, organic compounds	ND	Portion of fine organic particulate matter in the Los Angeles atmosphere attributable to direct particle emissions form vehicle exhaust is calculated to vary form 7.5 to 18.3%
Garnaud and others (1999)	A,R	Trace elements, major inorganic constituents, water-quality properties	standards, blanks	Particulate metal concentrations not appreciably varied in dry and wet fallout samples
Gay and Melching (1995)	A	Trace elements, major inorganic constituents, organic compounds, water-quality properties	standards	Precipitation samples collected to examine the quality of precipitation from storms
Germani and Zoller (1994)	A	Trace elements, major inorganic constituents	blanks	Mineral and ferrous metal particles constitute most of the material found on the first four stages of the cascade impactor samples
Grosjean (1983)	A	Organic compounds	blanks, controls	Approximately 85% of PAH levels would have been underestimated if sampling were limited to glass fiber filters
Gupta, Agnew, Gruber, and Kreutzberger (1981)	A,R	Trace elements, major inorganic constituents, organic compounds, water-quality properties	controls	Discussion of constituents of highway runoff, sources and migration of pollutants to receiving water, effects of pollutants and treatment methods
Habibi (1973)	A	Trace elements	replicates	Described methods used to assess lead emissions from vehicles
Halverson and others (1984)	A,R	Major inorganic constituents, organic compounds, water-quality properties	ND	Precipitation contributed most of nitrogen found in runoff, along with some sulfur and phosphorus

Table 5. Reports that address highway-runoff constituent loads and atmospheric deposition sources—*Continued*

Reference	Report type	Period of sampling	Type of sampling/method	Location/setting	Document method	
					Sample collec-tion	Analyt-ical
Harrison and Johnston (1985)	D/I	October 1981–June 1983	Bulk deposition/total deposition collectors	U.K./urban	Yes	Yes
Harrison and others (1985)	D/I	ND	Air/gas chromatography	Lancaster, U.K./urban; Hazelrigg, U.K./rural	Yes	Yes
Hedges and Wren (1987)	D/I	July 1983–July 1984	Bulk deposition/deposition canisters	Birmingham, U.K./urban	ND	ND
Herrick (1966)	M/I	ND	Dry deposition/dustfall collectors	ND	Yes	ND
Hewitt and Rashed (1990)	D/I	December 3, 1986–December 3, 1987	Bulk deposition/funnels covered with screens	Burton-in-Kendal, Cumbria, U.K./urban	ND	ND
Hicks and Matt (1988)	M/I	ND	Dry deposition/ND	ND	ND	ND
Hicks and others (1991)	M/I	ND	Dry deposition/filterpack sampler	ND	Yes	Yes
Hicks and others (1993)	R/S	ND	Bulk deposition/various	ND	Yes	ND
Ho and Tai (1988)	D/I	November 1979	Soil/trowel	Hong Kong/urban	Yes	Yes
Holdren and others (1993)	R/S	ND	Bulk deposition/ND	ND	ND	ND
Holsen and Noll (1992)	D/I	June 21,–September 29, 1991	Dry deposition/dry deposition collectors	Chicago, Ill./urban	Yes	Yes
Hopke (1991)	M/I	ND	Bulk deposition/ND	ND	ND	ND
Hvitved-Jacobson and Yousef (1991)	R/S	ND	Bulk deposition/ND	ND	ND	ND
James and Shivalingaiah (1985)	M/I	ND	Bulk deposition/ND	Hamilton, Ontarion, Canada/urban	ND	ND
Jensen and Laxen (1987)	D/I	January 1985–April 1986	Air/'M' Type samplers	London region/urban	Yes	Yes
Jones and Tinker (1984)	D/I	ND	Wet deposition/rain gauge, weir	Preston, U.K./urban	Yes	ND
Klappenbach (1991)	D/I	1982–89	Wet deposition/precipitation collectors	Great Lakes region/urban and rural	Yes	Yes
Klaus (1985)	D/I	ND	Vehicle emissions/impactors	ND	Yes	Yes

Reference	Investi-gation type	Chemical analyte	QA/QC	Comments
Harrison and Johnston (1985)	A	Trace elements, organic compounds	blanks	Documents a substantial decrease in pollutant deposition fluxes with distance from the highway
Harrison and others (1985)	A	Trace elements	blanks	Organic lead associated with atmospheric aerosols only is a minor component in comparison with gas-phase alkyllead or particulate inorganic lead
Hedges and Wren (1987)	A	Trace elements, major inorganic constituents	ND	Wind direction and seasonal changes affect deposition rates of certain metals
Herrick (1966)	A	ND	blanks	A revision for Recommended Standard Method for Continuing Dustfall Survey
Hewitt and Rashed (1990)	A,R	Trace elements, organic compounds	ND	Approximately 90% of lead emissions from fast-moving vehicles dispersed away from road; PAH compounds have >95% of lower molecular weight species dispersed away from road
Hicks and Matt (1988)	A	ND	ND	Modeling and measurement of dry deposition
Hicks and others (1991)	A	Organic compounds	blanks	Filterpack used to estimate dry-deposition rates on a routine basis
Hicks and others (1993)	A	ND	ND	Separate dry- and wet-deposition measurements more accurately characterize total deposition than bulk-deposition measurements
Ho and Tai (1988)	A	Trace elements, major inorganic constituents	blanks, replicates	Soil and grass samples used to estimate the extent of aerial deposition of metals in the roadside
Holdren and others (1993)	A	ND	ND	Overview of the selection of models to represent ecosystem responses to specified leveles of deposition
Holsen and Noll (1992)	A	Trace elements, major inorganic constituents, organic compounds	blanks, replicates	Coarse particles and the compounds associated with them are responsible for the majority of dry deposition
Hopke (1991)	A	ND	ND	Discussion of receptor models
Hvitved-Jacobson and Yousef (1991)	A	ND	ND	Smith et al. reported dust fall loads in the USA approximately 0.23 g/m^2/d, 0.16–1.53 at the central region and 0.07–0.18 in the southern region and 0.06–0.16 at the eastern region
James and Shivalingaiah (1985)	A,R	ND	ND	Discussion of runoff models used to simulate quantity and quality of storm water runoff
Jensen and Laxen (1987)	A	Trace elements	blanks, standards	Concentrations of particulate-bound lead in air measured to see decrease after phase-down of lead content in gasoline
Jones and Tinker (1984)	A,R	Major inorganic constituents, organic compounds, water-quality properties	ND	Discusses transport of pollutants from road surface by spray
Klappenbach (1991)	A	Trace elements, major inorganic constituents	ND	Maximum volume weighted mean deposition rates for Pb, Fe, Zn, Cu, Na occur during winter months
Klaus (1985)	A	Trace elements, major inorganic constituents, organic compounds	ND	Composition of flue gas deposits from an Otto-cycle and a diesel engine investigated

Table 5. Reports that address highway-runoff constituent loads and atmospheric deposition sources—*Continued*

Reference	Report type	Period of sampling	Type of sampling/method	Location/setting	Document method	
					Sample collec-tion	Analyt-ical
Kobriger and Geinopolos (1984)	R/S: FHWA	September 1978–October 1981	Bulk deposition/precipitation gauge, dustfall bucket, weirs, flumes, level sensing instruments	Milwaukee, Wisc./urban; Harrisburg, Penn./rural; Sacramento, Calif./urban; Efland, N.C./rural	Yes	Yes
Lamoree and Turner (1999)	D/I	February–April 1997	Vehicle emissions/MiniVol Portable Survey Samplers	St. Charles County, Mo./rural; St. Louis, Mo./urban	Yes	Yes
Lazrus and others (1970)	D/I	September 1966–March 1967	Bulk deposition/automated precipitation collector	32 stations across United States	Yes	Yes
Malmquist (1979)	D/I	April–October 1976	Bulk deposition/open beakers	Goteborg, Sweden/urban	ND	ND
Miguel and others (1998)	D/I	August 20–28, 1996	Vehicle emissions/stainless steel canisters	San Francisco Bay region, Calif./urban	Yes	Yes
Moe and others (1982)	D/I: FHWA	September 1977–September 1979	Bulk deposition/automatic recording rain gage, automatic water samplers, UC Davis stacked filter units	Dallas, Tex./urban	Yes	ND
Nader (1958)	D/I	ND	Dry deposition/dry deposition collectors	ND	Yes	Yes
Nikolaou and others (1997)	D/I	March 1993–March 1994	Air/CO sensors	Dallas, Lubbock, Houston, San Antonio, Tex./urban	Yes	Yes
Nilles and others (1992)	D/I	ND	Wet deposition/wet-dry deposition sampler, rain gage	United States/urban and rural	Yes	Yes
Nilles and others (1994)	R/S	1998–91	Wet deposition/wet-dry deposition sampler, rain gage	United States/urban and rural	Yes	Yes
Ondov and others (1982)	D/I	April 17–23, 1973; August 1973 December 1973–March 1974;	Vehicle emissions	ND	Yes	Yes
Pankow and others (1984)	D/I	March–April 1982; October–December 1982	Wet deposition/rain collector	Portland, Oreg./urban and semi-rural	Yes	Yes
Pankow and others (1998)	D/I	April–December 1997	Bulk deposition/multi-sorbent air-sampling cartridges	N.J./urban	Yes	Yes
Peters and Reese (1995)	D/I	April 14–June 30, 1992	Bulk deposition/wet-dry collector, dryfall collector, bulk collector	Lake Okeechobee, Clewiston, Fla./urban	Yes	Yes
Pirrone and Keeler (1993)	D/I	July 8–August 9, 1991	Bulk deposition/dichotomous sampler	Chicago, Ill./urban; Kankakee, Ill./rural	ND	ND

Reference	Investigation type	Chemical analyte	QA/QC	Comments
Kobriger and Geinopolos (1984)	A,R	Trace elements, major inorganic constituents, organic compounds, water-quality properties	controls	Discussion of constituents of highway runoff, sources and migration of pollutants to receiving water, effects of pollutants and treatment methods
Lamoree and turner (1999)	A	Organic compounds	blanks	Both PM20 and PM 2.5 the mass concentrations decreased with increasing distance downwind of the roadway
Lazrus and others (1970)	A	Trace elements, major inorganic constituents	ND	On basis of geographical distributions, lead, zinc, copper, iron, and manganese in atmospheric precipitation are derived primarily from human activity
Malmquist (1979)	A,R	Trace elements, major inorganic constituents, organic compounds	ND	Atmospheric fallout contributes substantially to the storm-water pollutants
Miguel and others (1998)	A	Organic compounds	ND	Gas- and particle-phase pollutant concentrations measured to determine PAH and black carbon emissions
Moe and others (1982)	A,R	Trace elements, major inorganic constituents, organic compounds, water-quality properties	ND	Particulate levels decreased sharply after rainshowers
Nader (1958)	A	ND	ND	No substantial differences measured among three different types of dustfall collectors
Nikolaou and others (1997)	A	Major inorganic constituents	ND	No evidence of increased carbon monoxide levels in vicinity of elevated or depressed freeways in comparison to at-grade level freeways
Nilles and others (1992)	A	Major inorganic constituents, water-quality properties	ND	Relative error increased for most analytes at lower concentrations; laboratory error is estimated to account for typically one-fifth of the overall collocated sampling error
Nilles and others (1994)	A	Major inorganic constituents, organic compounds, water-quality properties	duplicates	Colocation bias typically accounted for less than 25 percent of the overall measurement error for each site
Ondov and others (1982)	A	Trace elements, major inorganic constituents	ND	Lead, bromine, chloride, and barium can be used as markers of motor-vehicle contributions to pollution
Pankow and others (1984)	A	Organic compounds	blanks	Discussed design and use of a rain sampler
Pankow and others (1998)	A	Organic compounds	blanks, spikes, standards	Adsorption/thermal desorption with multi-sorbent air-sampling cartridges
Peters and Reese (1995)	A	Major inorganic constituents, organic compounds	blanks	Most of the Total-P in the dry deposition was Ortho-P, whereas only a small amount of the Total-P in the wet deposition was Ortho-P; inputs of insects to the bulk and dryfall-collectors factor affecting deposition estimates for P and NH3 + Org-N
Pirrone and Keeler (1993)	A,R	Trace elements, organic compounds	ND	Dry deposition of fine and coarse particles substantial source of trace metals discharged to sewer systems by storm water runoff

Table 5. Reports that address highway-runoff constituent loads and atmospheric deposition sources—*Continued*

Reference	Report type	Period of sampling	Type of sampling/method	Location/setting	Document method	
					Sample collection	Analytical
Randall and others (1981)	D/I	September 30, 1976–May 6, 1977	Bulk deposition/recording rain gages, automatic samplers, plastic funnels and containers	Virginia/urban	Yes	Yes
Revitt and others (1990)	D/I	July–September 1984	Bulk deposition/deposit gages, rain gage	Chilwell Gardens, Greater London/urban	ND	ND
Rice and Bricker (1996)	D/I	1991–93	Bulk deposition/wet-dry deposition collector	Catoctin Mt., Md./rural	Yes	Yes
Risley and Shanley (1994)	D/I	October 1986–December 1987	Wet deposition/wet-dry precipitation collector	Quabbin Reservoir region, Mass./rural	Yes	Yes
Rogge and others (1993)	D/I	May 1988	Vehicle emissions/vacuum sweeper truck	Los Angeles area/urban	Yes	Yes
Roorda-Knape and others (1999)	D/I	May 1995–August 1995	Vehicle emissions/ND	West of Netherlands/urban	ND	ND
Sanderson and others (1963)	D/I	November 1960–December 1961	Dry deposition/dustfall collectors	ND	ND	Yes
Sartor and others (1972)	R/S	ND	Street surface contaminants/ND	US/urban	ND	ND
Schroder and Hedley (1986)	D/I	May 11, 1982–May 13, 1982	Wet deposition/precipitation collectors	Denver, Colo./urban	Yes	Yes
Schroder and Malo (1987)	D	ND	Wet deposition/rain gage	ND	Yes	Yes
Schroder and Malo (1984)	D/I	ND	Bulk deposition/wet-dry collector	Raleigh, N.C./urban	Yes	Yes
Schroder and others (1989)	D/I	1985–88	Wet deposition/automatic wet-deposition sampler	Denver, Colo./urban	Yes	Yes
Schroeder (1995)	D/I	1986–87	Water samples/bailers	Fresno, Calif./urban	Yes	Yes
Schultz (1994)	D/I	June 15, 1988–August 31, 1989	Wet deposition/wet-dry automatic samplers	Cincinnati, Ohio/urban	Yes	Yes
Shahin and others (2000)	D/I	December 1993–October 1995	Dry deposition/automatic dry-deposition collectors	Lake Michigan region/urban	Yes	Yes

Reference	Investi-gation type	Chemical analyte	QA/QC	Comments
Randall and others (1981)	A,R	Trace elements, major inorganic constituents, organic compounds	ND	Washout of atmospheric contaminants occurred during the early stages of precipitation events
Revitt and others (1990)	A,R	Trace elements	ND	Contribution of local emissions to total deposition is considered and found to be important only for Zn; in rainfall metals are mainly particulate associated
Rice and Bricker (1996)	A	Trace elements, major inorganic constituents, water-quality properties	blanks, standards, duplicates	Contribution of large amounts of sulfate to watersheds by acidic deposition one of the underlying causes of acidification in watersheds
Risley and Shanley (1994)		Trace elements, major inorganic constituents, organic compounds, water-quality properties	ND	Discusses the effects of storm paths and variations within-storms on precipitation chemistry
Rogge and others (1993)	A	Organic compounds	ND	Fine particulate paved road dust is the third largest source of fine organic carbon particle emissions to urban atmosphere
Roorda-Knape and others (1999)	A	Major inorganic constituents, organic compounds	ND	Black smoke and NO_2 concentrations are higher close to motorways and decline with distance from the motorway
Sanderson and others (1963)	A	ND	duplicates	Comparison of dustfall collectors
Sartor and others (1972)	R	Trace elements, major inorganic constituents, organic compounds, water-quality properties	ND	Street surface contaminants contain high concentrations of materials known to cause problems of water pollution
Schroder and Hedley (1986)	A	Trace elements, major inorganic constituents, organic compounds, water-quality properties	blanks	During the beginning of a storm event, most of the inorganic constituents are at maximum concentration
Schroder and Malo (1987)	A	ND	blanks	Quality assurance program developed by the National Trends Network to collect long-term quality data
Schroder and Malo (1984)	A	Major inorganic constituents, water-quality properties	ND	Discusses the quality of wet deposition in the U.S.
Schroder and others (1989)	A	Trace elements, major inorganic constituents, organic compounds, water-quality properties	blanks	Precipitation acidity is associated with magnesium, fluoride, chloride, sodium, and calcium concentrations
Schroeder (1995)	A,R	Trace elements, major inorganic constituents, organic compounds, water-quality properties	standards	Wide variety of inorganic and organic contaminants generated in the catchment are removed by sorption within the top 4 cm of sediment in the recharge basin, and the contaminants have not degraded ground-water quality beneath the basin.
Schultz (1994)	A	Organic compounds, water-quality properties	ND	Urban wet deposition nitrate differs from non-urban deposition when compared on a monthly or seasonal basis, but not an annual basis
Shahin and others (2000)	A	Trace elements, major inorganic constituents	method detection limits, blanks, replicates	Automatic dry-deposition sampler developed that can make long term measurements

Table 5. Reports that address highway-runoff constituent loads and atmospheric deposition sources—*Continued*

Reference	Report type	Period of sampling	Type of sampling/method	Location/setting	Document method	
					Sample collec-tion	Analyt-ical
Shi and others (1999)	D/I	November 1996–December 1997	Dry deposition/scanning mobility particle sizers, electrical low pressure impactor, condensation particle counter, thermophoretic precipitator	Birmingham, U.K./urban	Yes	ND
Shivalingaiah and James (1982)	M/I	ND	Bulk deposition/ND	Hamilton, Ontarion, Canada/urban	ND	ND
Shivalingaiah and James (1983)	M/I	ND	Bulk deposition/ND	Hamilton, Ontarion, Canada/urban	ND	ND
Simcik and others (1997)	D/I	November 1993–October 1995	Dry deposition/automatic dry deposition collectors	Lake Michigan region/urban	Yes	Yes
Simmons and Pocock (1987)	D/I	November–December 1982; February–March 1983	Dry deposition/ deposit canisters	Walsall, West Midlands, U.K./urban	Yes	Yes
Sirois and Barrie (1988)	D/I	1979–82	Wet deposition/wet-only collector	Canada/urban	Yes	Yes
Stockham and others (1966)	D/I	February 1963–March 1964	Dry deposition/dustfall collectors	Chicago, Ill./urban	Yes	Yes
Tramontano and others (1987)	D/I	ND	Wet deposition/automatic collector	Lewes, Del./rural; Bermuda/rural	Yes	Yes
Vandenberg and Knoerr (1985)	D/I	January 1981–April 1982	Dry deposition/deposition buckets, deposition plates, petri dishes, filter paper	Duke Forest, N.C./rural	Yes	Yes
Ward (1990)	D/I	ND	Dry deposition, soil/ND	U.K./urban	ND	Yes
Warren and Birch (1987)	D/I	ND	Dry deposition and soils/Warren Spring Laboratory 'M' type sampling system and dustpan and brush	East London/urban	Yes	Yes
Westerholm and others (1988)	D/I	ND	Vehicle emissions/dilution tunnel	Sweden/urban	Yes	Yes
Williams (1987)	R/S	ND	Vehicle emissions/	U.K./urban	ND	ND
Willoughby and others (1991)	R/S	1989	Wet deposition/wet-deposition collectors	US/urban and rural	Yes	Yes
Willoughby (1995)	D/I	June 1992–August 1993	Wet deposition/wet-dry collector	Gary, Ind./urban	Yes	Yes

Reference	Investi-gation type	Chemical analyte	QA/QC	Comments
Shi and others (1999)	A	Organic compounds	ND	Total particle number concentration higher at roadside; decrease in particle number concentration was greater than that of the mass concentration
Shivalingaiah and James (1982)	A,R	ND	ND	SWMM (Storm water management model) III runoff quality algorithms used to determine pollutant accumulation
Shivalingaiah and James (1983)	A,R	ND	ND	Addition of atmospheric-dustfall subroutine used to simulate pollutant accumulation on individual subcatchments NEWBLD to SWMM3-RUNOFF model improved the computed pollutographs
Simcik and others (1997)	A	Organic compounds	method detection limits, blanks	Particle mass and elemental fluxes higher in Chicago than in rural areas
Simmons and Pocock (1987)	A	Trace elements, major inorganic constituents	ND	Metal deposition rates in urban areas are highly spatially variable
Sirois and Barrie (1988)	A	Organic compounds, water-quality properties	ND	Dry deposition estimated from total deposition
Stockham and others (1966)	A	Organic compounds	duplicates	Discusses the variability of dustfall analysis because of the container and the collecting fluid
Tramontano and others (1987)	A	Trace elements	blanks	Discusses the results of the analysis of trace metals in precipitatio
Vandenberg and Knoerr (1985)	A	Major inorganic compounds	standards	Wide range of surface deposition rates are estimated form the variety of deposition surfaces used in this study shows uncertainty of the surrogate surface-measurement techniques
Ward (1990)	A	Trace elements, major inorganic constituents, water-quality properties	blanks, replicates	Elements related to motor vehicles are elevated in surface soils due to dry and wet deposition of emission or wear of components
Warren and Birch (1987)	A	Trace elements	ND	Highest overall contamination occurs at a site with highest traffic density
Westerholm and others (1988)	A	Organic compounds	ND	A significant fraction of emitted PAH is formed in the combustion process (>50%)
Williams (1987)	A	Organic compounds	ND	Summarization of the contribution of motor vehicles to the emissions and air quality in terms of the more important air pollutants in the U.K.
Willoughby and others (1991)	A	Major inorganic constituents, organic compounds, water-quality properties	duplicates	No significant difference among laboratory determinations for calcium, magnesium, sodium, potassium, ammonium, chloride, nitrate, sulfate, hydrogen ion, and specific conductance
Willoughby (1995)	A	Trace elements, major inorganic constituents, organic compounds, water-quality properties	controls, blanks	Chemical quality of wet deposition monitored; annual loadings could be used to estimate the contribution of wet deposition to the total annual constituent loadings

Table 5. Reports that address highway-runoff constituent loads and atmospheric deposition sources—*Continued*

Reference	Report type	Period of sampling	Type of sampling/method	Location/setting	Document method	
					Sample collection	Analytical
Wu and others (1992)	D/I	June–July 1987; May and July 1988, May 1989	Dry deposition/deposition plates	Claremont, Calif./urban; Gettysburg, Penn./urban	Yes	Yes
Wu and others (1998)	D/I	August 1995–July 1996	Bulk deposition/automatic sampler, tipping bucket, nonrecording rain gage	Charlotte, N.C./urban and rural	Yes	Yes
Yu and others (1994)	D/I	June 5, 1990–July 9, 1991	Dry deposition/aerosol samplers, impactors	Chesapeake Bay region/rural	Yes	Yes
Zweidinger and others (1988)	D/I	May 1983	Vehicle emissions/roadside samplers	Raleigh, N.C. (U.S. Highway 70)/ urban	Yes	Yes

Reference	Investi-gation type	Chemical analyte	QA/QC	Comments
Wu and others (1992)	A	Trace elements, major inorganic constituents, organic compounds	blanks, duplicates	Surface resistance may be the rate-limiting factor in determining overall dry deposition
Wu and others (1998)	A,R	Trace elements, major inorganic constituents, organic compounds, water-quality properties	ND	Total suspended solids were higher at a bridge site than on typical urban highways
Yu and others (1994)	A	Trace elements, major inorganic constituents, organic compounds	blanks	Spatial and temporal differences of elemental concentrations examined
Zweidinger and others (1988)	A	Organic compounds	ND	Evaluated methods for estimating emission factors

Chapter 10. Statistical Approaches to Interpretation of Local, Regional, and National Highway-Runoff and Urban-Stormwater Data

By GARY D. TASKER and GREGORY E. GRANATO

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Statistical Approaches to Interpretation of Local, Regional, and National Highway-Runoff and Urban-Stormwater Data

By Gary D. Tasker *and* Gregory E. Granato

Abstract

Decision makers need viable methods for the interpretation of local, regional, and national-highway runoff and urban-stormwater data including flows, concentrations and loads of chemical constituents and sediment, potential effects on receiving waters, and the potential effectiveness of various best management practices (BMPs). Valid (useful for intended purposes), current, and technically defensible stormwater-runoff models are needed to interpret data collected in field studies, to support existing highway and urban-runoff-planning processes, to meet National Pollutant Discharge Elimination System (NPDES) requirements, and to provide methods for computation of Total Maximum Daily Loads (TMDLs) systematically and economically.

Historically, conceptual, simulation, empirical, and statistical models of varying levels of detail, complexity, and uncertainty have been used to meet various data-quality objectives in the decision-making processes necessary for the planning, design, construction, and maintenance of highways and for other land-use applications. Water-quality simulation models attempt a detailed representation of the physical processes and mechanisms at a given site. Empirical and statistical regional water-quality assessment models provide a more general picture of water quality or changes in water quality over a region. All these modeling techniques share one common aspect—their predictive ability is poor without suitable site-specific data for calibration.

To properly apply the correct model, one must understand the classification of variables, the unique characteristics of water-resources data, and the concept of population structure and analysis. Classifying variables being used to analyze data may determine which statistical methods are appropriate for data analysis. An understanding of the characteristics of water-resources data is necessary to evaluate the applicability of different statistical methods, to interpret the results of these techniques, and to use tools and techniques that account for the unique nature of water-resources data sets. Populations of data on stormwater-runoff quantity and quality are often best modeled as logarithmic transformations. Therefore, these factors need to be considered to form valid, current, and technically defensible stormwater-runoff models.

Regression analysis is an accepted method for interpretation of water-resources data and for prediction of current or future conditions at sites that fit the input data model. Regression analysis is designed to provide an estimate of the average response of a system as it relates to variation in one or more known variables. To produce valid models, however, regression analysis should include visual analysis of scatterplots, an examination of the regression equation, evaluation of the method design assumptions, and regression diagnostics. A number of statistical techniques are described in the text and in the appendixes to provide information necessary to interpret data by use of appropriate methods.

Uncertainty is an important part of any decision-making process. In order to deal with uncertainty problems, the analyst needs to know the severity of the statistical uncertainty of the methods used to predict water quality. Statistical models need to be based on information that is meaningful, representative, complete, precise, accurate, and comparable to be deemed valid, up to date, and technically supportable. To assess uncertainty in the analytical tools, the modeling methods, and the underlying data set, all of these components need be documented and communicated in an accessible format within project publications.

INTRODUCTION

Engineers, planners, economists, regulators, and others concerned with stormwater runoff from highways and urban areas often develop alternative plans to meet demands for desired quantity and quality of water at particular locations and times. Predictive procedures are needed for planning, permitting, and design of highway structures, as well as design of best management practice (BMP) structures (such as swales or retention ponds) and BMP maintenance procedures (such as street-sweeping programs). Predictive procedures include the development and application of conceptual models, simulation models, empirical models, and statistical models.

Any model, to be considered viable, must stem from an initial conceptualization of the system of concern. A conceptual model is a qualitative understanding of the sources and processes relevant to a problem. The model, which can commonly be represented by a diagram, is supported by common sense, scientific principles, data, and research to support the ideas. For example, expecting total pollutants in runoff to increase with increasing average daily traffic at a highway site—because vehicles are considered to be one of the primary sources of highway pollutants—is an example of a conceptual model. Analysis of available information, however, must substantiate the conceptual model to support development of more quantitative models through the application of empirical, deterministic, and (or) statistical techniques.

Stormwater-quality models have historically been used to characterize stormwater flow and quality, predict pollutant runoff loads, assess impacts on receiving waters, and determine the effectiveness of various BMPs to mitigate possible impairment of designated beneficial uses of receiving waters (Kobriger and others, 1981; Shelley and Gaboury, 1986; Driscoll and others 1990). Now, and in the future, valid, current, and technically defensible stormwater runoff models are needed to

- help in interpreting data collected by field studies,
- support existing highway- and urban-runoff planning processes (Kobriger and others, 1981, Driscoll and others 1990; Young and others, 1996; Granato and others, 1998),
- meet National Pollutant Discharge Elimination System (NPDES) requirements (Young and others, 1996), and
- provide systematic and economical methods for calculation of Total Maximum Daily Loads (TMDLs) (Shoemaker and others, 1997).

Sound statistical planning models that use data collected at monitoring stations representing the region of interest can be used to assist policy makers and public officials in the evaluations of alternative plans. Statistical planning models represent a structured, ordered, and quantitative approach. These models can provide information for debates over proper choices for water-management alternatives and to evaluate competitive alternatives. Statistical planning models are needed for quantitative local, regional, or national water-quality assessments that can be demonstrated to be valid (useful for intended purposes), current, and scientifically/technically defensible when based on readily available monitoring data, land use information, and information about water-quality management practices.

The general objective of this paper is to examine methods for water-quality modeling and to identify and describe statistical methods and procedures that may be used to predict concentrations and loads of chemical constituents and sediment in highway and urban runoff and the potential for effects in receiving waters in terms of the unique characteristics of water-resources data. Although the concentrations, loads and potential effects of runoff constituents are often examined on a site-specific basis, these issues are also examined within the context of regional and (or) national interpretations. This report is designed to provide general (and sometimes very basic) information in terms of the analysis of water-resources data for stormwater analysis, but it is not designed to be a textbook for statistical methods. Appendixes are provided to expand on certain methods discussed in the text, and references to suggested reading are provided where appropriate. Uncertainties in modeling are discussed, as well as the quality-assurance and quality-control measures that are necessary to address these uncertainties.

BACKGROUND

Simulation models, empirical models, regression models, and other statistical models historically have been used as approaches for predicting the quantity, quality, and loads of constituents in highway and urban runoff. Simulation models are used with model parameters that have a direct physical definition in an attempt to provide a detailed description of the physical processes and mechanisms that affect water quality. These models therefore require a considerable degree of detail in the description of the physical system. In simulation models, parameter estimation is not as data dependent as in statistical water-quality assessment models. On the other hand, empirical and statistical water-quality-assessment models provide a more general picture of water quality or changes in water quality. This picture could be in the form of a map of a water-quality statistic, or tables, or simply an equation with error bands on the parameters and predictions. Statistical regional water-quality models may also be used to estimate nonpoint-source loadings as inputs for more detailed water-quality simulation models (Ichiki and others, 1996). All these modeling techniques share one common aspect—the predictive ability of almost any model will be poor without suitable site-specific data for calibration (Shelley and Gaboury, 1986).

Criteria for model selection depend on modeling logistics as much as on data quality objectives (DQOs) and other technical considerations (Shoemaker and others, 1997). Logistical criteria include

- the availability of hardware and software to implement the model of choice,
- the availability of trained modelers to manipulate the model, to develop sound input parameters with an understanding of how they are used by the model, and to critically evaluate model results,
- organizational commitment to establish and support a model, to document the model, and to oversee subsequent applications of the model so that methods and results can be reviewed and accepted as valid, current, and technically defensible,
- organizational expertise with the model, to apply the model and to review applications of the model to maintain credibility of results, and
- available financial resources to support modeling efforts.

The resources needed to support a modeling effort increase in direct proportion to the complexity of the model chosen for analysis. A political criterion also is involved in the selection and use of modeling methods. To implement a successful modeling effort, the various interest groups involved in a project must be willing to accept modeling results. Even the most successful and sophisticated modeling effort will fail if the results are not understood and accepted by decision makers (Shoemaker and others, 1997).

A detailed description of each available runoff-quality model is beyond the scope of this report. Necessary information, however, is readily available in other publications. Driscoll and others (1990) discuss the application of different methods for national analysis of highway-runoff quality and related environmental effects. Hall and Hamilton (1991) describe many aspects of highway-runoff transport modeling. Bedient and Huber (1992) describe many of the hydrologic simulation models in use today. Young and others (1996) provide examples of simulation, empirical, and regression models, and the FHWA statistical model as applied to individual highway sites. Shoemaker and others (1997) provide a comprehensive guide describing most of the available predictive tools—including most applicable simulation, empirical, regression, and statistical models—for water-quality assessment within the TMDL process. A brief discussion of simulation, empirical, regression, and other statistical models, however, will provide information useful for statistical interpretation of local, regional, and national highway and urban stormwater-quality data.

Simulation models—including SWMM (Huber and Dickinson, 1988), STORM (U.S. Army Corps of Engineers, 1977), HSPF (Bicknell and others, 1993), and the Federal Highway Administration (FHWA) urban highway storm drainage model (Dever and others, 1983)—require detailed site-specific information and data to calibrate the model for current conditions. By using simulation models, highway engineers can evaluate the design of each highway—including the road surface, catch basins, and drainage structures—with respect to flow and water quality (Hall and Hamilton, 1991). Simulation models are also useful in estimating relations between variations in input parameters and resulting flows, constituent concentrations, and constituent loads in runoff. The validity of these estimates, however, depends upon a robust calibration of the model with site-specific data (Driscoll and others, 1990). For example, Zarrielo (1998) compared results of simulations made with nine uncalibrated runoff models to observed flows in two urban watersheds; although the modelers had very detailed information about site characteristics and precipitation, the resulting estimates of peak flow rates and total stormflow volumes differed from measured data by as much as 260 and 240 percent, respectively. Simulations are considered to be highly useful in the design phase or post construction-analysis phase of specific sections of a highway, but collection of the site-specific data and the high level of effort necessary to successfully implement these models are not practical for planning or management on a regional or national scale (Driscoll and others, 1990).

Empirical models include the U.S. Environmental Protection Agency (USEPA) Screening Procedures (Mills and others, 1985) and the Simple Method (Schueler, 1987). Empirical models involve the use of estimated concentrations (presumably derived from local studies and (or) the literature) multiplied by some fraction of local precipitation volumes (used to estimate runoff volumes) to estimate annual or storm loads of constituents of concern. Empirical models provide order-of-magnitude estimates of loads but do not indicate correlation among variables and do not provide estimates of the uncertainty in predictions without detailed site-specific data needed to estimate probability distributions of the precipitation/runoff volumes and concentrations used in the equation.

Highway-runoff regression models include those developed by the FHWA (Kobriger and others, 1981; Driscoll and others, 1990); State departments of transportation in Washington (Chui and others, 1982), California (Kerri and others, 1985), and Texas (Irish and others 1998); and the Ontario Ministry of Transportation (Thomson and others, 1996; 1997a). These models use information such as precipitation characteristics, highway-design features, traffic volumes, and interrelations between measured constituents to predict concentrations and (or) loads of highway-runoff constituents. The USGS regression method (Tasker and Driver, 1988; Driver and Tasker, 1990) uses the percentage of impervious area, rainfall statistics, and in some cases the mean minimum January temperature to estimate concentrations and (or) loads of urban-runoff constituents. This model also may be used for estimating highway-runoff quality in urban areas (Young and others, 1996).

Other statistical techniques have also been used as approaches for prediction of modeling urban- and highway-runoff quantity, quality, and loads. These techniques use measures of the central tendency of available data (such as the mean or median) and measures of the variability of data (the variance or coefficient of variation) to predict model outputs and the uncertainty thereof. The model formulated by Driscoll and others (1990), uses storm event statistics and the probability distribution of site event-mean concentrations (EMCs) to estimate runoff volumes, concentrations, and loads in runoff. Driscoll and others (1990) then use these loads and the probability distribution of streamflow volume at a given site to estimate potential dilution in receiving waters. Statistical models that use readily available rainfall statistics and water-quality data to produce a frequency distribution of concentrations, loads, and potential for receiving-water effects are useful because assessments of risk and return periods can be calculated (Driscoll and others, 1990).

The existing FHWA statistical pollutant loading and impact model approach described by Driscoll and others (1990) is, given appropriate input data, generally valid for intended purposes. This model uses site characteristics and other factors to calculate estimates of runoff volumes, loads, and receiving-water concentrations as a probability distribution. This model, however, is not designed for scientific or technical interpretation of study-site data in terms of the potential relations between constituents and (or) study-site characteristics. Therefore, other statistical models are necessary for scientific or technical interpretation of local, regional, and national highway- and urban-stormwater data.

Statistical techniques are commonly best suited to highway-runoff modeling needs at any scale (local, regional, or national). Population statistics and standard techniques for the analysis of error in predictions can be used to assess risk of decision error. Estimation of the error in predictions from empirical models or uncalibrated simulation models is, in reality, impossible, because inputs are complex and the effects on the error of outputs can be multiplicative. Use of simulation models requires a high degree of institutional expertise and experience, as well as a substantial modeling effort, for each site of interest. Many simulation models are suitable for specific highway applications, but the detailed input requirements and extensive modeling efforts required may preclude use for planning-level estimates. By comparison, use of existing statistical models minimizes the logistical burdens required for model application (Shoemaker and others, 1997). If the statistical model used is based on accepted statistical methods, is formulated from a valid, current, and technically defensible data set, and is documented and communicated in an accessible format, then these steps will ensure that model results will be accepted. The existence of a quantitative data set further lends credence to the acceptability of model results. The complexity of simulation models and the large range of reasonable input parameters inherent in the model calibration process can lead to differences in professional judgment, which can negatively affect acceptance of simulation-model results. Therefore, simple statistical models may be preferable to simulation models for many highway-runoff modeling needs.

Statistical analysis is also important to the design and implementation of highway- and urban-runoff data-collection programs that will yield results suitable for inclusion in local, regional, and national-synthesis efforts. Statistical analysis of available information is necessary to help determine the design of the sampling effort (random as opposed to systematic), the frequency of sampling, the number of and location of sites, and the quality of the resultant data (Averett and Schroder, 1994). For example, Thomson and others (1996; 1997b) used an extensive highway-runoff data set from Minnesota to determine that EMC samples from at least 15 to 20 storms are required to provide reasonable estimates of mean total suspended solids, total dissolved solids, total organic carbon, and zinc concentrations from each study site. Statistical methods can also be used to design and (or) optimize stormwater data-collection networks (Tasker and Raines, 1995). Statistical-analysis techniques are also necessary for the design, implementation, and interpretation of quality-assurance and quality-control (QA/QC) programs necessary to demonstrate that data collected are valid (useful for the intended purposes), technically defensible, and complete (Jones, 1999).

BASIC STATISTICAL CONSIDERATIONS

Proper classification of variables and an understanding of the characteristics of water-resources data are crucial for interpreting the results of individual studies and for combining these results in a regional or national synthesis of stormwater-quality data. Classification of the different types of variables being used to analyze data may determine which statistical methods are appropriate for data analysis. An understanding of the unique characteristics of water-resources data is necessary to evaluate the applicability of various statistical techniques, to interpret the results of these techniques, and to use tools and techniques that account for the nature of water-resources data sets. Understanding the methods and measures used to determine and analyze the population structure is also important. When necessary (as is common for water-resource and particularly for stormwater data sets), one must choose appropriate methods of data transformation to enable use of statistical techniques without violating the statistical assumptions underlying the methods chosen for analysis. Therefore, classification of variables of interest, an understanding of the statistical characteristics of water-resources data, a familiarity with the population structure and basic methods of analysis, and (when necessary) selection and proper use of population-transformation techniques are necessary to form valid, current, and technically defensible stormwater-runoff models.

Classification of Variables

Classification of variables is useful in several ways because the proper method of data analysis often depends on variable type. A variable can be classified by inherent mathematical structure (discrete or continuous), by statistical objectives of the study (response or predictor), and by level of measurement (nominal, ordinal, interval, or ratio).

A variable is discrete if there is a gap between two successively observable values in which an observed value is not possible (for example, an integer scale). A variable is continuous if there is always another observable value between any two observed values (for example, a real number scale). Examples of a discrete variable are the number of floods above a threshold, the number of exceedences of a water-quality standard, or the identification of a group. It is not possible to have 3.2 floods above a threshold, 11.7 exceedences of a standard, or to have a value between group A and group B. Examples of continuous variables are chloride concentration or the number of pounds of road salt applied per lane-mile of roadway per season. Discrete variables, however, can sometimes be treated as continuous if they cover a wide range with small gaps between observations. For example, the number of days per year with measurable rainfall could vary between 0 and 365. Furthermore, continuous variables may be grouped into categories and treated as discrete variables. For example, pH readings may be grouped into the categories of low, medium, and high.

A variable may also be classified according to the statistical objectives of the study without regard to the variable's mathematical structure. A variable that is described in terms of other variables in a regression model is called the response variable (or the dependent variable, or the predicted variable). Variables used to describe the response variable in a model are called predictors (or explanatory variables, carriers, or independent variables). For example, if one wishes to predict average nitrate concentration at a streamflow site on the basis of land-use characteristics of the upstream watershed, then average nitrate is the response variable, and land-use variables, such as percentage of urban or industrial land, would be predictors.

The level of measurement may also be used to classify variables. Nominal variables are variables whose observed values are labels for different unordered categories. For example, the "type" variable for a basin may be 1 for urban or 0 for nonurban. Ordinal variables are variables whose observed values are ordered with no implication of distance between different points on the scale. For example, Driscoll and others (1990) classified highway sites as either "urban"—average daily traffic (ADT) counts that are greater than or equal to 30,000 vehicles per day (VPD)—and "nonurban"—ADTs that are less than 30,000 VPD. Another example of an ordinal variable would be the use of the previously mentioned pH categories of low, medium, and high. Interval variables have equal differences between successive points on the measurement scale, but the zero point is arbitrary. In this case, one can compare differences in observed values. An example of an interval variable would be the increase in population density since the last census. Ratio variables have equal differences between successive points and a fixed zero. They allow one to compare differences in observed values and relative magnitude. For example, nitrate concentration measured at several monitoring sites in a region could be treated as a ratio-scale variable.

Characteristics of Water-Resources Data

The applicability of any given statistical procedure depends directly on assumptions about the characteristics of the data being explored. Results from statistical analysis may be meaningless or, even worse, misleading if data do not conform to the design assumptions of the statistical method used. Therefore, one must carefully consider which statistical methods are appropriate in terms of the data being evaluated. The unique features of water-resources data affect the suitability of interpretations made by the application of many classical statistical techniques. Pertinent characteristics of water-resources data (Helsel and Hirsch, 1992; Helsel, 1993; Hirsch and others, 1993), include the following:

- Nonrepeatability—Measurements are usually observational, not experimental. More specifically, statistical regularity cannot be demonstrated for water-resources data by repeating a controlled experiment because exactly recreating the many natural and anthropogenic influences that affect each measurement is impossible.
- A lower limit of zero—Negative values are not possible for many water-resources characteristics. For example, negative values for measured precipitation, flow, or constituent concentrations do not have meaning.
- Censored data sets—Limits in methods for sample collection and analysis cause data to be reported as either above or (more typically) below one or more reporting limits, which produce a censored population of data.
- Meaningful outliers—Valid measurements that are considerably higher or lower than most of the measured population are common among hydrologic data sets.

- Positive skewness—Data sets that are not symmetrical around mean or median values are typical for water-resources data sets because the combined effects of a lower bound of zero, censoring, and meaningful outliers tend to produce data sets in which the right tail of the distribution is extended and the left tail is truncated.
- Nonstandard distributions—Many statistical techniques are based on the assumption that the data (or in the case of regression models, the residuals) are normally distributed (the "bell-shaped" curve). The nonstandard distributions characteristic of water-resources data sets necessitate alternative tools for analysis.
- Autocorrelation—Natural and anthropogenic effects tend to cause conditions in which consecutive measurements tend to be strongly correlated.
- Interdependence—Changes in one characteristic of interest (such as rainfall intensity) cause changes in other characteristics (such as measured flows and concentrations).
- Temporal variation—Measured water-resources characteristics vary cyclically at timescales of hours, days, weeks, seasons, years, and even decades because of both natural and anthropogenic influences.

Therefore, data sets must be collected in a manner that will represent the underlying population distribution, and the statistical methods used to characterize the data must be appropriate for populations with these characteristics. Ancillary information and metadata (information about a given data set, including explanatory information and data-quality information) pertinent to the statistical characteristics of the sampled population need be documented and communicated in an accessible format with monitoring-study data to support interpretation methods.

Ancillary data are important to quantify possibly confounding variables that may preclude meaningful interpretation of data because statistical regularity cannot be demonstrated through controlled experiments. For example, Driscoll and others (1990) noted the effect of local land use on regression analysis to predict the median EMC of zinc from measures of average daily traffic on a site-by-site basis. When all sites (with average daily traffic greater than 30,000 vehicles per day) were included, regression analysis indicated a small negative slope with increasing traffic and an R^2 of about 0.04, indicating that EMCs for zinc would decrease with increasing traffic but that this relation was very weak. When one site (which was heavily influenced by a local zinc-smelting operation) was omitted, however, regression analysis indicated a strong positive slope and relatively strong relation between increasing traffic volume and increasing EMCs for zinc (R^2 was about 0.7). In this case, the local land use is the ancillary information necessary for meaningful interpretation of data based on the assumption that traffic characteristics would affect (if not control) zinc concentrations in highway runoff.

The effects of censored data can be especially problematic for interpretation of water-quality data. Laboratory detection limits change with time, can be dramatically different from laboratory to laboratory, and may even be different from method to method within a laboratory. For example, Garbarino and Struzeski (1998) indicate that detection limits for total recoverable copper in whole-water samples are 0.4, 5., and 0.3 micrograms per liter for the graphite furnace-atomic absorption spectrophotometry (GF-AAS), inductively coupled plasma-optical emission spectrometry (ICP-OES), and inductively coupled plasma-mass spectrometry (ICP-MS) methods, respectively. A number of methods may be used to compensate for the effects of one or more detection limits while applying statistical analysis tools to a data set (Gilliom and Helsel, 1986; Helsel and Gilliom, 1986; Helsel and Cohn, 1988; Helsel, 1990; Helsel and Hirsch, 1992). These methods of statistical analysis require knowledge of the detection limits truncating each data set. Detection-limit information, however, may not be available. For example, in compiling data to develop a pollutant-loading model, Driscoll and others (1990), noted that "it was virtually impossible to unequivocally determine the actual detection limit associated with each pollutant concentration." Driscoll and others (1990) could not determine the detection limits because this information was not explicitly documented in available ancillary data and because the data were produced by a number of different analytical laboratories over the years between the mid 1970's and the mid 1980's. Thompson and others (1996) also noted the difficulty in identifying detection-limit data in an extensive highway-runoff data set (416 storms from four sites monitored during 1976–83). Detection-limit artifacts also affect statistical properties of individual data sets. When a data set contains values reported as less than one or more detection limits an overestimation of central-tendency measures and an underestimation of dispersion measures will be caused by truncation of the lower tail of the true population (Driscoll and others, 1990). Also, because the relative uncertainty in the accuracy and precision of individual values tend to increase as reported concentrations approach the detection limit, the percent error expected for measurements near detection limits is much higher than for values well within the measurement range of the method of analysis (Granato and others, 1998).

The presence of meaningful high-end outliers (actual but extreme values) contributes to the positive skew and is a factor producing nonstandard distributions. High-end outliers represent times when, for example, regulatory criteria may be exceeded and the health of local ecosystems may be affected. These outliers, however, produce a host of potential problems for interpretation of data sets assembled for use in a regional or national synthesis.

Certain assumptions and conditions need to be considered in terms of the decision to include or exclude individual data points or even entire data sets, among which are the following:

- It is often assumed that outliers are not meaningful. This assumption may be misleading unless documented QA/QC information indicates problems with sample collection, processing, and (or) analysis that would justify elimination of suspect data.
- An outlier may be meaningful, but it may represent the effects of a process that should not be considered in a synthesis designed to characterize normal highway-runoff quality. For example, a chemical spill that occurs before or during a runoff-quality study may be representative of runoff quality and subsequent environmental effects at sites affected by spills, but the data may not be characteristic of "normal sites." In fact, the rate of substantial spills is about 0.0019 incident per lane kilometer per year (as estimated from the median of highway hazardous-materials incidents and public road mileage compiled by U.S. Environmental Protection Agency, 1999). Therefore, data from a spill site would incorrectly bias a national data set unless a sufficient number of sites were monitored to properly represent the probability of a spill at any given site. In another example, Driscoll and others (1990) eliminated data sets from sites affected by fallout from the eruption of Mt. Saint Helens in Washington State. Although these "meaningful outliers" were representative of the effects of volcanic eruption on the quality of highway runoff, this effect was not deemed suitable for estimation of typical highway-runoff quality in the United States.
- An extreme outlier may be meaningful and may represent the effects of a process that should be considered in a synthesis designed to characterize normal highway-runoff quality, but this effect may obscure effects of other process-related variables. The example of the effect of the highway site under influence of a local zinc smelting operation indicates the necessity for detailed documentation to describe surrounding land use, but this effect precludes development of meaningful relations between metal concentrations and average daily traffic for more normal highway conditions across the United States (Driscoll and others, 1990).

Elimination of outliers is considered a dangerous and unwarranted practice for the interpretation of water-quality data, unless one has substantial objective evidence demonstrating that the outliers are not representative of the population under study (Helsel and Hirsch, 1992). When statistical tests are used to detect outliers, these tests do not indicate that outliers represent errors; they do indicate that the population of measured vales is not necessarily a normal distribution. Excessive numbers of extreme values may cause significance levels of tests requiring the normality assumption to be in error. Therefore, use of a test requiring the normality assumption will produce inaccurate results when outliers affect population structure. Outliers may have high leverage and thus a strong potential for influencing the slope of a regression line (Helsel and Hirsch, 1992). If an outlier is discovered to have a strong influence on the slope of a regression line (the slope and (or) the correlation coefficient changes significantly when the point is omitted), then one must determine whether the outlier represents extreme values for a single process or if a secondary process is characterized by the outlier. Measurement and documentation of explanatory variables such as precipitation and flow (Church and others, 1999); real-time measures of water-quality characteristics such as specific conductance, pH, temperature, and turbidity (Spangberg and Niemczynowicz, 1992; Whitfield and

Wade, 1992; Granato and Smith, 1999); use of ratios between constituents of interest (Granato, 1996); and results from a comprehensive QA/QC program (Jones, 1999) can be used to identify and explain outliers in terms of the potential effect of real physicochemical processes as opposed to the effects of sampling artifacts.

The natural and anthropogenic processes controlling runoff quality and the methods for sampling, processing, and analysis often cause problems with autocorrelation (also referred to as serial correlation or correlation—the dependence of residuals in a time sequence because data reflect the effects of preceding conditions). One of the assumptions inherent in many regression techniques is that the residuals are independent (Helsel and Hirsch, 1992). Autocorrelation can be a problem within stormwater data sets because many of the variables used for analysis are pairs of data in a time series. For example, precipitation and flow, flow volume and concentration, and relations between measured constituents (total suspended solids and lead, for example) may be pairs of data in a time series. Time-series effects may also occur between subsequent storms. For example, Irish and others (1998) indicate that the duration, the volume of runoff per unit area, and the intensity of runoff per unit area of the preceding storm are significant causal variables in a regression model developed for highway-runoff loads of suspended solids and metals in Texas. Autocorrelation can be important because it affects the optimization of regression coefficients, affects estimates of population variance (invalidating results of hypothesis tests), and produces confidence and prediction intervals that are too narrow for the real population being sampled. To address autocorrelation problems, one may group data into time periods and use summary statistics in an analysis, use methods that are robust with respect to autocorrelation (Helsel and Hirsch, 1992), incorporate explanatory variables into predictive models that will account for potential effects of autocorrelation (Irish and others, 1998), or subsample from large data sets to eliminate autocorrelation.

Temporal variation may also increase variability in data and affect the comparability of data between sites. Seasonality is an obvious factor that may affect a population of stormwater samples at any given site. For example Driscoll and others (1990) segregated "snow washoff events" from other events for analysis and found that, for many constituents, snow washoff events had substantially higher median site EMCs, much wider confidence intervals, and a relatively few number of events than for the rest of the available data. More subtle temporal variations may affect relations between predictors and response variables and (or) contribute to the variability in measured water quality in a population of stormwater-quality samples. For example, Whitfield and Wade (1992) used results from automatic water-quality monitoring stations to detect daily cycles in receiving-water quality, as well as the effects of storms. In addition, the magnitude of seasonal variation would be expected to be a function of local climate and may therefore partly obscure relations between predictors (such as ADT) and response variables (such as constituent concentrations) if a statistical analysis includes sites with different patterns of temporal variation. For example, Driver and Tasker (1990) used the mean minimum January temperature as a predictor variable to partly account for differences in the magnitude of seasonal variation among sites in an analysis of National Urban Runoff Program (NURP) data.

Population Structure and Analysis

Sampling theory—the concept that one can monitor a given number of events and with this information estimate the properties of the underlying distribution—is based upon the concept of a probability distribution. The structure of a given population (the probability distribution) will determine which methods will be appropriate for statistical analysis and interpretation of water-resources data. If, for example, measured data fit a normal distribution, one measure of location (central tendency) and one measure of spread (variability) can be used to define the entire population. However, the applicability, robustness, and relative power of different measures of location, measures of spread, and measures of skewness depend upon the structure of data and the objectives of the analytical process.

The structure of data is often described by means of population-frequency distributions. If variables can be ascribed to a particular frequency distribution, then the known structure of the distribution has many potential uses (Athayde and others, 1983; Driscoll and others, 1990; Helsel and Hirsch, 1992), including the following:

- concisely reporting data in terms of population measures rather than total range (which may be misleading for data with outliers and multiple detection limits),
- examining the characteristics of the data (for example, the mean and standard deviation can be used to define the location and shape of a normal distribution),
- establishing the probability of any given value in the distribution (for example the probability of exceeding a water-quality standard),
- comparing results from different sites on a common basis,
- providing a framework for examining the transferability of data quantitatively, and
- testing hypotheses (for example, establishing whether concentrations of metals at sites with an ADT of less than 30,000 vehicles per day are statistically different from concentrations of metals at sites with an ADT greater than 30,000 vehicles per day).

The number of potential distributions is infinite (Ott, 1993). For example, McLaughlin (1999) provides equations for the probability distribution and cumulative distribution functions for more than 50 distributions in terms of the location, shape, and scale of each distribution. Figure 1 indicates generalized shapes of the probability-distribution and cumulative-distribution functions for the exponential, gamma, and normal distributions. Commonly, water-resources data can be characterized by relatively few distributions, and many of the available distributions are specialized variations of more general distributions (Helsel and Hirsch, 1992; Ott, 1993). For example, the lognormal frequency distribution is simply a normal distribution for data that have been transformed to logarithmic space so that the resulting distribution approximates that of the theoretical normal distribution.

Statistical-analysis methods can generally be classified as either parametric (methods in which a specified data distribution is necessary to support design assumptions) or nonparametric (methods that do not depend on a specified data distribution to establish their meaning). Nonparametric tests, because they are not as dependent on an assumed population distribution, may be more robust for data analysis. The power of parametric techniques is generally higher when the distributional assumptions are correct. In many cases, however, the relative advantage of parametric techniques decreases with increasing population size (Hirsch and others, 1993).

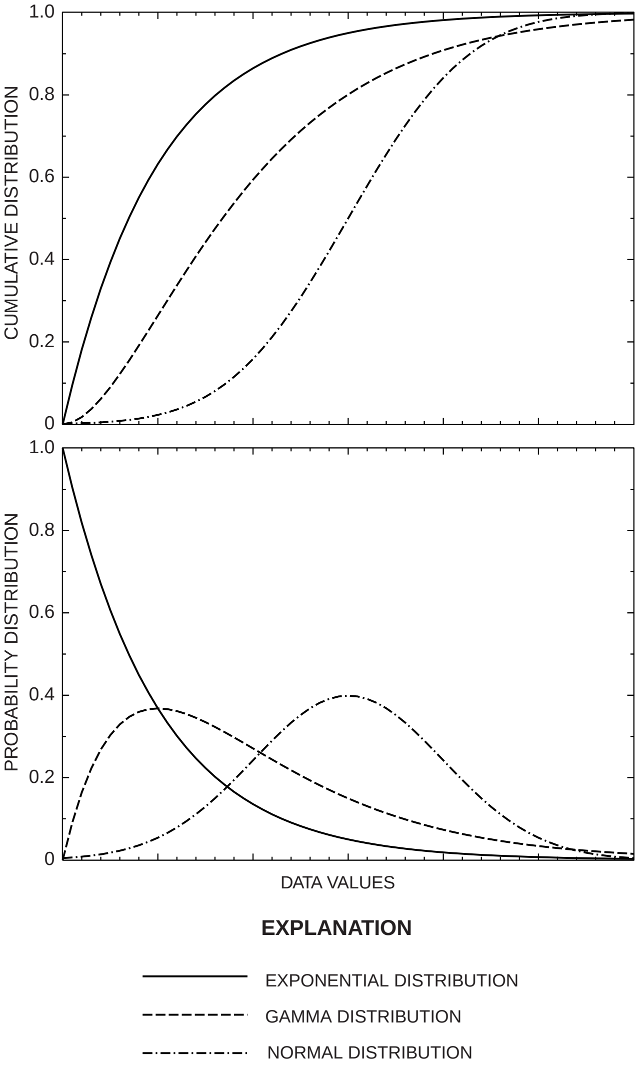

Figure 1. Example of the generalized shape of the probability and cumulative distributions of unitless, exponential, gamma, and normal populations.

Statistical measures of population location, spread, and skewness are summarized and defined in terms of the statistical basis and design assumptions that define each method in table 1. Helsel and Hirsch (1992) and Hirsch and others (1993) use these techniques to describe mathematical information for statistical analysis of water-resources data.

Table 1. Basic statistical techniques for parametric and nonparametric data analysis

[N, nonparametric; P, parametric]

Technique	Measure	Basis	Definition	Comments
Arithmetic mean (Average)	Location	P	The sum of all data divided by the sample size.	Can be affected by the presence of and (or) changes in the magnitude of one or more outlying observations. Representativeness depends upon the assumption that the data are normal (or at least unimodal and symmetric).
Median	Location	N	The middle value when data are ordered from lowest to highest.	When there is an even number of data points the median is the average of the two central observations. The median is also refered to as the 50th percentile.
Mode	Location	N	The data value that occurs with the highest frequency.	A data set may have more than one modal value.
Geometric mean	Location	P	The mean of the logarithms of data that is transformed back into original units.	Representativeness depends on the assumption that the data are normal (or at least unimodal and symmetric) in log space.
Trimmed (or weighted) mean	Location	P	The mean of censored data divided by the sample size after censoring.	Trimmed means (or weighted) means are computed once values judged as outliers have been eliminated (or weighted with a value of zero). It is typical to trim a given percentage from the bottom and top of the data in an attempt to apply systematic methods.
Range	Spread	N	The difference between the largest and smallest measurements in a set.	Although nonparametric, the range is affected by the presence of and (or) changes in the magnitude of one or more outlying observations.
Variance	Spread	P	The sum of the squared deviation of all measurements divided by one less than the total number of data points.	The variance can be unduly affected by the value of one or more outlying observations.
Standard deviation	Spread	P	The positive square root of the variance.	The standard deviation can be unduly affected by the value of one or more outlying observations.
Coefficient of variation (COV)	Spread	P	The ratio of the standard deviation over the mean.	A measure of spread normalized to the magnitude of the mean.
Interquartile range (IQR)	Spread	N	The difference between the 75th and 25th percentile values (by number of measurements) when data are ordered from lowest to highest.	Typically used as a measure of central spread because the 25th, 50th (median), and 75th percentiles split the data into four equal-sized quarters (by number of measurements). Other percentile ranges may be used as well.
Median absolute deviation (MAD)	Spread	N	The median of the absolute values of the difference between each data point and the data-set median.	The MAD, because it is the median of the population of absolute differences, is resistant to the effects of outliers.
Coefficient of skewness	Skewness	P	The third central moment divided by the variance cubed.	A positive value indicates that the population is right-skewed, and a negative value indicates left skew.
Quartile skew coefficient	Skewness	N	The difference between the range of each quartile (25th to 50th and the 50th to 75th) divided by the IQR	A positive value indicates that the population is right-skewed, and a negative value indicates left skew. Other percentile ranges may be used as well.

An understanding of the assumptions inherent in statistical measures, the methods used to calculated these measures, and their sensitivity to changes in location, spread, and skewness are important for interpretation of results of more complex statistical analysis. For example, in the calculation of a simple regression, the means and variances of each population of interest determine the slope and intercept of the resultant line equation (Hirsch and others, 1993). Furthermore, the simple measures of population characteristics covary with differing population structure. If a data distribution fits the normal distribution, then the mean, median, mode, and trimmed means should be equivalent if not equal (Helsel and Hirsch, 1992; Ott, 1993). If, however, a population is lognormal, then the geometric mean and median should be equivalent if not equal (Helsel and Hirsch, 1992). As unimodal populations become increasingly skewed to the left or right, the mean and trimmed mean will fall increasingly to the left or right of the median, respectively, and the mode will fall increasingly to the right or left of the median, respectively (Ott, 1993). Indices of spread also will have unique relations when data are normally distributed. For example, if data are normally distributed, then dividing the range by 4 should produce a value approximately equal to the standard deviation because about 95 percent of values should lie in the range of plus or minus 2 times the standard deviation (Ott, 1993).

For water-resources data, graphical analysis is an essential first step in the interpretation process. Use of graphical analysis can provide a visual summary of the data and can help reveal the most appropriate population structure and methods for analysis (Helsel and Hirsch, 1992). Graphical tools such as the scatterplot, the histogram, the boxplot, and the probability plot can be used to characterize data and find potential problems. For example, Driscoll and others (1990) present the event-mean suspended-solids concentrations and runoff volumes for the I-794 data set from Milwaukee, Wisconsin. A scatterplot (fig. 2), a boxplot (fig. 3), two histograms (fig. 4), and a probability plot (fig. 5) indicate that event mean suspended-solids concentrations are not normally distributed in linear space and that runoff volume does not control event mean suspended-solids concentrations at this site. Driscoll and others (1990) used probability plots to establish that the lognormal distribution was a sufficiently close approximation for highway-runoff-quality data to be included in their national highway-runoff-quality model. In this case, use of graphical analysis helped identify that a substantial number of below-detection-limit values were incorporated (without special notation) into some of the historical data sets and indicated that the below-detection-limit data did not fit the lognormal probability distribution and would affect population statistics (Driscoll and others, 1990). Helsel and Hirsch (1992) provide detailed descriptions about the use of graphs in exploratory data analysis (EDA). The National Institute of Science and Technology provides text and software for mathematical and graphical techniques to approach EDA (Croarkin and Tobias, 2000). A number of specification tests (methods to check that assumptions of the

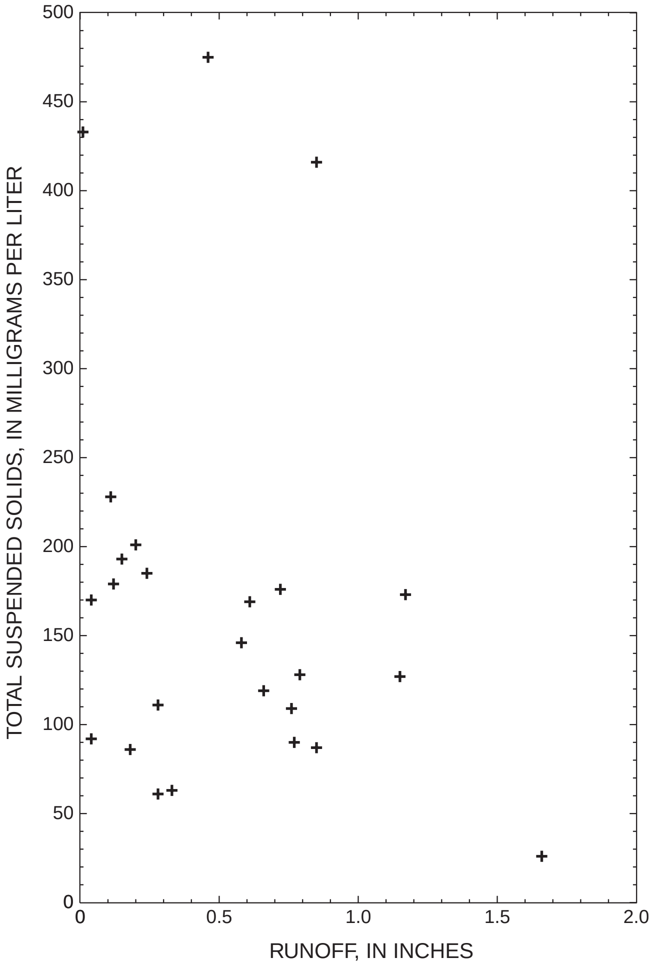

Figure 2. Example of a scatterplot of total runoff volume and event mean sediment concentrations from a highway-runoff monitoring study along highway I-794 in Milwaukee, Wisconsin (data from Driscoll and others, 1990).

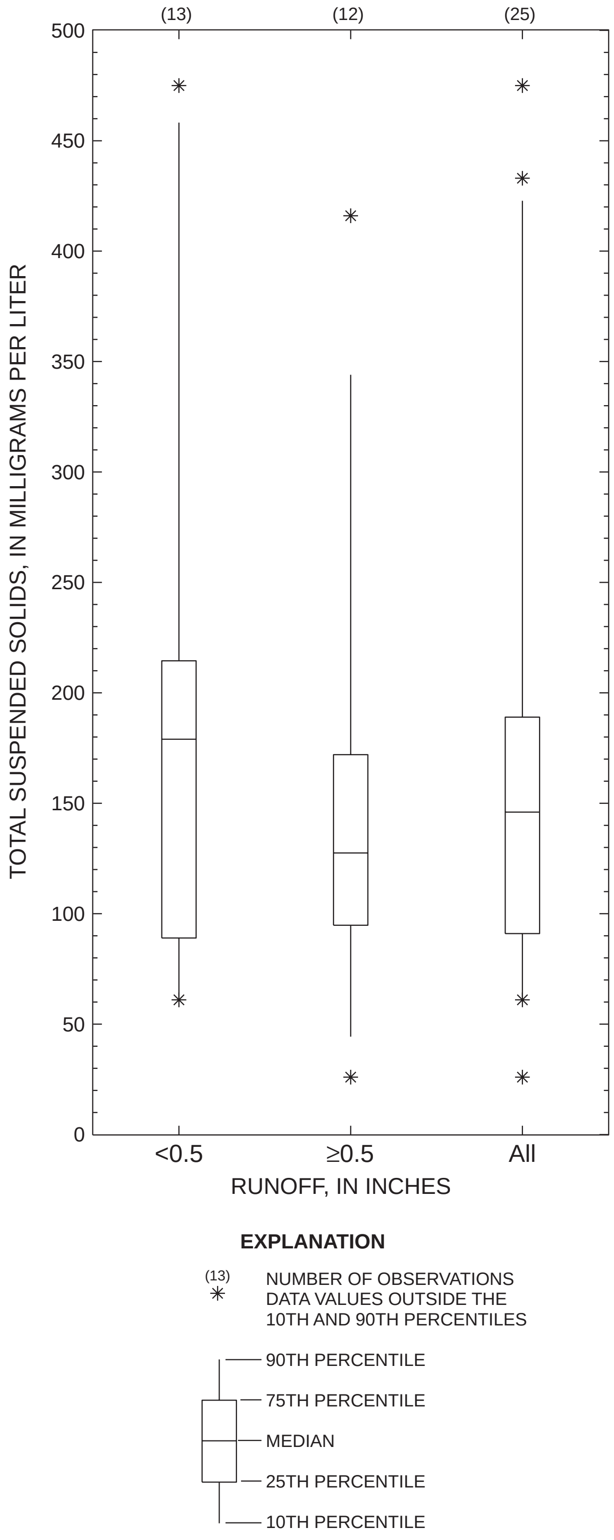

Figure 3. Example of a boxplot of total runoff volume and event mean sediment concentrations from a highway runoff monitoring study along highway I-794 in Milwaukee, Wisconsin (data from Driscoll and others, 1990).

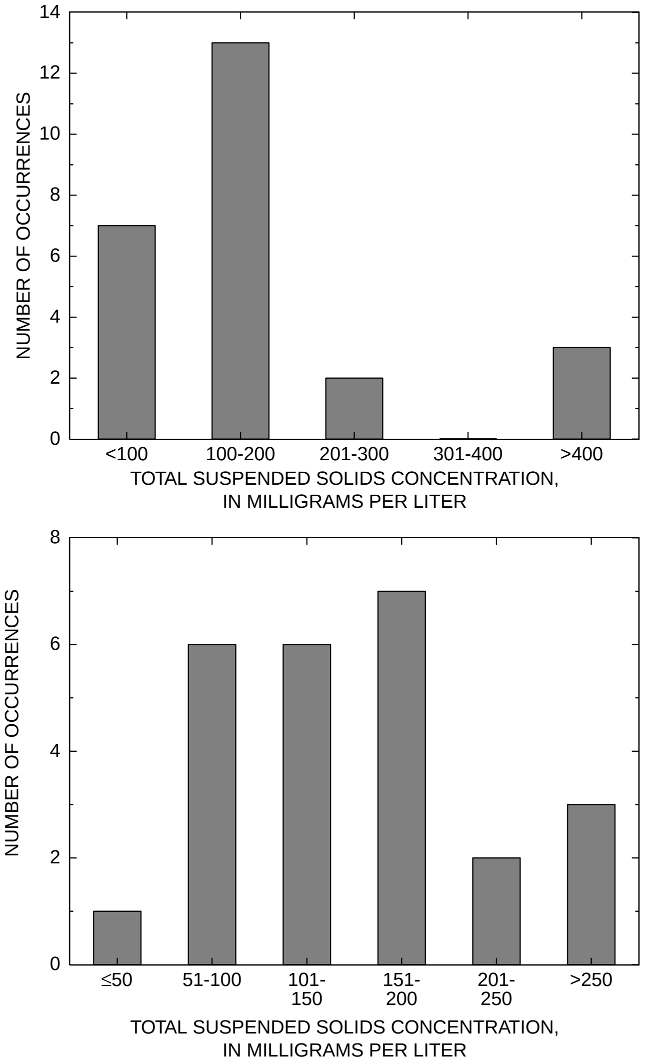

Figure 4. Example of two histograms (in groups of 50 and 100 milligrams per liter) of event mean sediment concentrations from a highway-runoff monitoring study along highway I-794 in Milwaukee, Wisconsin (data from Driscoll and others, 1990).

estimation method are valid) have been developed in recent years and may also be useful for examining runoff data before application of statistical-analysis techniques (Godfrey, 1988).

Within a discussion of population structure and statistical analysis, it should be noted the event mean concentration, or EMC, is not a statistical mean based on any implied probability distribution; rather the EMC is an operational definition used to characterize individual storm-event water quality. The EMC is defined as the total load of a stormwater-quality constituent divided by the total flow that occurs during the storm of

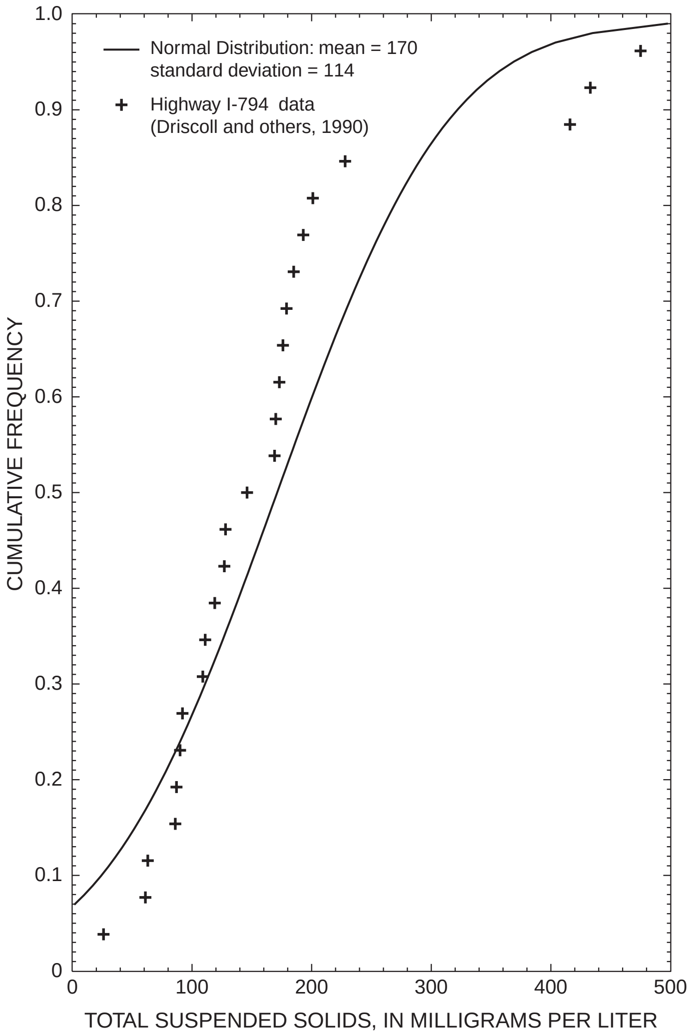

Figure 5. Example of a probability plot of event mean sediment concentrations from a highway-runoff monitoring study along highway I-794 in Milwaukee, Wisconsin (data from Driscoll and others, 1990).

interest (Huber, and others, 1979; Driscoll and others, 1990; Huber, 1993). In theory, an EMC would be obtained by collecting and homogenizing all runoff from a given event and then sending a representative subsample for analysis. In practice, the EMC representing each storm is determined from analysis of one flow-weighted composite sample or from a number of discrete samples that are flow-weighted mathematically (Driscoll and others, 1990; Huber, 1993). In either case, the EMC is not a parametric average, but a time- and flow-integrated estimate of stormwater quality.

Transformations

The general versatility, power, and mathematical elegance of parametric procedures designed for data that fit a normal distribution are usually advantageous in the application of statistical analysis. Mathematical transformations (used to redistribute population characteristics to approximate a normal distribution) are often employed to facilitate the use of normal (parametric) statistical-analysis techniques. Transformations are usually made for one or more of the following reasons: to simplify the model; to stabilize the variance; to normalize the data; or, for regression analysis, to define a transformed model with error distributions that fit the assumptions of the model. For regression models, transformation of the response variable is often desirable if the response variable is nonnegative and the range of observed values is one or more powers of 10. Log transformations are often useful for minimizing the standard error of the estimate (Driver and Tasker, 1990). If all the values are far from zero and the range of values is relatively small, however, transformation will have little effect. Nonparametric methods are generally invariant to measurement scale, so transformations do not alter data with respect to these methods (Helsel and Hirsch, 1992).

Transformations typically improve the symmetry of data by means of a mathematical function designed to alter the distance between observations on a line plot. The goal is to expand or contract the distance between the median and extreme values in the population of interest. Power functions (in which the transformed variable is raised to an exponent) and logarithms (natural and base 10) are usually used to transform data (Helsel and Hirsch, 1992). To reduce negative (left) skewness, powers of greater than 1 are used. To address positive (right) skewness powers less than 1 (the square or cubed roots) or logarithms are used.

Logarithmic transformations are especially useful for normalizing values that vary by orders of magnitude, and they dampen the effect of very large outliers on statistical estimators. In addition, the standard error of the transformed population can be expressed as a percent error when transformed back into original space. Logarithmic transformations, however, increase the relative weight of small data values and can magnify uncertainties in the true (or assigned) value of concentrations near detection limits (Stedinger and others, 1993).

Historically, populations of urban- and highway-runoff data can be characterized by the log-normal distribution (Athayde and others, 1983; Driscoll and others, 1990). EMCs of highway-runoff constituents indeed vary by more than one and as much as four orders of magnitude at and between sites. For example, Smith and Lord (1990) report that total suspended solids concentrations range from 4 to 1,156 mg/L (milligrams per liter), total organic carbon concentrations range from 5 to 290 mg/L, zinc concentrations range from about 0.01 to 3.4 mg/L, and chloride concentrations range from 5 to 13,300 mg/L. Driscoll and others (1990) used the natural logarithmic (ln) transform to normalize data used to develop their national highway-runoff-quality model. Athayde and others (1983) also indicated that urban-runoff data collected for the National Urban Runoff Program (NURP) generally could be characterized by use of the lognormal distribution. Thompson and others (1996) examined the effects of logarithmic and exponential transformation on the R^2 of various regression models designed to predict constituents from surrogate parameters; they found that these transformations demonstrate the best explanation (highest R^2) for the water-quality predictor variables but that untransformed models worked best for the constituents predicted by traffic volume. Driscoll and others (1990) graphically compared the probability distribution defined by the mean and standard deviation of the transformed population with individual points in the data set and tested the fit by means of the probability plot correlation coefficient (PPCC) test (Vogel, 1986). In that study, the lognormal distribution was found to be a satisfactory model for most runoff constituents at most runoff sites (Driscoll and others, 1990).

Athayde and others (1983) examined the mathematical properties of the lognormal distribution in terms of the ratio of the mean and percentile values in relation to the median as a function of typical coefficients of variation (COV; the ratio of the standard deviation to the mean). For a population with a COV of 1, the mean would be expected to be about 1.4 times the median, 90 percent of the data would fall in a range from about 0.25 to 3.9 times the median, and the interquartile range (about 50 percent of the data) would fall in a range from about 0.6 to 1.7 times the median (fig. 6). Historically, COVs of highway- and urban-runoff-quality constituent populations have ranged from about 1/4 to about 3, with typical values that are about 1 (Athayde and others 1983; Driscoll and others, 1990).

Mathematical properties of transformations may introduce error into the interpretation process if these properties are not properly addressed. When using logarithmic and exponential transformations, one must realize that statistical values such as the mean and standard deviation need to be calculated within the transformed data and then translated to original units (Helsel and Hirsch, 1992). Specifically, parametric statistics such as the mean and standard deviation cannot be transformed and subsequently used to estimate population characteristics in linear space. For example, the lognormal suspended-solids EMC population from the I-794 Milwaukee Wisconsin site described by Driscoll and others (1990) has a geometric mean of about 140 and a 95-percent confidence interval from about 40 to about 510. The standard deviation and COV (transformed from logarithmic space), however, are only about 1.9 and 1.3, respectively. It is apparent, therefore, that confidence-interval values must be calculated in log space and then transformed. Nonparametric statistics such as the median and quartiles, however, may be taken directly from the original or transformed data set because these statistics are associated with individual values in the data set.

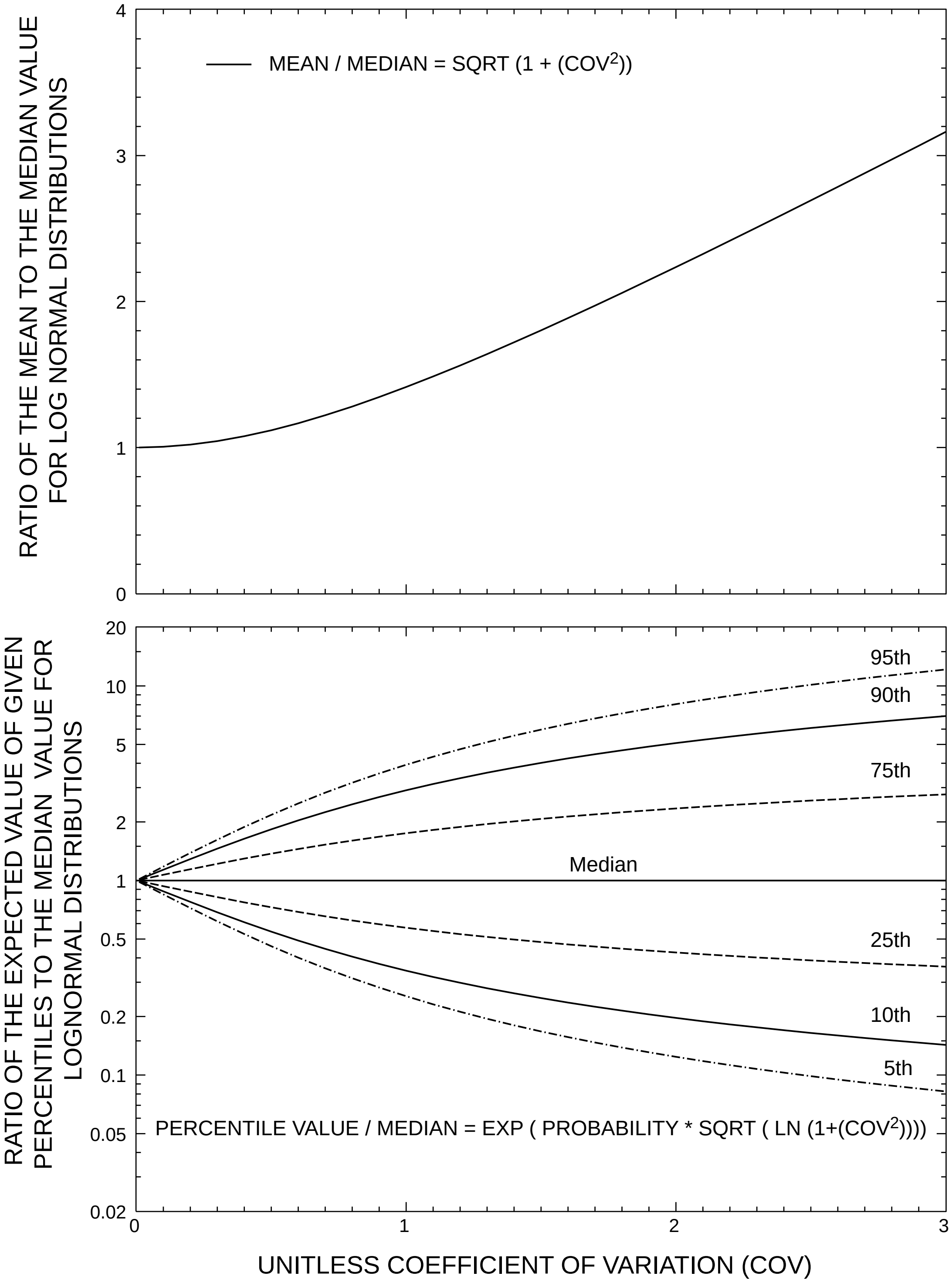

Figure 6. Properties of the lognormal (natural logarithm) distribution as a function of the population coefficient of variation (COV) modified from Athayde and others (1983).

Mathematical artifacts introduced by use of log transformation in regression analysis may also affect the predictive ability of resultant models. Transforming an unadjusted log-regression equation back into linear space (the original units, for example, milligrams per liter of suspended sediment) provides a median (the geometric mean) estimate, not a mean estimate of concentrations and (or) loads (Helsel and Hirsch, 1992). Ferguson (1986) summarized the problem in the context of estimating river loads from flow and concentration data and proposed a method for a bias correction factor (BCF). The BCF is a multiplicative term included in regression models that are formulated in logarithmic space and then transformed into original units; it is designed to prevent underestimation of concentrations or loads as an artifact of transformation. Further research indicates that several methods may be used to estimate a BCF and that a nonparametric method developed by Duan (1983) generally provides reasonable estimates for a BCF that is not affected by the structure of the data (Driver and Tasker, 1990; Helsel and Hirsch, 1992). Driver and Tasker (1990) used the Duan (1983) method to estimate BCF for storm-runoff loads, volumes, and selected constituent concentrations from NURP data and calculated BCFs that ranged from about 1.1 to 2.8 for their runoff models.

In the construction of regression models, the Box-Cox transformation (Box and Cox, 1964) can be used to stabilize variance and correct for nonnormality of a strictly positive response variable. John and Draper (1980) define a transformation that can be used when the response variable is not strictly positive. Aranda-Ordaz (1981) and Guerrero and Johnson (1982) define transformations that can be used when the response is binary (0 or 1) or a proportion between 0 and 1. For multiple regression models, a graphical device that can be helpful in deciding on a transformation for a predictor is a partial residual plot (Larsen and McCleary, 1972) in which the partial residuals (computed by taking the difference between the observed value and the components of the predicted value that exclude the variable of interest) are plotted against the predictor of interest. If the plot looks linear, no transformation is needed. If the plot shows some curvature, a transformation may be helpful. The practice of transformation optimization (finding the perfect root or power for transformation), however, is not encouraged because it is never known how well a sample represents the underlying population, and a generalized transformation that works reasonably well for all data of interest is better than multiple, slightly different transformations for each data set (Helsel and Hirsch, 1992). Alternatively, one may use other methods such as White's Specification Test, which is done by regressing squared residuals on the predictor variables and cross-products of the predictors. In this test, a significant regression implies that the specification is wrong or that heteroscedasticity of the residuals is related to the predictors (White, 1980).

REGRESSION ANALYSIS

Regression analysis is an accepted method for interpretation of water resources data and for prediction of current or future conditions at sites with characteristics that fit the input data model. The FHWA, State departments of transportation, and watershed managers need models to interpret data; predict runoff volumes, concentrations, and loads; and predict potential effects of runoff on receiving waters at sites for which data do not exist. In the following discussions, it is assumed that the purpose of the regional regression is for interpretation of data and for prediction of future responses, including possible extrapolation (that is, prediction outside the range of the sample data). If the regression model is not a reasonable representation of reality, then extrapolation could be erroneous. The purpose of the regression analysis will influence how predictors are selected for the regression model. Therefore, in selecting predictors for a possible regression model, one should choose variables that have a physical basis for explaining variations in the response, and the final regression coefficients should have a logical algebraic sign.

Historically, regression analysis was used for interpretation and prediction in several studies that represent the primary efforts for regional and (or) national characterization of highway runoff in the United States (table 2). To date, five studies (Kobriger and others, 1981; Chui and others, 1982; Kerri and others, 1985; Driscoll and others, 1990; Thompson and others, 1996) represent regional analysis of highway-runoff flow and quality based on data collected during the 1970's and early 1980's. Additionally, Young and others (1996) identified the urban-runoff regression equations developed by Driver and Tasker (1990)—identified as "the USGS method"—as applicable for estimating highway-runoff quantity and quality (table 2). The USGS method was developed from NURP data collected throughout the United States during the 1970's and early 1980s, but it does not include highway runoff as a specific land use. More recently, Irish and others (1996; 1998) interpreted data collected in the 1990's using regression analysis, but they were clear that these equations and related interpretations may be valid only in the local Austin, Texas, area. Typically, for all the models featured in table 2, runoff data from a substantial number of storms at a number of sites were compared to predict runoff coefficients, stormflow volume, constituent EMCs, storm loads, and (or) annual loads from a number of explanatory variables. These response variables are predicted from runoff constituents, hydrologic variables, highway-design features, land-use characteristics, and climate (table 2). Tasker and Driver (1988) used both ordinary and generalized least-squares regression methods. The highway studies featured in table 2, however, were limited to ordinary least-squares regression analysis.

The Analytical Process

Regression analysis is designed to provide an estimate of the average response of a system as it relates to variation in one or more known variables. Regression equations are often derived by use of computer programs that calculate the regression parameters and provide an estimate of the correlation coefficient (R^2— the proportion of the variability in the dependent variable explained by the predictor variable) without an investigation of the validity of the selected model. When this exercise yields a correlation coefficient that is close to 1, then it is often assumed that a good regression model has been selected. Many factors may produce high but invalid correlation coefficients. Regression analysis, therefore, should include visual analysis of scatterplots, examination of the regression equation, evaluation of the method design assumptions, and regression diagnostics (Helsel and Hirsch, 1992).

Examination of scatterplots is necessary to examine the relations between predictor and response variables and to assess response variability (Helsel and Hirsch, 1992). Scatterplots of interest include graphs of the response as a function of each predictor variable and graphs of the residuals as a function of predictor variables. For most regression methods, one must ensure that a linear relation exists between predictor and response variables. If relations are not linear, other, more linear predictors may be chosen; or as previously discussed, transformation methods may be used to increase the linearity of relations between variables. For some regression methods, one must determine whether the variability in the response variables is also a function of the magnitude of the predictor. Transformations are also used to reduce or eliminate problems of nonconstant variance. Partial residual plots (described in Appendix 1*A*) and the White Specification Test (White, 1980) are often useful in determining the appropriate transformation on the basis of the structure of residuals.

Often, it is also prudent to examine the effect of seasonality on highway- and urban-runoff data by use of scatterplots of each variable of interest and the regression residuals during the monitoring period. If seasonality exists, then explaining and quantifying this factor may increase the linearity in response to other predictors by removing seasonality from the response variable. Methods for quantifying seasonality are described in Appendix 1*B*.

Examination of the regression equation ensures that the model is logical, useful, and quantitative (Helsel and Hirsch, 1992). In a logical regression model, the coefficients will have a sign and magnitude that can be explained by a reasonable scientific hypothesis. When explanatory variables in a multiple regression equation covary, this multicollinearity will cause some predictors to have illogical values and (or) sign (Helsel and Hirsch, 1992). Methods for analysis of multicollinearity are described in Appendix 1*C*.

Regression statistics also provide information about the suitability of the model. Examination of the regression equation includes interpretation of the correlation coefficient to determine whether the resulting equation explains much of the variance in the data.

Table 2. Documented metadata for selected reports that document highway-runoff regression analysis

[**A**, area; **ADP**, antecedent dry period duration; **ADT**, average daily traffic; **Al**, aluminum; **AL**, annual loads; **AP**, annual precipitation; **ATC**, antecedent dry period traffic count; **As**, arsenic; **B**, boron; **BODx**, biochemical oxygen demand; **Cd**, cadmium; **Cl**, chloride; **COD**, chemical oxygen demand; **Cr**, chromium; **Cu**, copper; **D**, storm duration; **DQ**, discussed qualitatively; **DP**, dissolved phosphorus; **DS**, dissolved solids; **EMC**, event mean concentration; **Fe**, iron; **FR**, filterable residue (similar to TSS); **GLS**, generalized least squares regression; **Hg**, mercury; **HT**, highway type (indicating the degree of urbanization and (or) impervious area); **I**, storm intensity (flow divided by duration); **IA**, impervious area; **OG**, oil and grease; **OLS**, ordinary least squares regression; **LR**, TSS loading rate by climate; **LU**, land use; **MJT**, mean January temperature; **N**, total nitrogen; **Na**, sodium; **ND**, not documented; **NFR**, nonfilterable residue (dissolved solids); **NOx**, nitrate and (or) nitrite; **Ni**, nickel; **P**, precipitation volume; **PA**, pollution accumulation rate; **Pb**, lead; **PD**, population density; **PDUR**, preceding storm duration; **PI**, preceding storm intensity; **PQ**, preceding stormflow; **Q**, stormflow; **QD**, stormflow duration; **RC**, runoff coefficient; **SL**, storm loads; **SO4**, sulfate; **SS**, suspendid solids; **TDS**, total dissolved solids; **TKN**, total kjeldahl nitrogen; **TOC**, total organic carbon; **TP**, total phosphate; **TR**, total residue (similar to total solids); **TS**, total solids; **TSS**, total suspended solids; **TVS**, total volatile solids; **VDS**, vehicles during storm; **VSS**, volatile suspended solids; **Zn**, zinc; *, indicates that different equations were developed for different categories or a unified equation was developed with this variable as a nominal variable]

Reference	Year of data collection	Location/ environmental setting	Seasonality	Number of samples	Number of sites	Model	Output
Chui and others, 1982	1979–81	Washingon: eastern (semi-arid) and western (wet)	Winter sanding events considered	500	9	OLS	SL, AL
Driscoll and others, 1990	1976–84	National: 8 sites in Washington, 3 sites each in California and Wisconsin, 2 sites each in Florida, Minnesota, Pennsylvania, and 1 site each in Arkansas, Colorado, North Carolina, and Tennessee	Separated storms into snowmelt and nonsnowmelt events	Used site median EMCs from about 900 storms	24	OLS	Q, RC, EMC
Driver and Tasker, 1990	1977–83	30 urban areas nationwide in 3 regions designated by precipitation statistics	Developed equations for seasonal and annual loads	2,813	173	OLS GLS	Q,EMC, SL,AL
Irish and others, 1998	1993–95	Austin, Texas (semi-arid)	Date of storm and temperature were not significant	58	1	OLS	SL
Kerri and others, 1985	1975–81	California (arid to semi-arid)	ND	ND	3	OLS	SL
Kobriger and others, 1981	1976–77	National: 3 sites in Wisconsin (humid), and 1 site each in Pennsylvania (humid), Tennessee (humid), and Colorado (arid)	Deicing mentioned but not quantified	159	6	OLS	Q, QD, SL
Thompson and others, 1996	1976–83	Minnesota	Classified storms as rainfall, snowmelt, or mixed	416	4	OLS	Q, EMC

Table 2. Documented metadata for selected reports that document highway-runoff regression analysis—*Continued*

Reference	Response variables		Predictor variables						Uncertainty of estimates
	Runoff constituents	Hydrologic variables	Runoff constituents	Hydrologic variables	Highway characteristics	Land use	Climate	Other	
Chui and others, 1982	TSS			RC	VDS		LR*		Mean: ~200% Range: 0.3–1,650%
	COD, Cu, NOx, Pb, TKN, TP, TOC, VSS, Zn		TSS		ADT				ND
Driscoll and others, 1990		Q, RC		P				QD	Yes
		RC			Percent impervious				Yes
	BODx, Cd, Cl, COD, Cr, Cu, Fe, Hg, NOx, OG, Pb, TOC, TP, TKN, TS, TSS, VSS, Zn				ADT, HT*				
Driver and Tasker, 1990		Q		P		IA	R*, AP	A	Yes
	Cd, Cu, COD, DP, DS, N, Pb, SS, TKN, TP, Zn			P, D, I		A, IA, LU	R*, MJT		Yes
Irish and others, 1998	BODx, COD, Cu, Fe, NOx, OG, Pb, TP, TSS, VSS, Zn			ADP, D, I, PDUR, PI, PQ, Q	VDS, ATC				Yes
Kerri and others, 1985	COD, FR, Pb, TKN, Zn				VDS				Yes
	COD, NFR, Zn				TR				Yes
Kobriger and others, 1981		Q		ADP, P	HT*				DQ
		QD		D, ADP*	HT*				DQ
	PA				ADT				DQ
	TS			I	HT*				DQ
	BODx, Cd, Cl, Cr, Cu, COD, Fe, Hg, Pb, TKN, TOC, TP, TSS, TVS		TS		HT*				DQ
Thompson and others, 1996		Q		P					
	Al, As, BODx, Cd, Cl, COD, Cr, Cu, Fe, Hg, N, Na, Ni, NOx, Pb, SO4, TKN, TP, Zn		TDS, TOC, TSS, TVS		ADT				Examine potential leverage of outliers
	TDS, TOC, TSS, TVS			ADP, D, I, P, Q	ADT				ND

Table 2. Documented metadata for selected reports that document highway-runoff regression analysis—*Continued*

Reference	Comments
Chui and others, 1982	The regression equations provided adequate estimates of the central tendency of all storm loads, but were not accurate for predicting individual storm loads.
Driscoll and others, 1990	Regression analysis was used to examine factors that influence highway runoff characteristics. It was determined that there were not enough sites with consistent explanatory variables to quantitatively explore the effects of climate, atmospheric deposition, configuration, pavement (composition, quantity, or condition), design geometrics, right-of-way characteristics, drainage features, vehicle characteristics, maintenance practices, regulations, or surrounding land use characteristics.
Driver and Tasker, 1990	Flows and loads during individual storms, seasons and years were predicted for a number of constituents as a planning tool rather than for interpretation of cause and effect relations. Explanatory variables that would be readily available for planning purposes on a regional scale were used. Highways, as an individual land use, were not included in the analysis.
Irish and others, 1998	Regression analysis indicated that over 90 percent of the variation observed for most constituent loads may have been explained by in-storm-, antecedent dry period-, and preceding storm-variables. Date and time of storm, temperature, wind speed, and wind direction were not statistically significant predictors. Traffic mix, surrounding land use, curb height, guard-rail height, and maintenance activities could not be evaluated.
Kerri and others, 1985	ADP and ATC showed no statistical significance. B, Cd, NOx, OP, OG, TP, and TR cannot be estimated from explanatory variables
Kobriger and others, 1981	Sites were classified into 3 groups for regression: Type I—urban elevated bridge deck; Type II—curbed highways; and Type III—rural highways with flush shoulders. Equations were developed to estimate runoff volume, runoff duration, constituent accumulation during an ADP, pollution washoff, and constituent loadings (as a function of TS).
Thompson and others, 1996	Surrogate parameters were established to estimate most constituents. Also, models to predict surrogate parameters were developed. Additional data sets that were not used in the formulation of the model, were used to test and verify applicability of the models.

There is no general rule of thumb to determine a minimum acceptable correlation coefficient, but the risk of posing the wrong model must be considered in relation to the ability of the model to explain variance (Helsel and Hirsch, 1992). The *t*-ratio (the value of the estimate divided by the standard error of the estimate) also is a useful statistic. The *t*-ratio will usually indicate the significance of each coefficient so that the analyst can ensure that an apparent relation did not arise by chance when there is no real linear relationship. For OLS regression, *t*-ratio statistics that have an absolute value greater than 2 are generally considered to indicate a statistically significant non-zero relation between individual predictors and response variables (Helsel and Hirsch, 1992).

Regression diagnostics include methods designed to determine whether the equation posed as a model is dominated by a few outliers in the data set. An analyst can use regression diagnostic methods to find influential observations and study their effects. Examination of a scatterplot of the residuals will often identify the effect of outliers when there is only one predictor variable, but influential outliers are more difficult to recognize in plots from multiple regression analysis. Typical problems that affect the validity of regression models are curvature, outliers, and high-leverage points. Outliers, observations (or a subset of observations) that appear to be inconsistent with the remainder of that set of data, are fairly common in hydrologic data (Hirsch and others, 1993). Outliers should be checked for possible gross errors in measurement or mistakes in recording the observations, but rejecting them out of hand is not a prudent practice. Regression diagnostics are discussed further in Appendix 1*D*.

Linear Regression Methods

As previously discussed, water-resources data—and in particular, populations of urban- and highway-stormwater data—have statistical properties that require special treatment. Predictive modeling and interpretation of cause and effect relations of runoff quality and quantity may benefit from use of techniques applied in other water-resources studies. Some of the techniques and practical alternative methods for dealing with the realities of hydrologic data are discussed in the following sections. Applicable methods, classification of appropriate response and predictor variables, and general purpose and assumptions of each method are listed in table 3 with a reference to appendix that describe some mathematical details for each of the methods discussed. This table, which distinguishes among several statistical methods discussed herein on the basis of the type of data involved, can serve as a rough guide to help the researcher choose a method for study.

A method often used for predicting water quantity and quality is ordinary-least-squares (OLS) regression (Haith, 1976; Lystrom and others, 1978; Peters, 1984; Driver and Tasker, 1990; Irish and others, 1996; Jordan and others, 1997). The OLS model, however, requires several restrictive assumptions about the parameters and errors in the model, which are often not valid for hydrologic data. To fully implement OLS regression, one must demonstrate that the response variable (or the transformed values) is linearly related to predictors (or the transformed values), the data used to fit the model are representative of the population of interest, the variance of the residuals is constant, the residuals are independent, and the residuals are normally distributed (Helsel and Hirsch, 1992). Normally distributed errors are required, even with large samples, for the determination of prediction intervals - although certain empirical methods allow one to generate robust prediction intervals from OLS-determined residuals. Appendix 2*A* more fully describes the OLS regression model.

In some cases, transformations either may not adequately transform the error structure to fit the required distributional assumptions or may be undesirable because of the possible transformation artifacts (Helsel and Hirsch, 1992). Nonparametric regression provides a distribution-free alternative to OLS regression that does not require errors to be normally distributed. Nonparametric regression can refer to models with a prespecified functional form but with an unspecified error distribution or models with neither a prespecified functional form nor error distribution. Appendix 2*B* contains more details.

Stormwater data often include outliers, which may or may not be meaningful. Although it is often imprudent to remove outliers, they often exert a leverage that will limit the accuracy and precision of regression results for the bulk of data included in the regression model. Robust regression procedures deal with outliers by reducing their influence without necessarily rejecting them entirely from the analysis. In one sense, regression diagnostics and robust regression

Table 3. General guide to regression methods

Method	Response classification	Predictor classification	General purpose and assumptions	Appendix
Ordinary least-squares regression	Continuous	Usually continuous but nominal can be used in addition	Describes the relation between response and predictors. Errors are independent and identically distributed with no outliers. Normality of errors is required for hypothesis testing.	2A
Nonparametric regression	Continuous	Usually continuous but nominal can be used in addition	Describes the relation between response and predictors. Error distribution unspecified. Functional form may or may not be specified. Useful when errors are not approximately normally distributed.	2B
Robust regression	Continuous	Usually continuous but nominal can be used in addition	Describes the relation between response and predictors. Useful for detecting outliers and highly influential observations. Fits main portion of data, giving outliers little or no weight.	2C
Generalized least-squares regression	Continuous	Usually continuous but nominal can be used in addition	Describes the relation between response and predictors. Errors can be correlated and variances of errors may be different. Useful when observations of response variable are not independent or not measured with equal accuracy.	2D
Tobit regression	Part continuous, part nominal	Usually continuous but nominal can be used in addition	Describes the relation between response and predictors. Useful when response variable is censored below a detection limit.	2E
Logistic regression	Nominal	Usually continuous but nominal can be used in addition	Predicts probability of response being in one category or another.	2F
Contingency tables	Nominal	Nominal or ordinal groups	Describes the relation between nominal response and nominal or ordinal predictors.	2G
Ridge regression	Continuous	Usually continuous but nominal can be used in addition	Describes the relation between response and predictors. Useful when predictors exhibit high multicollinearity. Regression coefficients are biased.	2H
SPARROW	Continuous	Continuous	Nonlinear regression method to predict water quality for a stream reach based on spatially referenced predictors. The predictors are a function of the point and nonpoint sources and their location relative to the stream reach.	3A
Artificial neural networks	Continuous or nominal	Continuous or nominal	Flexible nonlinear nonparametric model for prediction. Any underlying model or functional relations may be impossible to extract. Data-in / predictions out black box.	3B

have the same goal of detecting outliers, but they approach the problem from different ends. Diagnostics use the classical fit of data to detect outliers and influential observations, whereas robust regression fits most of the data and detects outliers by their large residuals from the robust model. Robust regression techniques are discussed further in Appendix 2*C*. Some of the nonparametric methods discussed in Appendix 2*B* (Kendall-Theil and LOWESS smooth) also can be resistant to outliers (Helsel and Hirsch, 1992).

In analysis of stormwater quality, observations may not be independent in time and space. For example, Irish and others (1998) noted the effect of the volume, intensity, and duration of storm rainfall characteristics on the water quality measured during the next storm event. In using OLS regression, one assumes that observed values of the response variable are independent, resulting in independent residuals. In cases where this assumption is not approximately true, estimated generalized least-squares regression (GLS) can be used if the dependence of the residuals can be estimated from the data. For example, Tasker and Driver (1988) and Tasker and Raines (1995) show that when the observed response in a regional regression to estimate mean annual loads is obtained from at-site rainfall-load models, responses may have nonconstant errors and correlated errors. Appendix 2*D* describes one estimated GLS regression approach.

As previously mentioned, concentrations of water-quality constituents below one or more detection limits in water-resources data sets are not uncommon. These values are considered as censored values for statistical analysis. Concentrations reported as less than a detection limit censor the data at the limit of detection and relegate all values below the limit to the nominal scale. When only a few observations are in the censored range, either fabricating values at or below the censoring threshold or ignoring the values in the censored range has been done but generally, these practices are not acceptable. When the response variable is moderately censored (below 20 percent censoring), Hirsch and others,(1993) recommend the Kendall-Theil robust regression method (Appendix 2*C*) or Tobit regression (Appendix 2*E*). When the level of censoring exceeds about 20 percent, logistic regression (Appendix 2*F*) or contingency tables (Appendix 2*G*) are recommended (Hirsch and others,1993).

As discussed, multicollinearity will affect the results of regression analysis, causing some predictors to have a regression coefficient with large standard errors as an artifact of regression-equation optimization. Large standard error may result in coefficient estimates having the wrong sign or unreasonable values, and it generally results in coefficients being insignificant. When using OLS or GLS regression, one must often eliminate some potentially valuable and logical predictors from a regression model. A method for dealing with multicollinearity without predictor elimination is ridge regression (Hoerl and Kennard, 1970). A successful ridge regression analysis (Appendix 2*H*) produces slightly biased regressor coefficients with smaller variance. Thus, one may trade absence of bias for a stable set of regression coefficients in the presence of multicollinearity.

Nonlinear Regression Methods

In the previous section, the structure of the regression models was assumed to be linear in the predictor coefficients. In some areas of hydrology, the assumption of linearity may represent a distortion of the physical process being modeled. In such cases, a more theoretically based nonlinear model may be appropriate. In other cases, the analyst may wish to relax the linearity constraint for a more flexible model without knowledge of the form of the model.

Many regional regression studies relating water quality to basin attributes treat contamination sources as homogeneously distributed throughout the watershed in defining the predictors (basin attributes) (Lystrom, and others1978; Peters, 1984; Driver and Tasker, 1990). This treatment limits the usefulness of the models because it fails to account for spatial differences between sources and the water-quality monitoring points within a watershed. For example, consider the predictor "urban land use (in percent)" for two watersheds both with 10 percent urban land use. The urban land in one is in the lower part of the basin, immediately upstream from the water-quality monitoring point. In the other watershed, the urban land is in the upper part of the basin, far from the monitoring point. The simple predictor of percent urban land use fails to account for loss of contaminant mass during instream and overland transport, a factor that may be substantially different between the two watersheds.

Smith and others (1997) deal with this problem by developing water-quality predictors for point and nonpoint sources as functions of both river reach and land-surface attributes, as well as by considering rates of material transport. Predictor formulas describe the transport of contaminant mass from source to the end of a reach. This innovative technique, called SPARROW (SPAtially Referenced Regressions On Watershed attributes), has the potential for greatly improving the usefulness of regional regression models for water quality because it is able to include specific sources of contaminants and their location relative to the stream reach. It includes substantial refinements of a prototype method described in Smith and others (1993). Appendix 3*A* provides a more complete description of the method.

Artificial neural networks (ANN) include a class of flexible nonlinear models that can be used, like regression models, to predict responses from a set of predictors. Lingras and Adamo (1996) use ANN to estimate average and peak traffic volumes on the basis of road classes and short-duration counts. Zhang and Stanley (1997) and Thirumalaiah and Deo (1998) use ANN to forecast water quality and river stage on the basis of previous time steps, respectively. Artificial neural networks attempt to simulate the manner in which humans think (Hertz, Krogh, and Palmer, 1991). An ANN is composed of simple processing units, called neurons, arranged in layers. Each unit receives input from other units and converts the input to a single output, which it sends to other units. The conversion takes place in two stages: first, a net input is computed as a weighted sum of inputs, then an activity function transforms the net input into an output. The flexibility of ANN comes from one's being able to specify multiple layers of neurons with nonlinear activity functions and alternative methods for computing the net input. Observed values of predictors (inputs) and responses (targets) are used to "train" the ANN by iteratively adjusting the weights used by the neurons to produce output so that the sum of squared differences between output and target data is small.

ANN can over train (fit the observed data well, but not predict well for new data). For this reason, one should always set aside a portion of the observed data as a test data set that is not involved in any way with training the ANN, so that the ANN can be tested for predictive ability on new data. Just as in linear regression analysis, omission of important variables or inclusion of unimportant variables can be a problem. Artificial neural networks are data-in/predictions-out black boxes. Any underlying model or functional relation may be impossible to extract from the network. Appendix 3*B* gives more details about ANNs.

UNCERTAINTY, QUALITY ASSURANCE, AND QUALITY CONTROL

Uncertainty is an important part of any decision-making process. Success of a water-quality interpretive model depends on uncertain future meteorological, demographic, political, and technical conditions, all of which may affect future costs and benefits. In order to deal with problems of external uncertainty, the analyst first needs to know the severity of the statistical uncertainty inherent in the methods used to predict water quality. Statistical models need to be based on information that is meaningful, representative, complete, precise, accurate, and comparable to be deemed valid, up to date, and technically supportable. If sensitivity analyses reveal too much uncertainty in the predictions, new data and new methods may be needed, or safety factors based on prediction-interval estimates may be used. These criteria will also determine whether interpretations based on the model will be admissible as legal evidence.

Statisticians must deal with expected and unexpected uncertainties that can potentially affect interpretations made from a given data set. Expected uncertainty arises because many of the factors that affect the process are unknown or cannot be known with certainty. Statisticians can often address expected uncertainties, but these efforts are usually based on the assumption that data are collected and recorded correctly, thereby minimizing bias. Statistical measures of uncertainty are good for determining the level of noise (variability) in a data set, but they cannot detect bias without a population of "true" values with which to test the hypothesis. Unexpected uncertainty can arise from faulty computer programs, faulty application of inappropriate statistical techniques, and faulty data sets. Classical statistical measures cannot detect problems caused by unexpected uncertainty because statistical analysis is done under the assumption that the calculations are done correctly, that the correct model has been selected for the data, and that the data are representative of the environmental system under study. Thorough documentation, quality assurance, and quality control are necessary to ensure that bias is not introduced by the errors in the computer programs used for analysis, in the modeling effort, and in the data used for analysis. Prediction errors arise from natural heterogeneity, measurement errors, and structural differences between the real world and the methods used for predictions; therefore, quality-assurance and quality-control programs must be designed to quantify these sources of uncertainty. Quality assurance and quality control are necessary throughout any study-from design through data entry and interpretation (Jones, 1999). Increasingly legal and financial liability is driving modelers to implement rigorous quality-assurance and quality-control procedures at all stages of a modeling project (Van der Heijde, 1990).

Benchmarking of Analytical Tools

Results generated by the complex computer programs currently used for statistical analysis often are assumed to be correct because it is expected that the software companies have thoroughly tested their computer code under a number of different conditions (Landwehr and Tasker, 1999). If statistics that look reasonable but are, in fact, grossly incorrect are computed, this dangerous error is liable to remain undetected until applied to a real-world problem where the model noticeably fails. To prevent this situation, one can benchmark the statistical software to assess its reliability.

Benchmarking consists of applying a suite of statistical analyses to various standard data sets for which the values of the statistics are known with great precision and assessing whether the resulting values are in conformance. A discussion and review of how to do such assessments can be found in Sawizki (1994a) and McCullough (1998), who use the Statistical Reference Datasets (StRDs) recently published by the National Institute of Standards and Technology (1998). Wilkinson (1985) also proposed a collection of simple tests designed to uncover common flaws in statistical programs, including an example in which the variables are collinear and the difference in magnitude between variables was extreme but the magnitude of the observations for each variable was not unlike that found among common statistical problems.

Benchmarking studies to provide quality assurance and quality control to verify the operation of statistical software packages sound esoteric; but when such studies have been done, real problems have been discovered. For example, Sawitzki (1994b) reported on a joint effort by members of two working groups ("Computational Statistics of the International Biometrical Society" and "Statistical Analysis Systems" of the "GMDS," Deutsche Gesellschaft für Medizinische Informatik, Biometrie und Epidemiologie) to apply the Wilkinson tests to nine data-analysis systems, including some running on multiple platforms. The group demonstrated performance difficulties with each system, even between platform implementations of the same package. More recently Landwehr and Tasker (1999) completed a benchmark study of commercial statistical-software packages commonly used by the USGS and found that several analysis packages had more difficulty in providing computationally precise and (or) correct values than did others, and some were cumbersome to use in obtaining specific statistics. Therefore, quality assurance and quality control for interpretive efforts that make use of existing software should include documentation of the commercial software (including version and platform), documentation of benchmarking efforts, as well as scientific and technical reviews of the software selection and benchmarking efforts.

In general, the analyst should be aware of the specific question or questions to be answered by the analysis, as well as how a specific package is computing the answer it provides (Landwehr and Tasker, 1999). Quality assurance and quality control (using tools such as the ANASTY data set) is especially important when an analyst will write computer code to implement a statistical process, even if the code is written within the interface of an existing commercial software product that has been previously benchmarked. Quality assurance and quality control for code development includes verification of the structure and coding, model validation, record keeping, software documentation, and scientific and technical reviews.

Uncertainty in Modeling Efforts

Results generated by statistical models may appear to be more certain, more precise, and more authoritative than they really are because design assumptions and results (even realistic ones) can be stated with illusive precision and seeming accuracy. Models—like scientific theories—cannot truly be validated; they can only be invalidated when an exception or error is revealed by new data or circumstances. For example, Driscoll and others (1990) note that regression models have been criticized as poor predictors when applied beyond the original data set used to create the model. The analyst, therefore, has the responsibility to document efforts to

- examine the representativeness of data used to construct statistical models,
- assess uncertainties in models, and
- evaluate the potential predictive ability for sites not included in the construction of the model.

The application and documentation of these steps in the modeling procedure are essential for the transfer of a model to potential model users. Quality assurance and quality control in the processes used for data reduction, evaluation, and interpretation is as important as quality assurance and quality control for field and laboratory data-collection efforts (Brown and others, 1991). Quality assurance and quality control for modeling efforts include the procedural and operational framework used by an organization to ensure the technical and scientific adequacy of the tasks, and documentation thereof, to ensure that the results are fully reproducible and defensible. Modeling efforts are being used in the regulatory and legal domain, and the needs for model documentation describing the inherent uncertainty in predictions are increasing (Haan and others, 1990). Jones (1999) describes the quality assurance and technical review necessary to prepare data in a computerized database used to develop water-quality models.

A number of statistical tools are available to assess the uncertainties inherent in models during model development. The fit of a regression model is usually measured by means of the correlation coefficient, but a better measure of the model's predictive ability at unmonitored stations is the variance of prediction (Gilroy and others, 1990). This statistic is computed by estimating the mean or median variance of prediction for individual stations while using every station in the regression model. This computation is made on the basis of the assumption that the available stations are representative of the entire population of potential sites to be modeled. Irish and others (1996) note, however, that the standard error of forecasts (a measure of the spread of data points not used to formulate a regression model indicating the predictive ability of the coefficients in the model for data not included in the monitored population) is always larger than the standard error of the regression for modeled data. When the errors in a regression model are approximately normally distributed, standard errors of prediction and prediction intervals, which serve as a measure of the uncertainty in the predictions, can be computed on the basis of normal theory. Appendix 4*A* provides some details. When using methods that do not involve the assumption that errors are normal or do not specify an error distribution, the analyst may be able to use the bootstrap method (Efron and Tibshirani, 1986). The bootstrap is a simple, straightforward method for computing biases, standard deviations, and confidence intervals for almost any nonparametric problem (Efron, 1982). More details are given in Appendix 4*B*. Documenting a sensitivity analysis—determining how input parameters control model output—is necessary to indicate how uncertainty in input values will affect uncertainty in computed results. For example, Driver and Tasker (1990) provided uncertainty estimates for regional regression equations, which had coefficients of variation ranging from 0.2 to 0.65, standard errors of the estimate ranging from 79 to 145 percent, and average prediction errors ranging from -67 to 203 percent.

When developing a regional hydrologic regression for a fairly large geographic area, such as a state or several states, it is sometimes advantageous to subdivide the region into several homogeneous subregions in which the basic regression assumptions are more likely to be true than for the whole region. These regions may or may not have geographic boundaries. Geographic regions may be based on some general topographical or geological feature of the region or may be based on ecoregions (Omernik, 1995). Regions can also be defined on the basis of values of the predictors. Multivariate techniques of cluster and discriminant analysis have been used to define regions based on basin attributes (Tasker, 1982). Another possible method for dividing a large area into regions is referred to as the "region of influence method" (Tasker and Slade, 1994; Tasker and others, 1996) a method in which a unique regression equation is estimated for each site where a prediction is to be made. The regression equation is based only on data observed for sites with basin characteristics similar to the site where a prediction is to be made. Appendix 5 gives more details. Many of the characteristics that may be useful for regionalizing highway-runoff-quality data (including maps of climatic characteristics, receiving-water characteristics, and ecoregions) are provided as

Geographic Information System (GIS) coverages for the conterminous United States by Smieszek and Granato (2000). The process of regionalization needs to be documented, as well as the regional characteristics, so that practitioners using the model may properly assign any given site within an appropriate region.

Proper model application as part of a planning, design, or assessment effort also requires substantial documentation. Information that should be documented includes the statistical characteristics and design assumptions supporting application of the model. Model-performance parameters as defined in the previous paragraph should be documented in terms of an uncertainty estimate in the predictions made by the model when the model is applied. For example, Young and others (1996) apply the USGS method (Driver and Tasker, 1990) to estimate an annual load of suspended solids in a hypothetical case study to illustrate use of the method. Young and others (1996) use watershed area (one significant figure), land use by percent (one significant figure), and the impervious area (two significant figures) to compute a storm load of 397.4 kg (four significant figures). This storm load is then multiplied by the average number of storms (two significant figures) to compute an annual load of 55,636 kg (five significant figures). Young and others (1996) provide the exact results of these hypothetical computations to illustrate the method unambiguously. In reality, however, model results are expected to have an uncertainty that is compounded by use of input values with only one significant figure. Computed storm-loads for this hypothetical site are about 400 kg per storm with a 90-percent confidence interval from about 40 to about 2,000 kg per storm. Computed annual-loads for this hypothetical site are about 60,000 kg per year with a 90-percent confidence interval that ranges from about 6,000 kg to about 300,000 kg per year. Reporting the final rounded numbers and estimates of the uncertainty of the calculations provides the information necessary to evaluate the potential results from decisions based on these loads.

The analyst should also document an assessment of model suitability for site-specific conditions when models are applied. Regional regression models are designed to provide estimates for the average site with characteristics identified by predictor variables. One must determine that values of predictor variables for the site to be modeled fall within the range of data used to construct the models, and that no other distinguishing site characteristics would differentiate the site from the modeled population.

Uncertainty in Input Data

The quality of interpretations depends directly upon the quality and representativeness of available data. Statistical models are empirical models generally requiring large amounts of water-quality, land-use, and highway-related data for parameter estimation. Although a large amount of such data exist in this country, the data are in disparate databases and the comparability of this data is in doubt. De Vries and Klavers (1994) demonstrate that the reliability of modeling estimates is determined primarily by the quality of the monitoring strategy and that computation methods can be much less important than the data incorporated into a given model. Models, at best, are only as good as the uncertainty in the input data (Montgomery and Sanders, 1985). Furthermore, there is no guarantee that water-quality data, no matter how carefully collected, will be transferable to other areas and other circumstances (Sonnen, 1983). Harrop (1983) observed that the high uncertainty in highway-runoff-quality models was caused by "too much analysis being applied to too little data." Driscoll and others (1990) also noted that even with 31 sites and hundreds of monitored storms, many of the investigated factors—which theoretically should affect the quality of runoff—could not be quantitatively defined. Specifically, individual relations could not be defined because each site had a number of explanatory variables (including climate, traffic, highway-design features, and surrounding land-use characteristics) that were not held constant from site to site. In other words, it is difficult to develop meaningful models to quantitatively predict water quality from physical or chemical differences between sites unless the "noise" introduced by the sampling effort is much smaller than the "signal" produced by differences between sites. The NURP program recognized that interpretation of data would be questionable unless field programs at different sites provided consistent and sound data. Therefore, quality assurance and quality control elements were adopted as integral parts of each site/project workplan, including elements to address potential problems with the program, field monitoring and sample collection, laboratory analysis, data management, and data analysis (Athayde and others, 1983).

Standard least-squares methods for regression analysis depend on the assumption that the predictors are known without error. Nevertheless, measurement errors are inherent in most predictors used in regression analysis of environmental data. Measurement errors in the predictors may or may not be a problem in regional regression analyses. The effect of measurement errors can be ignored with little consequence when the variance of the measurement error is very small in relation to the variance in the predictor itself. Weisburg (1980), Seber (1977), and Davies and Hutton (1975) provide more details and methods for determining whether measurement errors are small enough to ignore.

When significant measurement errors are in the data set of predictors, use of the regional least-squares regression for prediction requires the predictions to be made by means of the same methods for measuring the predictors as used in the determination of the regression coefficients. For example, consider a regional regression in which the response, S, is annual sulfate load and predictors P and T are mean annual precipitation and average annual daily traffic flow, respectively. In addition, P is estimated from a contour map of the region based on 1930–60 data, and T is estimated from a regression on a sample short period count (Erhunmwunsee, 1991). As long as predictions from the regional model are made by use of the same methods for determining P and T, the measurement errors in P and T present little problem. However, if predictions from the regional model are made using P estimated from a nearby rainfall record or from a different contour map or if T is measured by means of some method different from the short-period-count regression, then the predictions from the regional least-squares model will not be appropriate. It follows that a problem exists when the observed predictors used to estimate the regression coefficients are measured using significantly different methods with different measurement errors. For example, consider a regional regression study covering several states in which each state uses a different method to estimate average annual daily traffic flow, T. In these cases, it is necessary to adjust the regression model for errors in the predictors.

The problem with using standard least-squares methods when measurement errors are in the predictors is that the observed predictors will correlate with the regression errors, resulting in biased estimates of the regression coefficients. An alternative to standard least squares that deals with the measurement errors in predictors is the method of instrumental variables (Johnston, 1972). Instrumental variables are variables that correlate with the predictor that contains measurement error and but do not correlate with the regression errors. Johnston (1972) and Fuller (1987) describe several methods for instrumental-variable estimation; SAS/ETS procedure MODEL (SAS Institute, 1988) can be used for the computations.

Therefore, to assemble a regional or national data set, one must ensure that the methods used to define both the predictor (explanatory) and response variables are the same, or that the different methods will produce results that are neither substantially or statistically different. Furthermore, it has been demonstrated that differences in monitoring objectives of past studies will affect the suitability of available data for inclusion in a regional or national synthesis because the monitoring objectives of those studies will affect the representativeness of the selected sites when compared to the total population of existing sites (Norris and others, 1990). This is because local studies are often designed for addressing local problems rather than for national characterization (Norris and others, 1990).

Availability of reliable runoff-quality data in an electronic format is necessary to facilitate future use of and interpretation of data collected. Driscoll and others (1990) and Thompson and others (1996) indicate the substantial difficulties involved in the collection, examination, quality assurance, quality control, and (when necessary) data entry of historical runoff data in their efforts toward local, regional, and national interpretation of highway-runoff data. In comparison, Driver and Tasker (1990) were able to assemble a much larger National Urban Runoff Program (NURP) data from the USGS and the USEPA with less effort because these programs were supported by quality-assurance and quality-control measures, and the data were stored in readily available national water-quality databases. The Transportation Research Board (1997) determined that development of consistent electronic data structures is a primary research need to standardize results of hydraulics, hydrology, and water-quality research efforts for future use. Data-collection activities, therefore, need be conducted within a framework of an established quality-assurance and quality-control program to demonstrate that data collected meet data-quality objectives and will be meaningful for interpretation of the characteristics of runoff quantity and quality (Jones, 1999). Many of the criteria for basic information, acceptable uncertainty, and quality-assurance and quality-control documentation described by Granato and others (1998) are essential for reliable interpretation of local, regional, and national runoff-quality data sets.

SUMMARY

Engineers, planners, economists, regulators, and other decision makers concerned with stormwater runoff need viable methods for the interpretation of local, regional, and national highway-runoff and urban-stormwater data. Stormwater-quality models have, historically, been used to characterize stormwater flow and quality, predict pollutant runoff loads, assess impacts on receiving waters, and determine the effectiveness of various best management practices to mitigate possible impairment of designated beneficial uses of receiving waters. Valid, current and technically defensible stormwater-runoff models are needed to interpret data collected by field studies; support existing highway and urban runoff planning processes, meet National Pollutant Discharge Elimination System requirements, and provide methods for calculation of Total Maximum Daily Loads, in a systematic and economical manner.

Historically, conceptual models, simulation models, empirical models, and statistical models of varying levels of detail, complexity, and uncertainty have been used to meet various data-quality objectives in the decision-making processes necessary for the planning, design, construction, and maintenance of highways and for other land-use applications. Water-quality simulation models attempt a detailed description of the physical processes and mechanisms by means of model parameters with a direct physical definition, and require as input a considerable degree of detail in the description of the physical system. In simulation models, parameter estimation is not as data dependent as in statistical regional water-quality-assessment models. On the other hand, empirical and statistical regional water-quality-assessment models provide a more general picture of water quality or changes in water quality over a region. Statistical regional water-quality models may also be used to estimate nonpoint-source loadings as inputs for more detailed water-quality simulation models. All these modeling techniques share one common aspect—the predictive ability of almost any model will be poor without suitable site-specific data for calibration.

An understanding of the classification of variables, the unique characteristics of water-resources data, and the concept of population structure and analysis is necessary to properly interpret the results of individual studies and to combine these results to form meaningful interpretations as part of a regional or national synthesis of stormwater quality data. Classification of variables being used to analyze data may determine which statistical methods are appropriate for data analysis. An understanding of the fundamental characteristics of water-resources data is necessary to evaluate the applicability of various statistical techniques, to interpret the results of these techniques, and to use tools and techniques which account for the unique nature of water-resources data sets. Understanding the methods and measures used to determine the population structure and analyze population characteristics also is necessary to form valid, current, and technically defensible stormwater runoff models.

Regression analysis is an accepted method for interpretation of water-resources data and for prediction of current or future conditions at sites that fit the input data model. The Federal Highway Administration, state departments of transportation, have successfully implemented regression models to interpret data; identify quantitative relations between constituents; predict runoff volumes, concentrations, loads; and predict potential effects of runoff on receiving waters at sites for which data do not exist. Regression analysis is designed to provide an estimate of the average response of a system as it relates to variation in one or more known variables. To date, highway- and urban-runoff studies have generally been limited to ordinary least squares (OLS) and generalized least squares (GLS) regression techniques. There are, however, a number of linear and nonlinear regression methods that may be appropriate for interpretation of local, regional, and national highway-runoff and urban-stormwater data when the classification of variables and the structure of the data violate the design assumptions of the OLS and (or) GLS methods.

Uncertainty is an important part of any decision-making process. Success of a water-quality interpretive model depends on uncertain future meteorological, demographic, political, and technical conditions, all of which may affect future costs and benefits. In order to deal with uncertainty problems, the analyst needs to know the severity of the statistical uncertainty of the methods used to predict water quality. Statistical models need to be based on information that is meaningful, representative, complete, precise, accurate, and comparable to be deemed valid, up to date, and technically supportable. If sensitivity analyses reveal too much uncertainty in the predictions, new data and new methods may be needed, or safety factors based on prediction interval estimates may be used. To ensure that decision makers can assess uncertainty in the analytical tools, the modeling methods, and the underlying data set, the analyst must document and communicate each of these components in an accessible format within project publications. These criteria will also determine whether interpretations based on the models developed will be admissible in a regulatory framework and (or) as legal evidence when necessary.

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APPENDIX 1. Regression Tools

A. Partial Residual Plots

Transformation of predictors in a multiple regression model can be used to achieve linearity and simplify the model. A graphical device that can be helpful in deciding on a transformation for a predictor is a partial residual plot (Larsen and McCleary, 1972). A partial residual plot for a predictor, x_t, in a multiple linear regression is a plot of the partial residual, computed by subtracting the effects of all variables except x_t, against x_t. For example, suppose we have the three-variable model

$$y_i = b_0 + b_1 x_{1,i} + b_2 x_{2,i} + b_3 x_{3,i} + e_i \quad (i=1, n), \tag{1}$$

and we wish a partial residual plot for variable x_3. The partial residual, $(y_i - b_0 - b_1 x_{1,i} - b_2 x_{2,i})$, is plotted against x_3. If the plot appears to be linear, then no transformation is needed. If the plot shows some curvature, then a transformation may be helpful. This plot is sometimes called a component-plus-residual plot because the partial residual, $(y_i - b_0 - b_1 x_{1,i} - b_2 x_{2,i})$, is equal to $b_3 x_{3i} + e_i$, which is easier to compute.

B. Seasonality

Data may exhibit seasonal patterns. One method for dealing with seasonal patterns is to develop different regressions for the different seasons. Barbe and Francis (1995) use this method for coliform concentrations in a river in Louisiana. Driscoll and others (1990) classified snowmelt storms separately from rainfall-runoff events, but they did not develop seasonality as a quantitative variable in their highway-runoff-quality models. Effects of seasonality sometimes can be reduced by dealing with deviations from seasonal means or by use of periodic functions. When a simple periodic function such as a cosine function is used to describe the cyclic variation, the model is

$$y_i = \beta_o + \beta_1 \cos\left(\frac{2\pi t_i}{\tau}\right) + \beta_2 \sin\left(\frac{2\pi t_i}{\tau}\right) + \varepsilon_i \ , \tag{2}$$

in which t_i is a time unit and τ is the cycle length in the same time units. Cycle lengths may be known (such as annual cycles, diurnal cycles, or tidal cycles) or may be estimated from the data. Tasker and Burns (1974) use a periodic function with estimated cycle lengths to model stream temperatures in New England. Other variables also may be included in the model. For example, Cohn and others (1992) use a periodic function to remove seasonality from a model to estimate nutrient loading in Chesapeake Bay.

C. Collinearity

Correlation among the predictors in a regression results in near redundancies among the predictors, and inferences based on the model can be misleading or erroneous. Multicollinearity is the problem of linear dependencies between predictors. Multicollinearity in a regression can cause prediction problems when predictions are extrapolated beyond the sample space of the predictors. When the sample X-space is 3 or more dimensions, it is especially difficult to recognize a collinearity problem.

One diagnostic for detecting possible collinearity problems is the variance inflation factor (*VIF*). It is computed as

$$VIF_j = \frac{1}{1 - R_j^2} \ , \tag{3}$$

where R_j is the coefficient of determination from the regression of X_j on the other explanatory variables. A guideline for serious multicollinearity problems is $VIF > 10$. Belsley and others (1980) and Belsley (1991) describe other useful methods for detecting multicollinearity. Treatment of the multicollinearity problem depends somewhat on the source of the multicollinearity. Sources may be related to the sampling design, constraints on the model, and model specification.

It is sometimes possible to deal with multicollinearity created by the sampling design by collecting new data to fill in sparse areas on the predictor space. For example, consider a regression of sulfate load with two predictors, drainage area (A) and percent of basin urbanized (U). If in designing the monitoring network, sites with large A tended to have small U and sites with large U tended to have small A, a negative correlation in A and U would result. This could be fixed by adding new sites in the network with small A and small U and sites with large A and large U.

Multicollinearity problems created by constraints on the model or model specification can sometimes be dealt with by redefining the predictors. For example, consider two regressors, drainage area (A) and stream length (L). Suppose further that in this region all basins with a large A also have a large L and basins with small A have small L, so that A and L are constrained by the population to have a positive correlation. It may be possible to create a new dimensionless shape variable, $Sh=L^2/A$, which is not correlated with A or L, which can be substituted for either A or L.

It is also possible to deal with multicollinearity by means of predictor elimination. For example, if predictors x_1, x_2, and x_3 exhibit strong multicollinearity, eliminating one of the predictors may reduce the problem greatly. Predictor elimination, however, may not be an attractive alternative if the analyst wishes to extract information regarding the roles of individual predictors.

D. Regression Diagnostics

Regression diagnostics are used to identify possible outliers. An analyst can use regression diagnostic methods to find influential observations and study their effects. Regression diagnostics aid in the systematic location of data points that are unusual or are highly influential in estimating regression parameters and standard errors. Diagnostics help to avoid misinterpretation of the regression model. Cook and Weisberg (1982; 1984) and Belsley and others (1980) give comprehensive treatments of regression diagnostics. Partial regression leverage plots are an important part of regression diagnostics. Two commonly used diagnostics, leverage and Cook's D are briefly discussed below.

Observations that are far from the center of the X-variable space are considered high leverage points because of their great potential to influence the regression results. The leverage of a point is defined as

$$h_{ii} = x_i(X'X)^{-1}x'_i \,. \tag{4}$$

The limits on h_{ii} are $(1/n)<h_{ii}<1$ and

$$\sum_{i=1}^{n} h_{ii} = p' \,.$$

Therefore the average $h_{ii}=\frac{p'}{n}$, and a suggested value to identify a point with high leverage, is $h_{ii}=2\frac{p'}{n}$. Leverage plays an important role in the calculation of influence statistics and standardized residuals.

Cook's D is a measure of the shift in the vector of predicted values of y when the ith observation is not used. It shows the influence of the observation on the regression estimates. Computationally, it is obtained as follows

$$D_i = \frac{r^2{}_i}{p'}\left(\frac{h_{ii}}{1-h_{ii}}\right). \tag{5}$$

A suggested cutoff value to flag influential data points is $D_i>4/n$.

APPENDIX 2. Linear Regression Methods

A. Linear Ordinary Least-Squares Regression

The linear model for relating a response variable, *Y*, to *p* predictors is

$$Y_i = \beta_0 + \beta_1 X_{i,1} + \beta_2 X_{i,2} + \ldots + \beta_p X_{i,p} + \varepsilon_i . \qquad (6)$$

Subscript *i* denotes an observation at site *i*. There are p predictors and $p' = (p+1)$ parameters to be estimated. Let *n* denote the number of observations or sites.

Denote the following matrices:

Y, a (n x 1) column vector of observed response,
X, a (n x p′) matrix of a column of ones followed by *p* columns of predictors,
β, is a (p' x 1) vector of parameters to be estimated, and
ε, is a (n x 1) column vector of random errors.

The linear model can be written in matrix notation as

$$\boldsymbol{Y} = \boldsymbol{X}\beta + \varepsilon , \qquad (7)$$

in which

$$\boldsymbol{Y} = \begin{bmatrix} y_1 \\ y_2 \\ \ldots \\ y_n \end{bmatrix} \qquad \boldsymbol{X} = \begin{bmatrix} 1 & x_{11} & x_{21} & \ldots & x_{k1} \\ 1 & x_{12} & x_{22} & \ldots & x_{k2} \\ \ldots & \ldots & \ldots & \ldots & \ldots \\ 1 & x_{1n} & x_{2n} & \ldots & x_{kn} \end{bmatrix} \qquad \beta = \begin{bmatrix} \beta_0 \\ \beta_1 \\ \ldots \\ \beta_k \end{bmatrix} \qquad \varepsilon = \begin{bmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \ldots \\ \varepsilon_n \end{bmatrix}$$

The usual assumptions about random vector of errors, ε, is that all the elements, ε_i, have a common variance, $\sigma^{2,}$, and are statistically independent. These assumptions can be written in shorthand as

$$\varepsilon \sim N(\mathbf{0}, \boldsymbol{I}\sigma^2). \qquad (8)$$

If the model is correct (another assumption), then

$$\boldsymbol{Y} \sim N(\boldsymbol{X}\beta, \boldsymbol{I}\sigma^2) . \qquad (9)$$

The regression coefficients, β, are best estimated as

$$\mathrm{b} = (\boldsymbol{X'X})^{-1}(\boldsymbol{X'Y}) . \qquad (10)$$

The predicted mean of the response variable at site k with basin characteristics $\boldsymbol{x}_k = (1, x_{k,1}, x_{k,2}, \ldots, x_{k,p})$ is

$$\hat{y}_k = \boldsymbol{x}_k \boldsymbol{b} . \qquad (11)$$

The variance of the prediction is $\mathrm{Var}(\hat{y}_k) = \sigma^2[1 + \boldsymbol{x}_k(\boldsymbol{X'X})^{-1}\boldsymbol{x}'_k]$.

B. Nonparametric Regression

The Kendall-Theil method (Helsel and Hirsch, 1992) is a nonparametric method for fitting a prespecified linear equation of the form:

$$Y=B_0+B_1X. \tag{12}$$

For each pair of points (x_i,y_i) and (x_j,y_j), such that $i<j$, a slope, $S_{ij}=\frac{(y_i-y_j)}{(x_i-x_j)}$, is computed and B_1 is set equal to the median of the computed slopes. Let $Y_{.5}$ and $X_{.5}$ denote the median of X and Y, respectively. The intercept, $B_0 = Y_{.5} - B_1X_{.5}$. Conover (1980) provides a method for estimating a confidence interval for B_1. Instead of using the median of the pairwise slopes, median (S_{ij}), one can use a weighted median of the slopes with weights proportional to the distance between the pairs of points. Birkes and Dodge (1993, p. 114) show that the nonparametric weighted median estimator is the value of B_1 that minimizes the sum

$$\sum_{i=1}^{n}\left(rank(y_i-B_1x_i)-\frac{(n-1)}{2}\right)(y_i-B_1x_i) \quad . \tag{13}$$

Equation 12 may be generalized to more than one predictor for a multiple regression problem. Nonparametric estimates of B_1, B_2, $\dots$, B_p are found by minimizing the sum

$$\sum_{i=1}^{n}\left(rank(y_i-(B_1x_{1i}+B_2x_{2i}+\dots))-\frac{(n-1)}{2}\right)(y_i-(B_1x_{1i}+B_2x_{2i}+\dots)) \quad . \tag{14}$$

An estimate of B_0 is obtained as the median of $y_i-(B_1x_{1i}+B_2x_{2i}+\dots)$. Birkes and Dodge (1993, p. 123) provide iterative procedures to find the values of B_1, B_2, $\dots$, B_p.

Regression smooths are nonparametric local averaging methods that require no prespecified model functional form. Three major smoothing methods for problems with one predictor are kernel smoothing, *k*-nearest neighbor (*k-NN*) smoothing, and splines (Härdle, 1990). Kernel smoothing uses local observations within a bandwidth to compute a weighted average defined by the kernel. The *k* nearest neighbors are used to estimate the local weighted average in *k-NN* smoothing. Splines are piecewise polynomials of order *k* that are smoothly joined. A cubic spline (k=3) is usually good enough for most problems. Average smooths tend to follow outlying points and are not particularly robust against outliers. However, one may choose median smooths (Helsel and Hirsch, 1992, p. 286) or LOWESS (Cleveland, 1979; Helsel and Hirsch, 1992, p. 288) when outliers are perceived to be a problem. LOWESS is an iterative procedure that progressively downweights outliers in computing the local weights.

The regression smooths described above are for problems with one predictor. Extending the local averaging smooths to problems with multiple predictors raises the problem of sparse data in local neighborhoods. Breiman and others (1984) proposed regression trees as a type of nonparametric, multiple-predictor smooth. Regression trees define a piecewise constant regression surface based upon neighborhoods defined by hyper-rectangles with sides parallel to coordinate axes. Friedman and Stuetzle (1981) describe projection pursuit regression, an extension of regression trees, that uses smoothing methods on linear combinations of predictors to form the regression surface. Research is needed to determine whether regression trees and projection pursuit regression would be useful in regional water-quality-assessment models.

C. Robust Regression

Robust regression methods are insensitive to the effects of outliers in the data; they are useful for detecting outliers by accentuating observations with large residuals from the robust model. Observations that are downweighted in the robust regression model require close examination for the reasons for downweighting. The parameter-estimation problem in regression analysis may be thought of as finding the estimates of β to minimize the sum of some function, ρ,

$$\sum_{i=1}^{n} \rho(z)\,, \tag{15}$$

where $z = \frac{y_i - \boldsymbol{x}_i\beta}{s}$ and s is a scale factor.

Robust procedures dampen the effects of outliers and tend to leave large residuals for the outliers. In robust estimation, the scale factor, *s*, must be a robust estimator of scale and not the standard deviation of the residuals because the standard deviation is relatively sensitive to outliers. Montgomery and Peck (1982, p. 367) suggest the robust estimator

$$s = \frac{median\left|e_i - median(e_i)\right|}{0.6745}\,, \tag{16}$$

where $e_i = y_i\text{-}x_i\beta$.

The least-squares estimator, corresponding to $\rho(z)=z^2$, is sensitive to outliers because it gives relatively greater weight to large residuals. On the other hand, the least-absolute-deviation estimator, corresponding to $\rho(z)=|z|$, is resistant to outliers but may give too much weight to small residuals. Huber (1973) proposed a compromise estimator that is robust yet relatively efficient if data are normal. It weights small residuals as a least-squares estimator and large residuals as an absolute-deviation estimator. The ρ function for Huber's estimator is

$$\rho(z) = \begin{cases} \frac{1}{2}z^2 & |z| \le t \\ \left(|z|t - \frac{1}{2}t^2\right) & |z| > t \end{cases}\,, \tag{17}$$

in which *t* is a constant usually equal to 2 or less. Parameter estimates are made from iteratively reweighted least squares. For example, the weights, *w*, in a weighted least-squares regression minimizing the sum of the function in equation 18 are

$$w(z) = \begin{cases} 1.0 & |z| \le t \\ \frac{t}{|z|} & |z| > t \end{cases}\,. \tag{18}$$

Because the weights depend on β, iteration is required until little or no changes in the parameters are observed. The parameters for many other functions that have been suggested for the robust regression problem (Andrews and others, 1972) also can be found by iteratively reweighted least squares.

One problem with robust methods is an apparent lack of agreement among authorities on how best to construct confidence intervals for the parameter estimates. Therefore, one important aspect of statistical regional models is not clearly determined for robust regression models.

D. Generalized Least-Squares Regression

In generalized least-squares (GLS) regression, β is estimated by

$$\tilde{\beta} = (\boldsymbol{X}^T \Lambda^{-1} \boldsymbol{X})^{-1} \boldsymbol{X}^T \Lambda^{-1} \boldsymbol{Y} \ , \tag{19}$$

in which Λ is the covariance matrix of errors, $E(\boldsymbol{ee}^T)$. The operational difficulty with this procedure is that Λ must be estimated from the data at hand. Stedinger and Tasker (1985) show that Λ can be estimated as

$$\Lambda = \gamma^2 \boldsymbol{I} + \Sigma \ , \tag{20}$$

where γ^2 is an estimate of the variance of the error inherent in the model, Σ is an estimate of the sampling-error covariance matrix, and I is an (n by n) identity matrix. The model error variance, γ^2, and regression coefficients, b, are found by iteratively searching for the best non-negative solution to the equation

$$E\{(\boldsymbol{Y} - \boldsymbol{X}\beta)^T \Lambda^{-1} (\boldsymbol{Y} - \boldsymbol{X}\beta)\} = n - k - 1 \qquad . \tag{21}$$

A leverage statistic in GLS analogous to leverage in OLS regression is the ith diagonal element of

$$H^* = \boldsymbol{X}(\boldsymbol{X}' \Lambda^{-1} \boldsymbol{X})^{-1} \boldsymbol{X}' \Lambda^{-1} \ . \tag{22}$$

The sum of the diagonal elements of H^* is equal to the number of parameters in the model; and a high-leverage site would be one in which the associated diagonal element is greater than 2 times the number of parameters divided by the number of observations, as a rule of thumb. A GLS version of Cook's D is

$$D'_i = \frac{e_i^2 h'_{ii}}{p'(\gamma_i - h'_{ii})^2} \ , \tag{23}$$

where h'_{ii} are diagonal elements of

$$\mathrm{H}' = \boldsymbol{X}(\boldsymbol{X}' \Lambda^{-1} \boldsymbol{X})^{-1} \boldsymbol{X}' \ . \tag{24}$$

D'_i is large if it exceeds about ($4/n$) (Tasker and Stedinger, 1989).

E. Tobit Regression

The tobit regression model for censored observations is

$$y_i = \left(\; (\boldsymbol{x}_i\beta + e_i) \qquad \text{if } (y_i > \text{threshold}) \right. \quad . \tag{25}$$

If one arbitrarily assumes a value for those observations of y below the threshold and uses the entire sample, or if one uses the subsample of observations when y_i is greater than the censoring threshold, the least-squares estimator of β is biased and inconsistent. However, maximum-likelihood estimators for the tobit regression model are available and are described in Judge and others (1985). Liu and others (1996) use tobit regression to predict atrazine concentrations in the Midwest. Hirsch and others (1993, p. 17.51) caution that application of tobit regression in hydrology is experimental.

F. Logistic Regression

In logistic regression, the response is a nominal variable with two possible values (0 and 1). For example, y_i is equal to zero if the value is below the detection limit and equal to 1 if the value is above the detection limit. In the model, the estimated response, $E(y|\boldsymbol{x})$, is a proportion between 0 and 1 and is given by

$$E(y|\boldsymbol{x}) = \frac{\exp(\boldsymbol{x}\beta)}{1 + \exp(\boldsymbol{x}\beta)} \quad . \tag{26}$$

The unknown β's are estimated by maximizing the log likelihood function

$$L(\beta) = \sum_{i=1}^{n} \{ y_i ln[\boldsymbol{x}\beta] + (1 - y_i) ln[1 - \boldsymbol{x}\beta] \} \text{ (Cox and Snell, 1989).} \tag{27}$$

Teso and others (1996) use logistic regression to estimate probability of pesticide contamination. Major statistics packages, such as SAS, Minitab, and STATIT, include procedures for fitting the logistic regression function. Thus, the logistic regression procedure can be used to estimate the likelihood of a water-quality characteristic being above or below a censoring threshold at a site with basin characteristics equal to $\boldsymbol{x}$.

G. Contingency Tables

Contingency tables can be used when both response and predictors are nominal or censored. The number of observed values falling within a cell defined by the response and predictor groups divided by the total observations in a group provides an estimate of the probability of a value being in the cell. If, for example, the effect of traffic volume on the potential for detection of cadmium was of interest, then this effect could be examined by use of the following (hypothetical) contingency table:

Contingency-table example using hypothetical cadmium concentrations in urban and rural highway runoff

[ADT, Average Daily Traffic; Cd, cadmium concentrations in micrograms per liter; VPD, vehicles per day]

Cadmium concentrations	Rural highway (ADT ≤30,000 VPD)	Urban highway (ADT>30,000 VPD)	Total
Cd < detection limit	A=15	B=8	A+B=23
Cd ≥detection limit	C=5	D=20	C+D=25
Total:	A+C=20	B+D=28	

In this hypothetical example, the probability of cadmium being greater than or equal to the detection limit is 5/20 = 0.25 for rural highways and 20/28 = 0.71 for urban highways. Helsel and Hirsch (1992) and other texts provide details for statistical analysis using contingency tables.

H. Ridge Regression

The ridge estimator of regression coefficients, β, is

$$\hat{\beta}_R = (\boldsymbol{Z}'\boldsymbol{Z} + \kappa\boldsymbol{I})^{-1}\boldsymbol{Z}'\boldsymbol{y}^{o} \quad , \tag{28}$$

in which constant κ is a biasing parameter to be determined, and Z and y^o are standardized versions of X and y, respectively. The choice of κ is the subject of several studies. Myers (1986) and Montgomery and Peck (1982) describe several methods for choosing κ.

Computations can be made by augmenting the standardized data and using ordinary least-squares methods as follows:

$$\boldsymbol{Z}_a = \begin{bmatrix} \boldsymbol{Z} \\ \sqrt{\kappa}\boldsymbol{I} \end{bmatrix} \qquad \boldsymbol{y}_a = \begin{bmatrix} \boldsymbol{y}^o \\ \boldsymbol{0} \end{bmatrix} \quad , \tag{29}$$

where $\sqrt{\kappa}\boldsymbol{I}$ is a *p* by *p* diagonal matrix with diagonal elements equal to the square root of κ and **0** is a *p* by 1 vector of zeros (Montgomery and Peck, 1982). The estimate $\hat{\beta}_R$ is then computed as

$$\hat{\beta}_R = (\boldsymbol{Z}_a{}'\boldsymbol{Z}_a)^{-1}\boldsymbol{Z}_a{}'\boldsymbol{y}_a \quad . \tag{30}$$

The use of ridge regression requires thoughtful study of the data and careful analysis, but it can be an effective method for dealing with multicollinearity problems.

APPENDIX 3. Nonlinear Regression Methods

A. SPARROW

In the SPARROW (SPAtially Referenced Regression On Watershed attributes) model (Smith and others, 1997), the stream network in a region is divided into many stream reaches and the instream load, L_i, of a constituent in a stream reach indexed by *i* is equal to the sum of contributions to the load from all upstream sources, $S_{n,i}$, so that

$$L_i = \sum_{n=1}^{N} S_{n,i} \ , \tag{31}$$

where *N* is the number of sources. Let *J*(*i*) represent the set of all stream reaches upstream from reach *i* and including reach *i* but downstream from all monitoring stations upstream from reach *i*. Let *K*(*i*) represent the set of all monitoring sites directly upstream from reach *i*. The source terms are determined by

$$S_{n,i} = \beta_n \sum_{j \in J(i)} X_{n,i,j} + \sum_{k \in K(i)} X_{n,i,k} \ , \tag{32}$$

in which β_n is a coefficient for source n and $\sum_{j \in J(i)} X_{n,i,j}$ is the predictor for source *n* and reach *i* associated with the upstream reaches *J(i)* or monitoring sites *K(i)*. The values for $X_{n,i,j}$ are given by

$$X_{n,i,j} = s_{n,j} \exp(-\alpha_1 Z_{1,j} - \alpha_2 Z_{2,j} \ldots - \delta_1 T_{1,i,j} - \delta_2 T_{2,i,j} \ldots) \ , \tag{33}$$

where $s_{n,j}$ is a measure of the contaminant mass from source n that is present in reach *j* or at monitoring site *k*, the α's are delivery coefficients associated with land-surface characteristics $Z_{i,j}$, and the δ's are decay coefficients associated with flowpath characteristics $T_{n,i,j}$. For point sources or monitoring sites, the α's are set equal to zero. For example, $s_{n,j}$ might be the mass of chlorides placed on the roads within the drainage of reach *j* or measured at monitoring site *k*; the $Z_{1,j}$ might be average soil permeability for the drainage area of reach *j*; and $T_{1,i,j}$ might be the stream length between reach *i* and reach *j*. The predictors are spatially referenced because the contribution from all reaches above a given reach is tied to the reach by the flowpath characteristic, $T_{i,j}$.

The parameters (β's, α's, and δ's) of this nonlinear regression technique are determined by means of SAS/ETS procedure MODEL (SAS Institute, 1988). Smith and others (1997) determine the standard errors of the parameters using bootstrap methods (Efron, 1982).

B. Artificial Neural Networks

An artificial neural network, or ANN (Hertz and others, 1991), is composed of simple processing units, called neurons, arranged in layers. Each unit receives input from other units and converts the input to a single output, which it sends to other units. The conversion takes place in two stages: first, a net input is computed as a weighted sum of inputs, then an activation function transforms the net input into an output. The flexibility of ANN comes from the analyst's being able to specify multiple layers of neurons with nonlinear activation functions and alternative methods for computing the net input. A multilayer perceptron (MLP) with three nodes in the input layer, three nodes in the hidden layer, and one output node is shown in figure *A*. The hidden layer is so named because it has no direct connection to the outside world.

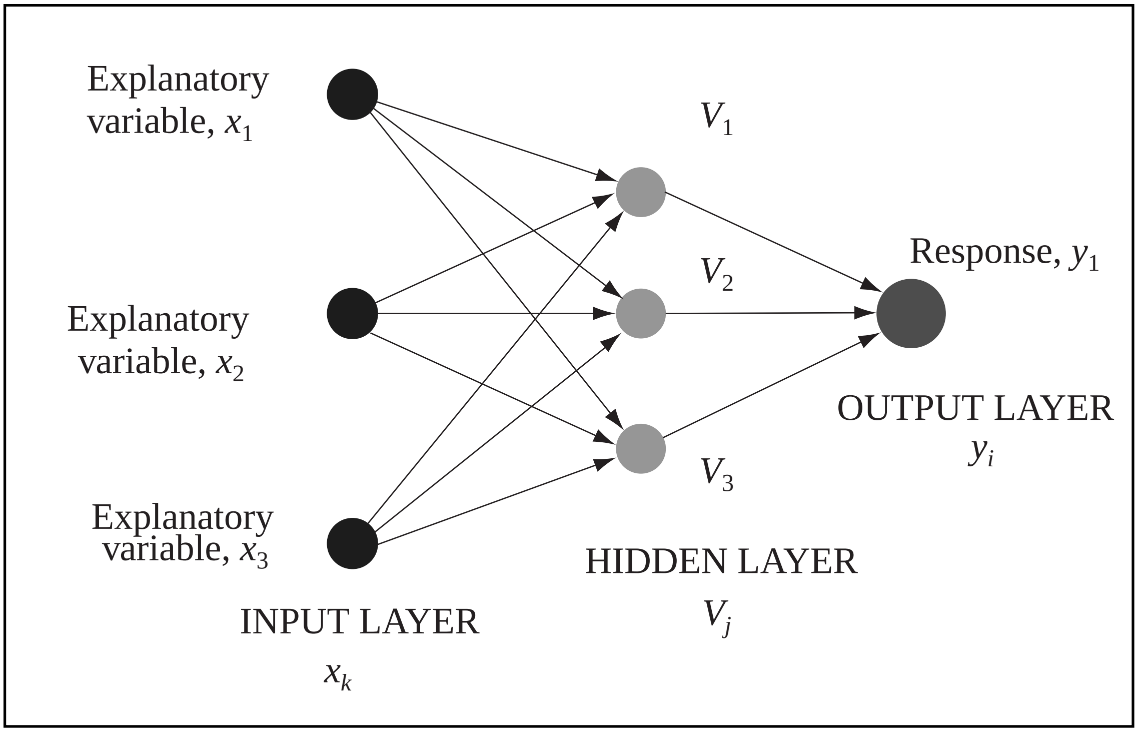

Figure A. Multilayer perceptron illustrating the function of an artificial neural network (ANN).

Each explanatory variable has one input node in the model. Denote the kth input variable as x_k and the number of hidden nodes as n_h. The net input to the jth hidden node is

$$a_j + \sum_{k=1}^{n_h} b_{jk} x_k \ , \tag{34}$$

where a_j and b_{jk} are intercept and weights from input k to hidden node j. The activation function, $g(u)$, for the hidden nodes is usually a smooth nonlinear function with a single-valued first derivative, such as the sigmoid function, $g(u)=\frac{1}{1+e^{-u}}$, or the hyperbolic tangent function, $g(u)=\tanh(u)$. For example, the estimated response, y_1, for the MLP in figure A with three input nodes, three hidden nodes with a hyperbolic tangent activation function, and one output node is

$$y_1 = c_1 + \sum_{j=1}^{3} d_{1,j} \tanh\left(a_j + \sum_{k=1}^{3} b_{jk} x_k \right), \tag{35}$$

where c_1 and $d_{1,j}$ are intercept and weights from hidden node j to output 1. The activation function for the output node in this example is the linear function, $g(u)=u$.

Observed values of predictors (inputs) and responses (targets) are used to train the ANN by iteratively adjusting the weights used by the neurons to produce output so that the sum of squared differences between output and target data is small. The method used is called back-propagation with a conjugate gradient training algorithm (Hertz and others 1991). Neural Connection 2.0 (SPSS, Inc., 1997) software was used for the calculations. Alternatively, one could estimate the intercepts and weights in equation 35 using nonlinear regression methods (Sarle, 1994). ANN can overtrain (fit the observed data well, but not predict well for new data). For this reason, a portion of the observed data is used as a validation data set that is not used in training the ANN. Artificial neural networks are data-in/predictions-out black boxes. Any underlying hydrologic model or hydrologically significant functional relation may be impossible to extract from the network.

APPENDIX 4. Uncertainty Analysis

A. Uncertainty—Normally Distributed Errors

The predicted response at unmonitored site k with basin characteristics $x_0 = (1, x_{0,1}, x_{0,2}, .., x_{0,\mathrm{p}})$ is

$$\hat{y}_0 = \boldsymbol{x}_0 \boldsymbol{b} \ . \tag{36}$$

The standard error of the prediction in OLS regression is

$$S(\hat{y}_0) = \sigma \sqrt{1 + \boldsymbol{x}_0 (\boldsymbol{X}'\boldsymbol{X})^{-1} \boldsymbol{x}'_0} \ . \tag{37}$$

In GLS regression the standard error of prediction is:

$$S(\hat{y}_0) = \sqrt{\hat{\gamma}^2 + \boldsymbol{x}_0 \boldsymbol{X}' \hat{\Lambda}^{-1} \boldsymbol{X}^{-1} \boldsymbol{x}'_0} \ . \tag{38}$$

A 100(1-α) prediction interval would be

$$\hat{y}_0 - T \le y_0 \le \hat{y}_0 + T \ , \tag{39}$$

where

$$T = t_{\frac{\alpha}{2},\,(n-p')} S(\hat{y}_0) \ , \tag{40}$$

and where $t_{a/2,\, n\text{-}p'}$ is the critical value from a t-distribution for n-p' degrees of freedom. The use of the t-statistic requires the errors to be approximately normally distributed. If a log transformation had been made so that $y_0 = \log_{10}(q_0)$, then the prediction interval would be

$$10^{\hat{y}_0 - T} \le q_0 \le 10^{\hat{y}_0 + T} \ . \tag{41}$$

When a log transformation has been made and the standard error in log units follows a normal distribution, the standard error may be expressed in percent of the predicted value in the original untransformed units. Denote σ as the standard error in log (base 10) units, S_{org} as the standard error in original units, and $E(q|x_k)$ as the predicted value of q, in original units, given x_k, and $x_k = (1, x_{k,1}, x_{k,2}, ..., x_{k,p})$ is a vector of basin characteristics at site k. The standard error in percent, S_{percent}, is given by

$$S_{percent} = 100 \frac{S_{org}}{E(q|x_k)} = 100\sqrt{(e^{5.302\sigma^2} - 1)} \qquad \text{(Aitcheson and Brown, 1957).} \tag{42}$$

Sometimes it is said in OLS that two-thirds of the points lie within one standard error of estimate of the regression function. This is true for the log unit standard error of estimate, σ, but it generally is not correct for S_{percent}, because the errors in log space are symmetrically distributed under the assumption of normality of the log errors, but the errors in original units are skewed. One can, however, calculate a +percent and -percent errors with the following formulas:

$$S_{plus} = 100(10^{\sigma} - 1) \quad \text{and} \tag{43}$$

$$S_{minus} = 100(10^{-\sigma} - 1) \ . \tag{44}$$

The three formulas (42, 43, and 44) above apply not only to the standard error of estimate for an OLS regression but also to the standard error of the model, $\hat{\gamma}$, in GLS regression, and standard error of a prediction in both OLS and GLS.

B. Uncertainty—Non-Normally Distributed Errors

Consider the general regression model

$$y_i = g(\boldsymbol{x}_i, \beta) + \varepsilon_i \qquad \mathrm{i} = 1, 2, 3, ..., \mathrm{n} \ , \tag{45}$$

where $g(\boldsymbol{x}_i, \beta)$ is a function of known form, x_i is a vector of known predictors, and β is a vector of unknown coefficients. The ε_i are independent errors drawn from an unspecified distribution, *F*, centered at zero, that may not be normally distributed. Having observed y_i for *i*=1, 2,..., *n*, β is estimated by minimizing the sum of some function, ρ, of the errors

$$\hat{\beta} : \min \sum_{i=1}^{n} \rho(y_i - g(\boldsymbol{x}_i, \beta)) \ . \tag{46}$$

Such a model may be too complicated for standard analysis, but a bootstrap method similar to that described below can be used.

1. Compute the observed residuals: $\hat{\varepsilon}_i = y_i - g(\boldsymbol{x}_i, \hat{\beta})$
2. Draw a bootstrap sample by randomly selecting, with replacement, from the observed residuals, a bootstrap sample of residuals, $\hat{\varepsilon}°_1, \hat{\varepsilon}°_2, \ldots, \hat{\varepsilon}°_n$, compute $y_i° = g(\boldsymbol{x}_i, \hat{\beta}) + \hat{\varepsilon}_i°$ and calculate $\hat{\beta}°$.
3. Repeat step 2 *Z* times to obtain bootstrap replications $(\hat{\beta}°)_1, (\hat{\beta}°)_2, \ldots, (\hat{\beta}°)_Z$.

Let $\hat{\beta}°_{mean} = \sum_{b=1}^{B} \frac{(\hat{\beta}°)_b}{Z}$; then, an estimate of β's covariance matrix is

$$cov(\hat{\beta}) = \frac{1}{Z-1} \sum_{b=1}^{B} ((\hat{\beta}°)_b - \hat{\beta}°_{mean})((\hat{\beta}°)_b - \hat{\beta}°_{mean})' \ . \tag{47}$$

A nonparametric (1-α) confidence interval for a prediction can be approximated by taking the (1-α) central portion of *Z* predictions based on the bootstrap replications from step 3.

APPENDIX 5. Region of Influence Method

In this method of developing site-specific predictions with a data set spanning a large geographic area, the regression equation for a site is computed using data from a unique region called the region of influence by Burn (1990a, 1990b) and suggested by Acreman and Wiltshire (1987). The unique subset of monitoring sites that make up the region of influence for each prediction site is made up of the *Ns* nearest neighbors. The method is an attractive alternative to the more traditional methods because it can be easily updated by simply updating the water-quality data in a database file from which the method draws its basic data; furthermore, extrapolation errors tend to be small because predictions by definition occur near the center of the space of the predictors. In this method, the nearness of two neighbors is not measured by the physical distance between the sites, but rather by a distance defined in terms of the watershed characteristics. This distance between any two sites, indexed by *i* and *j*, is determined by the Euclidean distance metric;

$$d_{ij} = \left(\sum_{k=1}^{p} \left(\frac{x_{ik} - x_{jk}}{sd(X_k)} \right)^2 \right)^{1/2} , \tag{48}$$

in which, d_{ij} is the distance between the watershed characteristics at sites *i* and *j*, *p* is the number of watershed characteristics needed to calculate d_{ij}, X_k represents the *k*th watershed characteristic, $sd(X_k)$ is the sample standard deviation for X_k, and x_{ik} is the value of X_k at the *i*th site. The d_{ij}'s between the prediction site *i* and all monitoring sites *j* = 1, 2,..., *n* in a region is determined, and the *Ns* monitoring sites with smallest *dij* make up the region of influence for site *i*. For this method to work, the value of *Ns* should be large enough to have enough degrees of freedom in the regression to estimate two or three parameters. The method is computer intensive and requires some subjective judgement for selecting *Ns* and the attributes used in the distance metric.

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