National Water Quality Assessment
Pesticide National Synthesis Project

Methods for Comparing Water-Quality Conditions Among National Water-Quality Study Units, 1992-1995

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ABSTRACT

The National Water-Quality Assessment is based on intensive investigations of stream and ground-water quality in selected major hydrologic basins (study units) of the United States. One objective of the national assessment is to comparatively evaluate water-quality conditions within and among the different study units. Methods were developed to compare the water-quality conditions of 20 study units that were studied during 1992-1995. Two approaches were taken: (1) water-quality conditions for each study unit were ranked in relation to the findings for all study units, and (2) water-quality conditions for each study unit were compared to established criteria for the protection of human health and aquatic life.

Separate rankings were developed for several major characteristics of water quality by using selected combinations of measured values for individual constituents or properties. The water-quality characteristics that were evaluated for streams were nutrients and pesticides in water, organochlorine pesticides and polychlorinated biphenyls in bed sediment and tissue, semivolatile organic compounds and trace elements in bed sediment, fish community degradation, and stream habitat degradation. The water-quality characteristics that were evaluated for ground water were nitrate, pesticides, volatile organic compounds, dissolved solids, and radon. The water-quality rankings are relative strictly to the distribution of conditions measured at sampling sites included in developing the method. Sites in the first 20 National Water-Quality Assessment study units include a broad range of environmental settings, but are not a statistically representative sample of the Nation. > To supplement the relative rankings, established water-quality criteria were used to indicate where particular constituents may have adverse effects, and thus merit further investigation. Established water-quality criteria, which provide consistent benchmarks for national comparisons of individual constituents, were selected from a variety of sources and applied to specific constituents in the specific medium (water or sediment) appropriate for each criterion.

INTRODUCTION

The National Water-Quality Assessment (NAWQA) Program of the U.S. Geological Survey (USGS) is designed to assess the status of, and trends in, the quality of the Nation's surface- and ground-water resources, and to link the status and trends with an understanding of the natural and human factors that affect the quality of water (Hirsch and others, 1988; Leahy and others, 1990; Gilliom and others, 1995). The study design balances the unique assessment requirements of individual hydrologic systems with a nationally consistent design structure that incorporates a multiscale, interdisciplinary approach. The building blocks of the national assessment are investigations in major hydrologic basins of the Nation, designated as study units. The goal for the first phase of investigation in each study unit is to characterize, in a nationally consistent manner, the broad-scale geographic and seasonal distributions of water-quality conditions in relation to major contaminant sources and background conditions.

The NAWQA study units cover about 40 percent of the conterminous United States, encompass 60 to 70 percent of both national water use and the population served by public water supplies, and include diverse hydrologic systems that differ widely in the natural and human factors that affect water quality. The study units are divided into three groups, which are studied on a rotational schedule of 3-year periods of intensive data collection. About one-third of the study units are in the intensive data collection phase at any given time, and the 9-year cycle is designed to be repeated perennially. The first complete cycle of intensive data collection in the study units began during 1992 and 1993 and is scheduled to be completed in 2002.

The national assessment goals of NAWQA are being accomplished in two main ways. First, the accumulation of consistent and comparable water-quality assessments for the most significant hydrologic systems of the Nation will stand alone as a major contribution to our knowledge of regional and national water-quality conditions. Second, the NAWQA national synthesis builds on and expands the findings from individual study units by combining and interpreting results from multiple study units together with historical information reported by the USGS and other agencies and researchers. National synthesis analyses produce regional and national assessments for priority water-quality issues.

One component of the NAWQA strategy for analyzing and reporting findings is to produce summary reports on water-quality conditions in each study unit at the end of each intensive study cycle. The first cycle of intensive data collection for the first 20 NAWQA study units occurred during 1992-1995. In concert with the national assessment goals, the summary reports highlight findings specific to each study unit in a consistent format. In particular, each study-unit summary report includes standardized analyses of how water-quality conditions in the particular study unit compare with those in other study units and with established criteria for the protection of human health and aquatic life.

Purpose and Scope

The purpose of this report is to describe methods used to compare water-quality conditions for streams and ground water among the 20 NAWQA study units that were studied during 1992-1995 (fig. 1). The resultssupport consistent comparisons among study units and can be used to identify and prioritize water-quality issues for further investigation.

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OVERVIEW OF APPROACH

Comparisons of water-quality conditions among NAWQA study units were made by two different approaches: (1) relative ranking of major water-quality characteristics, and (2) evaluation of individual constituents in relation to established water-quality criteria. The relative ranking system was developed solely with data collected from the study units evaluated. The relative ranking system has the advantage of providing a simplified and highly aggregated evaluation of major water-quality characteristics in relation to other areas studied, but has the disadvantages of being entirely relative to the development data, of not being directly related to an absolute scale of high and low water quality, and of not retaining the identity of individual constituents. The evaluation of individual constituents in relation to established water-quality criteria has the advantage of yielding constituent-specific comparisons to fixed thresholds chosen to define the terms high and low, but has the disadvantages that criteria are not available for many constituents, derivations of criteria are inconsistent and not always comparable, and some potential influences on water quality, such as the effects of mixtures, are not considered. Together, the relative rankings and criteria comparisons provide a complementary assessment of water-quality conditions.

NAWQA Design

Interpretation of results from a relative ranking of water-quality conditions is highly dependent on the nature of the areas and hydrologic systems included in the analysis and how they were sampled. Although it was not the intent of this study to fully characterize how conditions in the first 20 NAWQA study units relate to those in the rest of the Nation, it is useful to compare some general characteristics to gain a perspective on this relationship.

Study-Unit Characteristics

The first 20 NAWQA study units were selected to establish a balance of many factors, including population and water use, importance of water-quality issues, and geographic distribution. Examination of cultural and environmental characteristics of study units in relation to the rest of the Nation provides a perspective on the relevance of water-quality findings in the study units to other parts of the Nation. Table 1 shows that, relative to their area of 16 percent of the conterminous United States, the first 20 NAWQA study units contain a proportionally high share of the Nation's population (20 percent) and water use (22 percent), which is also consistent with the greater significance of agricultural and urban land use in study units compared with the rest of the Nation. In general, the 20 study units are widespread throughout the United States and include a broad diversity of environmental settings, but the study units are biased toward areas where the population, water use, and agricultural and urban land uses are greater-than-average.

Sampling Design

Relative rankings of water-quality characteristics for NAWQA study units, and comparisons of constituent concentrations to water-quality criteria were based on data from a consistent sampling design to support equitable comparisons among study units. The analyses described in this report focus on results from the most standardized components of the NAWQA study design. The complete design of these components, including site selection, sampling strategy, and analytical strategy, is described in Gilliom and others (1995), and only a brief outline is provided here.

Streams

The national study design for surface water focuses on water-quality conditions in rivers and streams (hereinafter referred to only as streams) using the following interrelated components:

- Water-column studies assess physical and chemical characteristics, which include suspended sediment, major ions and metals, nutrients, organic carbon, and dissolved pesticides.
- Bed sediment and tissue studies assess trace elements and organic contaminants that are hydrophobic (tend to associate with particles and accumulate in biological tissues rather than be dissolved in water).
- Ecological studies evaluate characteristics of biological communities and physical habitat in streams.

Sampling designs for all three components rely on coordinated sampling of varying intensity and scope at integrator sites, which are chosen to represent water-quality conditions of streams with large basins often affected by complex combinations of land-use settings, and at indicator sites, which are chosen to represent water-quality conditions of streams associated with specific environmental settings. The most complete data collection for the three components is at a selected core of three to five integrator sites and four to eight indicator sites in each study unit, which constitute the fixed-site monitoring network for regular collection of samples over time. A subset of two to five sites in each study unit, usually one integrator site and two to four indicator sites, is sampled more intensively than the rest, and these are the only sites where pesticides in water are routinely measured. All 226 stream sampling sites used to compare water quality among study units, and included in this report, are part of the fixed-site monitoring network of one of the first 20 study units. A listing of all sites and their characteristics is shown in appendix A, and the distribution of sites among study units is shown in table 2.

The 226 stream sampling sites in the first 20 study units include a wide range of stream sizes, types, and land-use settings in major regions of the Nation, but the sites were not selected to be a statistically representative sample of the Nation's streams. The water-quality rankings developed for these sites are relative strictly to the distribution of water-quality conditions found at the sites that are included in the analysis of each characteristic. Data requirements for analysis of each water-quality characteristic further restrict the number of stream sites that are included for a particular characteristic. Thus, the results for each characteristic are relative only to the subset of sites for which there are adequate data. Stream sites included in the analysis of each water-quality characteristic are indicated in appendix A. Most water-quality characteristics for streams were evaluated using data from the majority of sites in the fixed site network. Only pesticides in water were evaluated for a much smaller subset.

Figures 2 and 3 show the distribution of land-use characteristics for NAWQA stream sites compared with all basins of a similar size in the conterminous United States. The basin-size categories represent the ranges of the smallest 50 percent (fig. 2) and largest 50 percent (fig. 3) of the 226 NAWQA sites. Land use was determined from a classification of land cover derived from spectral information collected in 1990 by Advanced Very High Resolution Radiometer (AVHRR) on National Oceanic and Atmospheric Administration earth-orbiting satellites (U.S. Geological Survey, 1993). The AVHRR data were used to identify over 150 land-cover classes, which were grouped into eight land-use categories: agriculture, range, forest, water, wetland, barren, tundra, and snow. Urban land use was identified from the 1990 population data as land areas with population density greater than 386 people per square kilometer. The amounts of each land use in each basin were determined by overlaying basin boundaries on a 1-km resolution grid of land use. The drainage basin boundaries for each size category in the conterminous United States were determined by using automatic basin delineation tools and a 1-km resolution digital elevation model of the conterminous United States.

NAWQA sites with relatively small drainage basins (17-1,243 km2), have a greater prevalence of basins with large proportions of agricultural and urban land compared with all similarly sized basins in the United States, particularly the subset of pesticide sites (fig. 2). NAWQA sites with large basins (1,244-221,497 km2), which are mainly integrator sites, also have a greater prevalence of agricultural land compared with similarly sized basins in the United States (fig. 3), although the pattern is less clear than for the smaller basins. This bias toward agricultural and urban land use is the expected consequence of the NAWQA design.

Ground Water

The national study design for ground water focuses on water-quality conditions in major aquifers and in recently recharged shallow ground water associated with current and recent land uses:

- Aquifer surveys assess the quality of water in the major aquifer systems of each study unit. Aquifer surveys are referred to as "study-unit surveys" in Gilliom and others (1995) and in some study-unit reports as "subunit surveys."

- Land-use studies assess the quality of recently recharged shallow ground water associated with specific combinations of land uses and hydrogeologic conditions.

Generally, each aquifer survey and and use study consists of sampling about 30 randomly selected sites (wells or springs) within the geographic area and aquifer zone targeted for the specific study. One sample was collected from most of the sites. For the first 20 study units, results from 36 aquifer surveys and 56 and use studies were used to compare water-quality conditions among study units.

All ground-water study areas and their characteristics are listed in appendix B. The 36 aquifer surveys have mixed land-use influences. Of the 56 land-use studies, 41 targeted agricultural settings, 14 targeted urban settings, and 1 targeted a forested setting. Most water-quality characteristics were evaluated for all ground-water studies. Although suitable geographic delineation of aquifer boundaries throughout the United States is not available to enable comparison of NAWQA ground-water study areas to ground-water resources of the entire United States (as it was for stream drainage basins), the focus of the NAWQA ground-water design on agricultural and urban settings is similar to surface water.

For evaluating water-quality characteristics and comparing constituent concentrations to established water-quality criteria, aquifer surveys and land-use studies were reclassified according to two categories of ground-water resources:

- Drinking-water aquifers (DWA), which are currently used as sources of drinking water (though wells sampled by NAWQA were not necessarily drinking-water supply wells).
- Shallow ground water (SGW), which is recently recharged ground water that may or may not be currently used as a source of drinking water.

Classification of NAWQA ground-water study areas as DWAs or SGW was determined as follows:

- All land-use studies, which were specifically designed to study shallow ground water underlying particular land uses, were classified as SGW studies.
- land-use studies also were classified as DWA studies if the sampled wells tap water in an aquifer currently used for drinking-water supply.
- All aquifer surveys, except for one, were classified as DWA studies. The lone exception, which is in the Georgia-Florida coastal plain, targets a shallow aquifer that is not presently used for drinking water and, therefore, was classified solely as a SGW study.
- Selected aquifer surveys also were classified as SGW studies if the wells sampled showed evidence of being influenced by recent recharge and were of generally comparable depth to land-use study wells in the same area.

Classification and characteristics of 92 ground-water study areas in the first 20 NAWQA study units are listed in the appendix B. A total of 62 study areas were classified as DWAs and 66 study areas were classified as SGW, with 36 in both categories. The distribution of ground-water studies among study units is shown in table 2.

Relative Ranking of Water-Quality Conditions

Methods for ranking water-quality conditions in a consistent and comparable manner among all study units were developed for each of several major characteristics of water quality by using selected combinations of measured values for individual constituents or properties that relate to the particular characteristic. For each water-quality characteristic, the measured constituents or properties that represent the particular characteristic were chosen and, if necessary, grouped into a few major factors that define the characteristic. The purpose of grouping is to simplify the data and reduce computational problems with nondetections and high variability, while also producing a balanced assessment of each water-quality characteristic. For example, the constituents used to define pesticides in streams are grouped into two factors, herbicides and insecticides. For some characteristics, such as nutrients in streams, each factor consists of only a single constituent. A few characteristics, such as nitrate in ground water, are represented by only a single factor determined by a single constituent Water-quality characteristics and the factors included in each are summarized in table 3.

For a particular stream site or ground-water study area, the water-quality score was computed for each characteristic according to:

where

> WQS_i = the water-quality score for characteristic i
> n_i = the number of factors i
> FSV_f = the factor summary value for factor f
> NM_f = the NAWQA median of FSV_f for all stream sites or ground-water study areas.

Although scores for all water-quality characteristics were computed by equation 1, the method of determining the FSV_f for different water-quality characteristics varied, depending on the constituents involved and the sampling design. The general procedure for determining FSV_f and for applying equation 1 is summarized below, but variations and details are explained later in separate discussions of each characteristic.

- The value of each factor was determined for each individual sample collected at a site. For factors that include several constituents, this evaluation is commonly a sum of concentrations or a percent age of detections.
- A factor summary value (FSV_f) for a site (such as an annual median or other percentile) was computed for each factor from the factor values for all samples collected at each stream site or ground-water study area. Factor summary values were computed somewhat differently for different characteristics. For example, the annual 75th percentile was calculated as the factor summary value for herbicides and insecticides at stream sites because of the strong seasonality of pesticide concentrations, whereas the annual median was used for nutrients.
- The NAWQA median (NM_f was determined from factor summary values for all NAWQA stream sites or ground-water study areas. Median values for each factor are reported with

varying significant figures, depending on laboratory reporting practices and whether or not the value was interpolated.

- The factor summary values for each site or study area were standardized by dividing FSV f for each site by the corresponding value of NM f, thus expressing the score for the factor as a multiple of the NAWQA median. The standardized factor scores were summed for each site (streams) or study area (ground water) CLASS="Blue"> and divided by the number of factors to derive the final water-quality score (WQS i) for the particular water-quality characteristic i.

For each NAWQA stream site and ground-water study area, the water-quality scores for each characteristic were categorized by the national quartiles of the scores for the particular characteristic. A rank of 1 (lowest scores, "best" water quality) through 4 (highest scores, "worst" water quality) was assigned to each site or study area, for each water-quality characteristic, on the basis of the quartile in which the site or area score occurred. In the study-unit summary reports, final ranks are displayed on separate maps for each water-quality characteristic with site-location symbols color coded according to rank.

Comparison of NAWQA Results to Water-Quality Criteria

In addition to evaluating general characteristics of water quality by relative comparisons, established water-quality criteria were used as fixed benchmarks for evaluation of NAWQA results and to indicate where particular constituents might cause adverse effects, thus meriting further investigation. The term "water-quality criteria," as used in this report, refers to commonly used standards or guidelines established by national or international agencies or organizations in North America that have regulatory responsibilities or expertise in water quality. Thus, the term is used in a general sense in this report and does not necessarily refer to U.S. Environmental Protection Agency (USEPA) water-quality criteria for protection of human health and aquatic organisms.

Water-quality criteria are established for specific constituents, such as nitrate or a particular pesticide, and in a specific medium, such as water or sediment. Furthermore, water-quality criteria may be divided into two general categories: those for protection of human health and those for protection of aquatic life. For summarizing study-unit results in a nationally comparable manner, aquatic-life criteria were applied to concentrations of constituents measured in the water and bed sediment of streams, and human-health criteria were applied to concentrations of constituents measured in drinking water aquifers.

There is no single source of established and consistently derived criteria for all constituents. Moreover, different types of criteria may have different sampling and analytical requirements. In many instances, the characteristics of water-quality data collected for NAWQA studies, such as sampling frequency or analytical strategy, do not exactly match the requirements of a particular type of water-quality criteria. Although these can be crucial issues in regard to regulatory monitoring and enforcement, water-quality criteria are used in this study only as indicators of potential problems. The established criteria provide consistent benchmarks, with which most water-quality managers are already familiar, for national comparison of individual constituents.

In the study-unit summary reports, NAWQA results are compared to water-quality criteria in two ways. First, on maps for each water-quality characteristic, sites are highlighted if any individual criterion was exceeded for any constituent included in the particular characteristic. Second, in a tabular summary, the distributions of all measured concentrations of each constituent in the study unit are shown in relation to corresponding criteria values and to the national range of concentrations measured in all 20 study units.

RELATIVE RANKING OF STREAM WATER QUALITY

The water-quality characteristics that were evaluated for streams are nutrients in water, pesticides in water, organochlorine pesticides and polychlorinated biphenyls (PCBs) in bed sediment and tissue, semivolatile organic compounds (SVOC) in bed sediment, trace elements in bed sediment, fish community degradation, and stream habitat degradation (table 3). The methods for ranking each water-quality characteristic are described below, preceded by general characteristics and methods for each type of media evaluated.

Water Data for concentrations of constituents in stream water consist of multiple measurements over a period of 1 to 3 years during 1993-1995 at each sampling site in the fixed-site monitoring network. For each particular site, data are available from several different types of sample collection strategies that were designed for different purposes. The primary types of samples are listed below.

- Fixed frequency--collected on a predetermined time schedule without regard to flow conditions or other significant biases. The frequency varies among sites and seasons, from as frequent as twice weekly, to as sparse as bimonthly or quarterly when expected variability is low.
- High flow--individual samples collected during selected high-flow conditions within a particular season to supplement fixed-frequency samples.
- Low flow--individual samples collected during selected extreme low-flow conditions within a particular season to supplement fixed-frequency samples.
- Storm hydrograph (not used in the analysis described here) -- multiple samples collected during an individual storm runoff period, usually several samples within 1 to 3 days.

Data used for evaluating nutrient and pesticide water-quality characteristics were restricted to fixed-frequency, high-flow, and low-flow samples to make the analysis as consistent as possible among sites and to avoid biases caused by extensive and extreme storm hydrograph data for some periods at some sites. Most of the data used are from fixed-frequency samples. For nutrients, there are 2 to 3 years of data at about a monthly sampling frequency for most sites. For pesticides, there are commonly 1 to 2 years of data at a minimum monthly sampling frequency, supplemented by more frequent sampling during 3- to 6-month seasonal periods. Pesticide data are available only for a subset of two to five intensive sampling sites in each study unit.

Concentration values for evaluating water-quality characteristics were simplified by determining the monthly median concentration for each month within the period of record analyzed. This approach gives equal weight to each month with data, regardless of the amount of data. Thus, for months with one sample, the median is the value for that sample, for months with two samples, the median is the mean of the two values, and so forth, using the standard method for determining medians. Concentrations for nondetections were set to zero prior to computing medians. Reduction of data to monthly medians decreases the influence of extreme events and uneven sampling frequency.

Nutrients in Stream Water

Comparison of nutrients among NAWQA stream sites was based on three factors: ammonia, nitrite plus nitrate, and total phosphorus concen-trations in water (appendix C). The period of record was restricted to a 2-year period (April 1993 to March 1995), and the analysis was limited to sites that had samples in at least 12 months during that period. Of the 226 NAWQA fixed sites, 219 met these data requirements (see appendix A). The relative regularity and completeness of the data sets for nutrients justified inclusion of all months with available data during the defined 2-year period.

For each site included in the analysis, monthly median values were determined from the measured concentrations for each of the three factors:

$$MC_{f,m} = med\{C_{f,1} \ldots C_{f,n_{sm}}\}$$

where
$MC_{f,m}$ = the median concentration of factor f in month m
$C_{f,1} \ldots C_{f,n_{sm}}$ = the measured concentrations of factor f in samples 1 through n_{sm}
n_{sm} = number of samples in month m .
In most months, only one sample was collected, and $MC_{f,m}$ is merely the single measured concentration.
The factor summary value for each factor was determined for each site as the median of all monthly median concentrations:

$$FSV_f = med\{MC_{f,1} \ldots MC_{f,nm}\}$$

where nm is the number of months with data. The national median for each nutrient factor was determined from the factor summary values at the 219 sites:

- Ammonia: 0.035 mg/L
- Nitrite plus nitrate: 0.58 mg/L
- Total phosphorus: 0.060 mg/L

The nutrient score for each site was calculated by equation 1 as the average of standardized factor values (ratio of FSV_f to NM_f). Nutrient scores for all sites were categorized according to ranks 1 to 4 on the basis of quartiles of the national distribution of NAWQA site scores. Categories are summarized in table 4.

Pesticides in Stream Water

Comparison of pesticides among NAWQA stream sites was based on two factors: total herbicide concentration and total insecticide concentration (including selected degradation products). Pesticides included in these totals are listed in appendix D. Samples selected for this computation were required to include pesticide analysis by gas chromatography/mass spectroscopy, which accounted for most detections.

For each sample, concentrations of all detected herbicides and all detected insecticides were summed separately to yield total concentrations for each of these factors. Similar to nutrients, medians for each factor in each month were computed from the resulting values:

$$MC_{f,m} = med\left\{ \sum_{p=1}^{np} C_{p,1} \ldots \sum_{p=1}^{np} C_{p,nsm} \right\}$$

where
MC f, m = the median concentration of factor f in month m
C p,1...C p, n sm = the detected concentrations of pesticide p in samples 1 through nsm
np = number of herbicides or insecticides detected in each sample 1 through nsm.

Monthly medians for each site were grouped into 1-year periods, usually starting with the onset of sampling at the particular site (most commonly March or April of 1993 or 1994). For a site to be included in the national analysis, it had to have at least 1 year with more than six monthly medians and a reasonable probability that no missing months would affect the 75th percentile for the year. Several sites that met these criteria were excluded because there were other similar sites in the same study unit, which could introduce undo bias into the national analysis. Of the 226 NAWQA stream sites, 61 were selected (see appendix A), 56 of which have 9 or more months of data in at least 1 year, and 5 of which have 7 or 8 months of data in at least 1 year.

For all sites, annual 75th-percentile concentrations were determined from the monthly medians of both factors (total herbicides and total insecticides) for the first year of data:

$$AC_{f,1} = prob_{0.75}\{MC_{f,1} \ldots MC_{f,nm}\}$$

Where
AC f, 1 = the 75th-percentile concentration of factor f in year 1
nm = the number of months with data.
Each of the 61 sites was then evaluated to determine if there were second or third years with enough data to compute valid 75th percentiles. Subsequent years were retained in the national analysis if the year included at least 4 months of data and had one of the following characteristics:

- Data for as many months as the first year and covered the same portion of the year.
- Data for fewer months than the first year, but the 75th percentile was higher than the first year.
- Data for fewer months than the first year and a lower 75th percentile, but the months available

included all or the most important months for determining the 75th percentile (on the basis of the first year and nearby sites).

Decisions on including or excluding additional years of data were made independently for herbicides and insecticides because their seasonal timing frequently differs.

The factor summary values for herbicides and insecticides were determined for each site as the median of annual values for years 1 through ny:

$$FSV_{\text{[illegible]}} = med\{AC_{\text{[illegible]}} \ldots AC_{\text{[illegible]}}\}$$

The national median for each pesticide factor was determined from the factor summary values at the 61 sites:

- Total herbicides: 0.297 mg/L
- Total insecticides: 0.012 mg/L

The pesticide score for each site was calculated by equation 1 as the average of standardized factor summary values (ratio of FSV f to NM f). Pesticide scores for all sites were categorized according to ranks 1 to 4 on the basis of quartiles of the national distribution of NAWQA site scores. Categories are summarized in table 5.

Table 5. Water-quality scores and ranks for pesticides in stream water

[≤, less than or equal to; >, greater than]

[illegible]	[illegible]	[illegible]
1 (best)	≤25	≤0.43
2	>25 – 50	>0.43 – 1.75
3	>50 – 75	>1.75 – 6.69
4 (worst)	>75	>6.69

Bed Sediment and Tissues

Most data for bed sediment and tissues of aquatic organisms consist of one sample from one or more media (sediment, fish, or clam) for each site. Most sites had data for sediment and either fish or Asiatic clams (genus Corbicula) collected at approximately the same time. If multiple samples of a given medium (sediment, fish, or clam) were collected at a site, the median total concentration of constituents in that medium was used for that site. The site median for each medium was determined by equation 7. Samples were grouped by year of sampling, the median concentration was determined for each year, and the site median is the median of the available annual medians:

$$FSV_{\text{[illegible]}} = med[med\{TC_{\text{[illegible]}} \ldots TC_{\text{[illegible]}}\}_{\text{[illegible]}}$$

$$\ldots med\{TC_{\ldots}\ldots TC_{\ldots}\}]$$

where

TC f,s = the total concentration for factor f in sample s

ny = the number of years with data

nsy = the number of samples in a year.

Organochlorine Pesticides and PCBs in Bed Sediment and Tissue

Comparison of organochlorine pesticides and PCBs in stream bed sediment and biological tissue among NAWQA stream sites was based on three factors: total concentration in bed sediment, total concentration in fish tissue, and total concentration in clam tissue. One, two, or all three of these media might have been analyzed at a particular site. Compounds included in this analysis are listed in appendix E. Samples of a medium with missing data for any one of the most commonly detected analytes (total DDT, total chlordane, dieldrin, or total PCBs) were excluded because sums for these samples might be biased low. Total DDT was considered missing if concentrations of any of the p,p¢-isomers of DDT, DDD, and DDE (typically the most abundant com-ponents of this mixture) were missing. Total chlordane was considered missing if concentrations for any one of its components (cis- and trans-chlordane, cis- and trans-nonachlor, and oxychlordane) were missing. Of the 226 stream sites in the NAWQA fixed-site monitoring network, 202 had adequate samples from at least one sediment or tissue medium (see appendix A).

For each sample of each medium, the total concentration of organochlorine pesticides and PCBs was calculated by summing the concentrations of all detected compounds. The total concentration in fish tissue was normalized by dividing by lipid content. This normalization decreases the bias that might result from comparing different species in the fish-tissue data set, and is reasonable because of the significant correlation between total concentration and fish lipid content (Spearman rho=0.31, p=0.0003). The clam-tissue data also were normalized to be consistent with the fish data. The correlation between total concentration and lipid content in clam tissue is about the same as in fish tissue (Spearman rho=0.38, p=0.039), although the sample size is much smaller.

The factor summary value for each available medium was computed for all sites by equation 7. National comparison values were determined for total organochlorine pesticides and PCBs in each medium at the 202 sites. For fish tissue, the comparison value was determined as the median of the factor values for all sites that had adequate data. Exact medians could not be determined for bed sediment and clam tissue, however, because more than 50 percent of the samples had no detections. The lowest detected concentration for each medium was used in place of the median for these factors, but the values used are not far removed from the 50th percentile (median). The national comparison concentrations of organochlorine pesticides and PCBs are:

- Bed sediment: 0.7 mg/kg total sediment (56th percentile)
- Fish tissue: 2,780 mg/kg lipid (median)
- Clam tissue: 218 mg/kg lipid (59th percentile)

The score for organochlorine pesticides and PCBs for each site was calculated by equation 1 as the average of the standardized factor summary values (ratio of FSV f to NM f or the alternate comparison value). If samples from all media were not available from a site, WQS was computed from as many media as possible. Individual site scores were categorized according to ranks 1 to 4 on the basis of percentiles of the national distribution of NAWQA site scores. Scores were zero for 32 percent of the sites. All of these sites were included in the lowest category, and only 18 percent of the sites were included in the second category. Categories are summarized in table 6.

Table 6. Water-quality scores and ranks for organochlorine pesticides and PCBs in bed sediment and tissue

[≤, less than or equal to; >, greater than]

[illegible]	[illegible]	[illegible]
1 (best)	≤32	0.00
2	>32 – 50	>0.00 – 0.63
3	>50 – 75	>0.63 – 9.67
4 (worst)	>75	>9.67

Semivolatile Organic Compounds in Bed Sediment

Comparison of SVOCs in bed sediment among NAWQA sampling sites was based on three factors: total polycyclic aromatic hydrocarbons (PAH), total phenols, and total phthalates. Compounds included in the analysis of each factor are listed in appendix F. Several analytes were corrected for laboratory contamination by subtracting the 95th percentile concentration in laboratory blanks from the measured concentration in each environmental sample. The corrections applied to these analytes were:

bis (2-Ethylhexyl) phthalate: 100 ug/kg
Di-n -butyl phthalate: 54 ug/kg
Butylbenzyl phthalate: 64 ug/kg
Phenol: 27 ug/kg
Diethyl phthalate: 25 ug/kg

Of the 226 NAWQA fixed sites, 198 have sufficient data for SVOC comparison (see appendix A).

The factor summary value for each site was computed by equation 7, after summing the detected concentrations of compounds in each factor group in the sample from that site. The national median for each SVOC factor was determined from the factor summary values at these sites. The national median concentrations of SVOCs in bed sediment are:

PAHs: 104 ug/kg
Phenols: 73 ug/kg
Phthalates: 20 mg/kg

The SVOC score for each site was calculated by equation 1 as the average of the standardized factor summary values (ratio of FSV f to NM f). Individual site scores were categorized according to ranks 1 to 4 on the basis of quartiles of the national distribution of NAWQA site scores. Categories are summarized in table 7.

Table 7. Water-quality scores and ranks for semivolatile orgar compounds in bed sediment

[≤, less than or equal to; >, greater than]

[illegible]	[illegible]	[illegible]
1 (best)	≤25	≤0.45
2	>25 – 50	>0.45 – 1.58
3	>50 – 75	>1.58 – 5.43
4 (worst)	>75	>5.43

Trace Elements in Bed Sediment

Comparison of trace elements in bed sediment among NAWQA sampling sites was based on nine elements: arsenic, cadmium, chromium, copper, lead, mercury, nickel, selenium, and zinc (appendix G). Of the 226 NAWQA fixed sites, 198 had data for trace elements in bed sediment (see appendix A).

The factor summary value for each element at each site was computed using equation 7. The national median for each trace-element factor was determined from the factor summary values at the 198 sites. The national median concentrations of trace elements in bed sediment are:

Arsenic: 6.35 ug/g Cadmium: 0.4 ug/g Chromium: 62ug/g Copper: 26 ug/g Lead: 24.3 ug/g Mercury: 0.06 ug/g Nickel: 25ug/g Selenium: 0.7 ug/g Zinc: 110ug/g

The trace element score for each site was calculated by equation 1 as the average of the standardized factor summary values (ratio of FSV f to NM). Individual site scores were categorized according to ranks 1 to 4 on the basis of quartiles of the national distribution of NAWQA site scores. Categories are summarized in table 8.

Table 8. Water-quality scores and ranks for trace elements in bed sediment

[≤, less than or equal to; >, greater than]

[illegible]	[illegible]	[illegible]
1 (best)	≤25	≤0.85
2	>25 – 50	>0.85 – 1.07
3	>50 – 75	>1.07 – 1.57
4 (worst)	>75	>1.57

Fish and Habitat

Water-quality scores for fish community degradation and stream habitat degradation were based on previously published index systems for rating stream quality. To retain comparability of factor values for individual sites with existing index systems, values for individual factors for each site were summed instead of averaged, as was done for other water-quality characteristics. Rankings by quartiles are the same using either averages or sums. The characteristics of the index systems and their application to NAWQA data are described below.

Fish Community Degradation

The water-quality score for fish community degradation is based on a modification of the Index of Biotic Integrity (IBI), which was developed by Karr (1981) to assess the biological condition of streams. The IBI is a broadly based ecological index that integrates a number of fish community attributes and is sensitive to different sources of degradation (Fausch and others, 1990). Although the IBI must be modified for use in different ecological regions (Miller and others, 1988), the approach retains the same basic ecological foundation. The IBI is based on assumptions of how fish communities respond to increasing environmental degradation (Fausch and others, 1990; Yoder and Rankin, 1995). The attributes that are assumed to increase with increasing environmental degradation are:

> The proportion of individuals that are members of tolerant species;
> The proportion of trophic generalists, especially omnivores;
> The proportion of individuals that are members of introduced species; The incidence of externally evident disease, parasites, and morphological anomalies, excluding blackspot; and
> The proportion of individuals that do not require silt-free substrate to spawn.

Of these five attributes, information is available from NAWQA data and the literature for all except the reproductive-habitat requirements associated with item 5. Therefore, comparison of fish communities among NAWQA stream sites is based on the first four factors only. Of the 226 NAWQA fixed sites, 172 have sufficient data to evaluate these factors (see appendix A).

The factor summary value (FSV f) for each factor was assigned a value of 1, 3, or 5 according to whether the measured percentage at a site approximated, deviated moderately from, or deviated strongly from the expected percentage at a comparable site that has been relatively undisturbed. Expected percentages for undisturbed conditions were estimated from previous studies. Factor summary values were summed to determine the total value for the fish community at each site. If the value for one of the four factors was missing, or considered to misrepresent conditions at that site, that factor was omitted and the sum of the remaining three factors was multiplied by 1.33. The result is a unitless value ranging from 4 to 20, and the larger the number, the greater the degradation.

The national median (NM) determined from the values for fish communities at the 172 sites was 10. The score for fish community degradation (WQS) at each site was computed by a modification of equation 1, dividing the factor summary values by the national median, rather than averaging the standardized factor summary values:

$$WQS = \frac{\sum FSV}{NM}$$

Individual site scores were categorized according to ranks 1 to 4 on the basis of quartiles of the national distribution of NAWQA site scores. Categories are summarized in table 9.

Stream Habitat Degradation

Several approaches to assessing stream habitat conditions have been developed for biomonitoring programs (Rankin, 1995). Three commonly applied habitat indices are (1) the Rapid Bioassessment Protocol (Plafkin and others, 1989), (2) the Riparian, Channel, and Environmental Inventory (Peterson, 1992), and (3) the Qualitative Habitat Evaluation Index (Rankin, 1989). These indices, however, may not be broadly applicable beyond the regions for which they were developed. Rankin (1995) recommends seven metrics that could be widely used as indicators of habitat condition: substrate type, instream cover, stream modification, riparian vegetation, bank erosion, streamflow, and characteristics of geomorphic channel units such as pool, riffle, and run. Stauffer and Goldstein (1997) suggest that habitat index approaches should reflect dominant geomorphic processes of stream systems to improve upon making assessments of environmental change across large geographic areas. Characteristics of stream channel and bank geomorphology and riparian vegetation can be used as diagnostic factors to assess environmental changes in stream systems (Simon and Downs, 1995). Environmental changes can be the result of natural occurrences such as floods, or of human activities such as bridge construction, dredging, or land use. Environmental changes of sufficient magnitude and extent can initiate stream-channel and stream-bank responses in the size, shape, and morphology of channel features and in the condition of riparian vegetation (Simon and Hupp, 1992).

Comparison of habitat conditions among NAWQA stream sites was based on four factors: stream modification, bank erosion, bank vegetative stability, and riparian vegetation density. Of the 226 NAWQA fixed sites, 181 have sufficient data to eval-uate these factors (see appendix A). Stream modifica-tion refers to alterations to a stream channel that include, but are not limited to, channelization, artifi-cial banks, and artificial stream beds. Streams were classified as unmodified (low degradation) when there was no observable channel alteration along or near the sampled reach; moderately modified when streams have had modifications some distance upstream or downstream from the sampled reach; and highly modified for streams that had modifications within the sampled reach.

Bank erosion was assessed by using recorded observations of multiple types of bank failure along a reach. These observations were grouped by percentile, and bank erosion at each site was classified according to low (<25th percentile), moderate (25th-75th percentile), or high (>75th percentile) groupings.

Vegetative bank stability was assessed using the procedures described in Meador and others (1993). A mean vegetative bank-stability rating was calculated from the sampling points along a stream reach at each site, then classified according to three groupings: low (4.0-3.5), moderate (3.4-2.5), and high (< 2.5) stability.

The relative density of woody riparian vegetation (all species combined) was calculated for the reach using the formula:

$$RD = \frac{100?m^{[illegible]}}{(PTD)^{[illegible]}}$$ where:

RD = relative density of riparian vegetation

PTD = mean point-to-tree distance for a reach, in meters.

On the basis of the distribution of computed densities for all sites, the density values for each site were classified into three groups: low (>75th percentile), moderate (25th-75th percentile), or high (<25th percentile).

Each habitat degradation factor was assigned a value of 1 (low), 3 (medium), or 5 (high) on the basis of the factor classifications determined for each site. The four factors then were summed to determine the factor summary value for habitat degradation at each site. If the value for one of the four factors was missing, or considered to misrepresent conditions at that site, that factor was omitted and the sum of the remaining three factors was multiplied by 1.33. The result is a unitless value ranging from 4 to 20, with higher numbers representing greater degradation.

The national median of the factor summary value, determined from the values for habitat degradation at the 181 sites, was 12. The score for habitat degradation at each site was computed by equation 8. Individual site scores were categorized according to ranks 1 to 4 on the basis of quartiles of the national distribution of NAWQA site scores. Categories are summarized in table 10.

Table 10. Water-quality scores and ranks for stream habitat degradation

[≤, less than or equal to; >, greater than]

[illegible]	[illegible]	[illegible]
1 (best)	≤25	≤0.75
2	>25 – 50	>0.75 – 1.00
3	>50 – 75	>1.00 – 1.16
4 (worst)	>75	>1.16

Table 10. Water-wulaity scores and reanks for stream habitat degradation.

[≤, less than or equal to; >, greater than]

RELATIVE RANKING OF GROUND-WATER QUALITY

The water-quality characteristics that were evaluated for ground water are nitrate, pesticides, volatile organic compounds (VOCs), dissolved solids, and radon (table 3). Water-quality characteristics were evaluated for ground water using an approach similar to that for streams, but with water as the only medium and with each characteristic evaluated on the basis of only one factor. Thus, FSVf is reduced to FSV in equations for ground water. Data from a minimum of 10 sampling sites (wells or springs) were required for a ground-water study to be included in the analysis. For ground water, only the data from the most recent sampling of each well or spring were included so that bias toward sites with multiple samples was eliminated. Classification and characteristics of the 92 qualifying ground-water study areas in the first 20 NAWQA study units are listed in appendix B. A total of 62 study areas are classified as drinking water aquifers (DWA) and 66 are classified as shallow ground water (SGW), with 36 in both categories.

Nitrate in Ground Water

Comparison of nitrate in ground water among NAWQA ground-water study areas was based on measured concentrations of dissolved nitrite plus nitrate, which are strongly dominated by nitrate in most samples. The factor summary value (FSV) for each study area was determined as the median of concentrations in samples from all wells and springs in the study area:

where

C 1 ...Cnw = the concentration of dissolved nitrite plus nitrate in a single sample each from wells (or springs) 1 through nw.

n w = the total number of wells (or springs) in the study area.

The national median for each group of study areas was determined from the factor summary values. The national median concentrations of nitrate in ground water are:

Drinking water aquifers (DWA): 1.0 mg/L
Shallow ground water (SGW): 2.0 mg/L

The nitrate score for each study area was calculated by equation 1 as the ratio of the study-area median concentration to the national median. The national median used in this calculation was determined by the classification of the study area as either a DWA or an SGW. In some cases, a study area was classified as both, and two nitrate scores were calculated. Study-area scores were categorized according to ranks 1 to 4 on the basis of quartiles of the national distribution of NAWQA study-area scores. Categories are summarized in table 11.

Pesticides in Ground Water

Comparison of pesticides in ground water among NAWQA ground-water study areas was based on the detection frequency of one or more pesticide compounds in samples collected in each study area. Pesticides included in this analysis are listed in appendix D. Most of the pesticides detected in ground water were herbicides.

The factor summary value for each study area was determined as the percentage of wells or springs in which at least one pesticide was detected:

$$FSV = 100\left|\frac{\sum_{i=1}^{n_w} D_i}{n_w}\right|$$

where

n w = the total number of wells (or springs) in the study area

D i = 1 if any pesticide was detected in a single sample from well (or spring) i, or 0 if no pesticides were detected.

Adequate data were available for pesticides for 62 DWAs and 66 SGW study areas (see appendix B).

The national median for each group of study areas was determined from the factor summary values. The national median detection frequencies of pesticides in ground water are:

Drinking water aquifers (DWA): 39.6 percent
Shallow ground water (SGW): 45.9 percent

The pesticide score for each study area was calculated as the ratio of the study-area detection frequency to the national median, using equation 1. The national median used in this calculation was determined by the classification of the study area as either a DWA or an SGW. In some cases, a study area was classified as both, and two pesticide scores were calculated. Study-area scores were categorized according to ranks 1 to 4 on the basis of quartiles of the national distribution of NAWQA study-area scores. Categories are summarized in table 12.

Volatile Organic Compounds in Ground Water

Comparison of VOCs in ground water among NAWQA study areas was based on the detection frequency of one or more VOCs in samples collected at each study area. Compounds included in this analysis are listed in appendix H.

The factor summary value for each study area was determined as the percentage of wells or springs in which at least one VOC was detected:

$$FSV = 100\left(\frac{\sum_{i=1}^{n_w} D_i}{n_w}\right)$$

where

n_w = the number of wells (or springs) in the study area

D_i = 1 if any VOC was detected in a single sample from well (or spring) i, or 0 if no VOCs were detected.

Adequate data were available for VOCs for 45 DWAs and 50 SGW study areas (appendix B).

The national median for each group of study areas was determined from the factor summary values. The national median detection frequencies of VOCs in ground water are:

Drinking water aquifers (DWA): 10.0 percent
Shallow ground water (SGW): 12.2 percent

The VOC score for each study area was calculated as the ratio of the study-area detection frequency to the national median, using equation 1. The national median used in this calculation was determined by the classification of the study area as either a DWA or an SGW. In some cases, a study area was classified as both, and two VOC scores were calculated. Study-area scores were categorized according to ranks 1 to 4 on the basis of quartiles of the national distribution of NAWQA study-area scores. Categories are summarized in table 13.

Dissolved Solids in Ground Water

Comparison of dissolved solids in ground water among NAWQA study areas was based on measurements of residue on evaporation of filtered samples at 180°C. The factor summary value for each study area was determined as the median concentration in samples from all wells and springs in the study area:

Table 13. Water-quality scores and ranks for volatile organic compounds in ground water.

The national median for each group of study areas was determined from the factor summary values. The national median concentrations of dissolved solids in ground water are:

Drinking water aquifers (DWA): 298 mg/L

Shallow ground water (SGW): 290 mg/L

The dissolved-solids score for each study area was calculated as the ratio of the study-area median concentration to the national median, using equation 1. The national median used in this calculation was determined by the classification of the study area as either a DWA or an SGW. In some cases, a study area was classified as both, and two dissolved-solids scores were calculated. Study-area scores were categorized according to ranks 1 to 4 on the basis of quartiles of the national distribution of NAWQA study-area scores. Categories are summarized in table 14.

Table 14. Water-quality scores and ranks for dissolved solids in ground water

[≤, less than or equal to; >, greater than]

[illegible]	[illegible]	[illegible]	
		[illegible] [illegible]	[illegible] [illegible]
1 (best)	≤25	≤0.69	≤0.67
2	>25 – 50	>0.69 – 1.00	>0.67 – 1.00
3	>50 – 75	>1.00 – 1.32	>1.00 – 1.46
4 (worst)	>75	>1.32	>1.46

Table 14. Water-quality scores and ranks for dissolved solids in froundwater.
[≤, less than or equal to; >, greater than]

Radon in Ground Water

Comparison of radon in ground water among NAWQA study areas was based on measured concentrations of radon 222. The factor summary value for each study area was determined as the median concentration in samples from all wells and springs in the study area:

$$FSV = med\{C_{w} \ldots C_{nw}\}$$

where

C f,1 ...C nw = the concentration of radon in a single sample each from wells (or springs) 1 through nw.

Adequate data were available for radon 222 for 47 DWAs and 43 SGW study areas (see appendix B).

The national median for each group of study areas was determined from the factor summary values. The national median concentrations of radon in ground water are:

Drinking water aquifers (DWA): 450 pCi/L Shallow ground water (SGW): 470 pCi/L

The radon score for each study area was calculated by equation 1 as the ratio of the study-area median concentration to the national median. The national median used in this calculation was determined by the classification of the study area as either a DWA or an SGW. In some cases, a study area was classified as both, and two radon scores were calculated. Study-area scores were categorized according to ranks 1 to 4 on the basis of quartiles of the national distribution of NAWQA study-area scores. Categories are summarized in table 15.

COMPARISON OF NAWQA RESULTS TO WATER-QUALITY CRITERIA

Results from NAWQA studies can be compared to established water-quality criteria to supplement the relative rankings for the highly aggregated water-quality characteristics with an absolute and more specific indication of which individual constituents may be of concern and, thus, merit further investiga-tion. As noted previously, water-quality criteria consist of commonly used standards or guidelines that have been established by agencies or organizations with regulatory responsibilities or expertise in water quality. Generally, a criterion is assumed to be a threshold concentration at which there is some estimated significant risk of adverse effects on the basis of evidence from toxicological studies, with an increasing risk of adverse effects at concentrations above that threshold.

Each water-quality criterion is based on a finite data set of measured effects, but the quantity and type of data vary, depending on the constituent and the type of criterion. The scope of these data is limited to effects of individual constituents, almost always (except for sediment criteria) measured in laboratory studies. The criteria used in this report were developed by considering acute and chronic toxicity to aquatic organisms (for aquatic-life criteria) or chronic toxicity and carcinogenicity for humans (for human-health criteria). These criteria generally do not consider certain more complex issues related to toxicity, such as the effect of chemical mixtures on toxicity and the potential for endocrine-disrupting effects on development, reproduction, and behavior of fish and wildlife populations. In addition, criteria have not been established for many constituents. Thus, the absence of criteria exceedances (concentrations that exceed one or more water-quality criteria) at a site does not necessarily mean that there are no issues of concern at that site.

Different types of criteria have different sampling and analytical requirements. For example, USEPA chronic water-quality criteria for the protection of aquatic organisms are designed for comparison with the 4-day average concentration of a contaminant in a water body. Sampling and analytical requirements for determining compliance with federal drinking-water standards depend upon the water system, the compound, and the frequency of exceedances (Code of Federal Regulations, v. 40, part 141, subpart C). Data collected for the NAWQA Program do not always match the conditions specified or implied in the definition of a particular type of criterion. These conditions can include the sample collection or processing method, the frequency of collection, and the type of chemical analysis. Although differences in methods and sampling may limit the use of NAWQA data in regulatory monitoring and enforcement in some situations, they do not preclude the comparison of NAWQA data to water-quality criteria to signal potential water-quality problems.

Established water-quality criteria are consistent benchmarks for national comparisons with observed concentrations for many individual constituents considered important in management of water resources. Because most of the streams sampled are not used as primary drinking-water sources, and because aquatic life is a vital resource in virtually all streams, water and bed-sediment concentrations for streams are compared with aquatic-life criteria to identify potential water-quality problems at NAWQA stream sites. Ground-water concentrations, on the other hand, are compared to human-health criteria.

The water-quality criteria referred to in this report were compiled from various sources developed by federal or international agencies in North America, including USEPA, the Canadian Council of Resource and Environment Ministers, and the International Joint Commission (IJC) of Canada and the United States. State and Canadian provincial criteria were not used because of the wide variability in the methods used in their derivation. If more than one type of criterion was available for a constituent, several rules were used to prioritize criteria. In general, USEPA criteria were given preference over criteria from other agencies. Also, USEPA standards (enforceable regulatory limits) were given preference over USEPA criteria and guidelines (issued in an advisory capacity). For constituents in sediment, a slightly different approach was used because no single type of sediment-quality guideline is generally accepted in the scientific literature, and there may be substantial differences (up to three orders of magnitude) between different guideline values for a given constituent. Therefore, on the basis of the available criteria for a given constituent, procedures developed by USEPA are used to determine a threshold concentration above which there was a high probability of adverse effects on aquatic life.

Aquatic-Life Criteria for Stream Water

Aquatic-life criteria for stream water were evaluated for ammonia, the only nutrient species with an established aquatic-life criterion, and for all pesticides with established criteria. Regarding nutrients, a significant limitation is the lack of available water-quality criteria that reflect the eutrophication influences of nutrient enrichment on streams, such as nuisance algal growth, reduced water clarity, and depressed dissolved oxygen; thus, these types of effects are not considered in the analysis of nutrient effects on streams at NAWQA sites. For pesticides, the most significant weaknesses are that (1) no criteria are available for many pesticides and (2) existing criteria assess the effects of single chemicals only and do not consider effects of chemical mixtures. Nonetheless, the criteria used here represent the state-of-the-art in defining acceptable water quality for specific uses. Because of the above limitations, however, the available criteria do not take into account all potential effects on aquatic life in streams from nutrients or pesticides.

The three types of aquatic life criteria used are USEPA chronic water-quality criteria for protection of aquatic organisms (U.S. Environmental Protection Agency, 1986, 1991), Canadian water-quality guidelines (Canadian Council of Resource and Environment Ministers, 1996), and Great Lakes water-quality objectives (International Joint Commission, 1977). All criteria values used for nutrients and pesticides in stream water are for protection of freshwater aquatic life. The USEPA chronic water-quality criterion for protection of aquatic organisms is the estimated highest concentration of a constituent that aquatic organisms can be exposed to for a 4-day period, once every 3 years, without deleterious effects. If no USEPA chronic water-quality criterion for protection of aquatic organisms exists for a given constituent, then Canadian water-quality guidelines are used, if available. The older Great Lakes water-quality objectives are used only if neither USEPA chronic water-quality criteria for protection of aquatic organisms nor Canadian water-quality guidelines are available for that constituent. The Canadian water-quality guidelines and the Great Lakes water-quality objectives are defined as specifying maximum concentrations that should not be exceeded at any time.

Data for ammonia and pesticide concentrations in streams were simplified to a time series of monthly median concentrations, as previously described for the development of water-quality scores. Monthly medians were compared to water-quality criteria to identify sites with the greatest potential water-quality effects attributable to ammonia or pesticides and to estimate the number of months during a year that one or more criteria were exceeded. This approach is an approximation for examining broad patterns and prioritizing further investigations. The frequency of exceedances is reduced by using monthly medians rather than individual sample values because individual high values might not influence a monthly median. For NAWQA study-unit summary reports, stream sites are designated as having an exceedance if the median concentration in any month exceeds the criterion for ammonia or for any pesticide.

Ammonia in Water

The only applicable aquatic-life criterion for nutrients in streams is for ammonia. In water, ammonia exists in equilibrium between its un-ionized form and the ammonium ion; this equilibrium is dependent on temperature and pH. The USEPA water-quality criterion for protection of aquatic organisms is based on toxicity of un-ionized ammonia, so its value varies with temperature and pH. The USGS measures the sum of un-ionized ammonia and ammonium ion in solution, and expresses concentrations in units of milligrams of nitrogen per liter (mg/L as N). The USEPA chronic water-quality criterion for protection of aquatic organisms for ammonia, expressed in this form, varies from 0.07 to 2.1 mg/L as N, depending on temperature and pH (U.S. Environmental Protection Agency, 1986). Computation of the appropriate criterion value was made for each month at each site, using median water temperature and pH, according to methods reported by the U.S. Environmental Protection Agency (1986). The criterion was then compared with the monthly median dissolved-ammonia concentrations for the period of record.

Pesticides in Water

Aquatic-life criteria have been established for only 28 pesticides (table 16) of the 83 pesticides included in analysis of NAWQA water samples (appendix D). Of these, 6 have USEPA chronic water-quality criteria for protection of aquatic organisms, 21 have Canadian water-quality guidelines or Canadian interim guidelines, and 1 has a Great Lakes water-quality objective. The minimum data requirements for a site to be included in comparisons with pesticide water-quality criteria were the same as those imposed for evaluating the relative water-quality scores with the additional requirement that there be at least 8 months of data for a year to be included. If data for a site met the requirements for more than 1 year, data from all suitable years were included in the analysis. For each year of data for a site, the number of months with exceedances was divided by 12 to estimate the percentage of the year with one or more criteria exceeded.

Aquatic-Life Criteria for Bed Sediment

Aquatic-life criteria were evaluated for two groups of constituents in bed sediment: (1) organochlorine pesticides and PCBs and (2) SVOCs. Sediment-quality guidelines have been proposed by several agencies and organizations in different parts of the United States and Canada to assess potential effects of sediment contamination on aquatic life. A number of different approaches have been used to develop these guidelines, and no single approach is generally accepted (Persaud and others, 1993; U.S. Environmental Protection Agency, 1996c). For a given constituentin sediment, the available guideline values can vary by as much as 3 orders of magnitude. Therefore, the criteria used in this analysis were selected using procedures developed and used by U.S. Environmental Protection Agency (1996c) to analyze data in the National Sediment Inventory. These procedures use the available sediment-quality guidelines for a given constituent to classify sites into probability-of-adverse-effects classes (or tiers) on the basis of measured concentrations at those sites. 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.

In the NAWQA data analysis, criteria were determined using the procedures described by the U.S. Environmental Protection Agency (1996c) for establishing tier 1 sites. For two pesticides and three SVOCs at some sites, the USEPA procedures had to be modified slightly to suit the available data, as described below.

The USEPA procedure for classifying sites calls for assembling available sediment guidelines for a given constituent and designating each guideline as either an upper screening value (above which adverse effects may be severe or frequent) or a lower screening value (above which adverse effects may begin or occur occasionally). The first step in determining tier 1 classification for organic constituentsis to determine whether the measured concentration exceeds the USEPA proposed sediment-quality criterion (SQC) for protection of benthic organisms (available only for acenaphthene, dieldrin, endrin, fluoranthene, and phenanthrene) with site-specific adjustment for total organic carbon in sediment. For organic constituents with no USEPA SQC, or for any site without information on the total organic carbon content of the bed sediment, the USEPA procedure for tier 1 classification requires that the second lowest of the upper screening values be exceeded. Thus, tier 1 classification requires some consistency among available sediment guidelines in that two upper screening values must be exceeded for a site to be classified in tier 1. The U.S. Environmental Protection Agency (1996c) used the following upper screening values in its analysis of data in the National Sediment Inventory:

> USEPA SQC (with a default value of 1 percent total organic carbon in sediment for sites with no organic carbon data).
> USEPA sediment-quality advisory level (SQAL) for freshwater aquatic life (with a default value of 1 percent total organic carbon in sediment for sites with no organic carbon data).
> Effects range-median (ER-M) developed by Long and others (1995).
> Probable effect level (PEL) developed by MacDonald (1994) for the Florida Department of Environmental Protection.
> Apparent effects threshold-high (AET-H) developed by Barrick and others (1988).

For NAWQA data analysis, the USEPA procedures were slightly modified to facilitate the most consistent site-to-site comparisons possible and to include the greatest possible number of constituents. Total organic carbon measurements were available for about 93 percent of NAWQA sites, thus allowing assessment of tier 1 classification from the USEPA SQC using site-specific organic carbon data for the five compounds with USEPA SQCs. For the remaining 7 percent of NAWQA sites, the five compounds with USEPA SQCs were evaluated using organic carbon values estimated from data for nearby sites (instead of using the default 1-percent sediment organic carbon value and applying the second-lowest upper screening value). This modification makes comparisons of USEPA SQCs for the sites with missing organic carbon data as similar as possible to other sites in the national data set. In addition, although not used in the USEPA procedures described in U.S. Environmental Protection Agency (1996c), Canadian freshwater PEL values (Environment Canada, 1995) were included as a sixth upper screening value for the determination of tier 1 criteria values for NAWQA data analysis. Also, some additional ER-M values from Long and Morgan (1991) were used for a few constituents that do not have ER-M values listed in Long and others (1995). Use of the Canadian PEL values and the additional ER-M values increases the number of constituents for which at least two upper screening values were available. Inclusion of the Canadian PEL values also increases the number of upper screening values determined specifically for freshwater species.

Most of the bed-sediment chemistry data for NAWQA stream sites are based on one sample per site. For sites with multiple samples, median values were computed as described in the development of water-quality scores (WQS). In the study-unit summary reports, sites are designated as exceeding an aquatic-life criterion if the concentration of one or more constituents exceeds the applicable tier 1 boundary concentration.

Organochlorine Pesticides and PCBs in Bed Sediment

Following the procedures described above, sufficient criteria were available to determine a criterion (tier 1 boundary concentration) for the most commonly detected organochlorine pesticides and PCBs. Criteria used are listed with references in table 17. Note that criteria are included for total chlordane (the sum of cis-chlordane, trans-chlordane, cis-nonachlor, trans-nonachlor, and oxychlordane) rather than for the individual components of this mixture. Similarly, criteria are included for total DDT (the sum of o,p¢-DDD, p,p¢-DDD, o,p¢-DDE, p,p¢-DDE, o,p¢-DDT, and p,p¢-DDT) and for p,p¢-DDE (which is the most commonly detected component of total DDT) rather than for all individual isomers of DDT and metabolites. In table 17, the values listed for USEPA SQC have a default value of 1-percent sediment organic carbon.

Semivolatile Organic Compounds in Bed Sediment

Following the procedures described above, sufficient criteria were available to determine a criterion (tier 1 boundary concentration) for 18 of 66 SVOCs analyzed in NAWQA studies (appendix F). Criteria used are listed with references in table 18. The USEPA SQC and

USEPA SQAL values listed in table 18 have a default value of 1-percent sediment organic carbon.

Human-Health Criteria for Ground Water

Most concern about contaminants in ground water stems from the potential effects of contaminants on drinking-water supplies. Accordingly, human-health criteria are the focus for evaluating potential problems and determining the need for further investigation of ground-water quality. Only USEPA criteria were used to assess human health effects associated with drinking-water contaminants. There is no single type of USEPA criteria available for the broad array of constituents measured in NAWQA studies. Therefore, four types of USEPA criteria are used for evaluating NAWQA ground-water data: (1) maximum contaminant level (MCL), (2) secondary maximum contaminant level (SMCL), (3) risk specific dose (RSD), and (4) lifetime health advisory (HA-L). Values for these criteria were obtained from U.S. Environmental Protection Agency (1996a,b). The MCL is the maximum permissible level of a contaminant in water that is delivered to any user of a public water system. The SMCL is a guideline for contaminants that can adversely affect the odor or appearance of water for drinking-water use. The RSD is a guideline for potential carcinogens on the basis of drinking-water exposure over a 70-year lifetime; an RSD value is always associated with a specified cancer risk (maximum acceptable incidence of excess cancer). The RSD values used for NAWQA analysis are associated with a cancer risk of 1 in 100,000. The HA-L is a guideline for drinking-water exposure over a 70-year lifetime, considering noncarcinogenic adverse health effects. More detail on these types of criteria, their derivation, and their underlying assumptions is provided in Nowell and Resek (1994). For some constituents, more than one of these four criteria are available. For these constituents, the MCL was used if available; otherwise, the lowest of the SMCL, RSD (at 1 in 100,000 cancer risk), and HA-L values was selected.

Criteria for all constituents that have an established MCL, SMCL, RSD, or HA-L were compared with concentrations in ground-water sampled from NAWQA study areas. Comparisons were limited to study areas that are classified as representative of drinking-water aquifers. Criteria are compared to single measurements from individual sampling sites (wells or springs). Because ground water moves and changes relatively slowly, even a single sample can provide a useful evaluation of ground-water quality in relation to criteria designed for long-term exposure. The percentage of sampling sites at which one or more constituents exceeded the a pplicable criteria was computed for each ground-water study area.

Of the constituents considered for NAWQA ground-water quality scores, human-health criteria are available for nitrite plus nitrate, dissolved solids, some pesticides, and some VOCs. The MCL for radon is under review by the USEPA and is not used in this analysis. Of 83 pesticides analyzed (appendix D), 13 have MCLs, 5 have RSDs, 28 have HA-Ls, and 37 have no established USEPA human-health criteria. The 60 VOCs analyzed (appendix H) include four trihalomethane compounds (bromodichloromethane, dibromochloromethane, tribromomethane, and trichloromethane), which were summed and compared to the MCL for total trihalomethanes. Of the remaining 56 VOCs analyzed, 23 have MCLs, 3 have RSDs, and 12 have HA-Ls. No USEPA human-health criteria have been established for 18 of the analyzed VOCs. The human-health criteria used for nitrite plus nitrate and dissolved solids are listed in table 19, for pesticides in table 16, and for VOCs in table 20.

APPLICATION OF WATER-QUALITY RANKINGS AND CRITERIA FOR SUMMARIZING NAWQA RESULTS

Scores for each water-quality characteristic were computed for each NAWQA stream site and ground-water study area with adequate data. Sites (or study areas) were assigned a rank of 1 to 4 on the basis of the quartiles of the scores for all NAWQA sites in the 20 study-units investigated during 1992-1995. *The lowest category, with a rank of 1, contains* the 25 percent of sites with the lowest scores for the particular water-quality characteristic, and thus, generally represents the *best* quality for the particular characteristic in comparison with other NAWQA sites. The highest *category, with a rank of 4,* contains the 25 percent of sites with the highest scores, and thus, the poorest quality for the particular characteristic in comparison with other NAWQA sites. Symbols plotted on a map at the site or study area location show the quartile classification, with color coding to facilitate visual comparisons within and among study units. *Concentrations of individual constituents are compared with* established water-quality criteria for each water-quality characteristic, and stream sites or ground-water study areas with exceedances are indicated.

Results for the Central Columbia Plateau study unit (fig. 1) are presented and summarized as an example of the format used in study-unit summary reports (Williamson and others, 1998). Figure 4 shows results for water-quality characteristics of streams in the Central Columbia Plateau study unit. Figure 5 shows results for characteristics of ground-water study areas in the Central Columbia Plateau study unit. Four ground-water studies were done in the Central Columbia Plateau--three land-use studies of shallow ground water and one aquifer survey of public supply wells throughout the study unit. All four are classified as drinking-water aquifers (DWA) because the three land-use studies assessed shallow ground water that is tapped by domestic wells in the area. In study-unit summary reports, all ground-water study areas are evaluated for water-quality characteristics and all those classified as DWAs are included in comparisons with water-quality criteria.

SUMMARY AND CONCLUSIONS

Methods were developed to compare the water-quality conditions within and among 20 study units of the National Water-Quality Assessment (NAWQA) Program that were investigated during 1992-1995. Comparisons were made using two different approaches: (1) a relative ranking of major water-quality characteristics, and (2) an evaluation of individual constituents relative to established water-quality criteria. The relative ranking system was developed solely with data collected from the study units evaluated; the individual constituents were evaluated on the basis of established criteria, which are fixed values that are independent of the data from the study units.

For relative rankings, major characteristics of water quality were evaluated by using selected combinations of measured values for individual constituents or properties. Water-quality characteristics evaluated for streams were nutrients in water, pesticides in water, organochlorine pesticides and PCBs in bed sediment and tissue, semivolatile organic compounds in bed sediment, trace elements in bed sediment, fish community degradation, and stream habitat degradation. Water-quality characteristics evaluated for ground water were nitrate, pesticides, volatile organic compounds, dissolved solids, and radon.

Scores were computed for each water-quality characteristic for all stream sites and ground-water study areas for which adequate data were available. A rank of 1, 2, 3, or 4 was assigned to each characteristic for each site or study area on the basis of the quartiles of the water-quality scores for all sites or study areas. The rankings of water-quality conditions are based strictly on the values for the characteristics of stream sites and ground-water study areas included in the method-development data set. In general, the 20 NAWQA study units are widespread throughout the United States and include a broad diversity of environmental settings, but they are biased toward areas with greater-than-average population, water use, and agricultural and urban land use. The rankings serve as an initial comparative framework for summarizing the results of each study unit in relation to the other study units.

The water-quality rankings are designed to be updated and refined as the data on which they are based become more complete. As additional NAWQA studies are completed, data from many more sites in different areas of the Nation will be added to the database. Over time, updated evaluations will be increasingly representative of the Nation's water resources. Separate rankings can be developed (using the same general process) for more specific subcategories of the Nation's water resources, such as urban or agricultural streams, so that more specific questions about particular types of hydrologic systems can be addressed. In addition, the representation of water-quality characteristics can be improved, such as by standardizing contaminants by toxicity.

Established water-quality criteria were used as benchmarks for comparison and to indicate where particular constituents may cause adverse effects and thus merit further investigation. Established water-quality criteria were selected from a variety of sources and applied to specific constituents in the specific medium (water or sediment) appropriate for each criterion. Water-quality criteria change over time, however, as existing criteria are modified in response to new data, and legislative mandates and new criteria are added. The selection process described in this report will guide continued evaluation and updating of criteria used for assessing the environmental significance of NAWQA results.

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USGS
National Water Quality Assessment
Pesticide National Synthesis Project

Methods for Comparing Water-Quality Conditions Among National Water-Quality Study Units, 1992-1995

By Robert J. Gilliom, David K. Mueller, *and* Lisa H. Nowell
U.S. Geological Survey Open-File Report 97-589

FOREWORD

The mission of the U.S. Geological Survey (USGS) is to assess the quantity and quality of the earth 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. Assessment of water-quality conditions and trends is an important part of this overall mission.

One of the greatest challenges faced by water-resources scientists is acquiring reliable information that will guide the use and protection of the Nation's water resources. That challenge is being addressed by Federal, State, interstate, and local water-resource agencies and by many academic institutions. These organizations are collecting water-quality data for a host of purposes that include: compliance with permits and water-supply standards; development of remediation plans for specific contamination problems; operational decisions on industrial, wastewater, or water-supply facilities; and research on factors that affect water quality. An additional need for water-quality information is to provide a basis on which regional- and national-level policy decisions can be based. Wise decisions must be based on sound information. As a society we need to know whether certain types of water-quality problems are isolated or ubiquitous, whether there are significant differences in conditions among regions, whether the conditions are changing over time, and why these conditions change from place to place and over time. The information can be used to help determine the efficacy of existing water-quality policies and to help analysts determine the need for and likely consequences of new policies.

To address these needs, the U.S. Congress appropriated funds in 1986 for the USGS to begin a pilot program in seven project areas to develop and refine the National Water-Quality Assessment (NAWQA) Program. In 1991, the USGS began full implementation of the program. The NAWQA Program builds upon an existing base of water-quality studies of the USGS, as well as those of other Federal, State, and local agencies. The objectives of the NAWQA Program are to:

- Describe current water-quality conditions for a large part of the Nation's freshwater streams,

rivers, and aquifers.
- Describe how water quality is changing over time.
- Improve understanding of the primary natural and human factors that affect water-quality conditions.

This information will help support the development and evaluation of management, regulatory, and monitoring decisions by other Federal, State, and local agencies to protect, use, and enhance water resources.

The goals of the NAWQA Program are being achieved through ongoing and proposed investigations of 60 of the Nation's most important river basins and aquifer systems, which are referred to as study units. These study units are distributed throughout the Nation and cover a diversity of hydrogeologic settings. More than two-thirds of the Nation's freshwater use occurs within the 60 study units and more than two-thirds of the people served by public water-supply systems live within their boundaries.

National synthesis of data analysis, based on aggregation of comparable information obtained from the study units, is a major component of the program. This effort focuses on selected water-quality topics using nationally consistent information. Comparative studies will explain differences and similarities in observed water-quality conditions among study areas and will identify changes and trends and their causes. The first topics addressed by the national synthesis are pesticides, nutrients, volatile organic compounds, and aquatic biology. Discussions on these and other water-quality topics will be published in periodic summaries of the quality of the Nation's ground and surface water as the information becomes available.

This report is an element of the comprehensive body of information developed as part of the NAWQA Program. The program depends heavily on the advice, cooperation, and information from many Federal, State, interstate, Tribal, and local agencies and the public. The assistance and suggestions of all are greatly appreciated.

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NAWQA Pesticide
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Methods for Comparing Water-Quality Conditions Among National Water-Quality Study Units, 1992-1995

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U.S. Geological Survey Open-File Report 97-589

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Multiply	By	To obtain
kilometer (km)	0.6214	mile
square kilometer (km^2)	0.3861	square mile

Temperature is given in degrees Celsius (°C) which can be converted to degrees Fahrenheit (°F) by the following equation: °F = (1.8 x °C) + 32

Abbreviations and Acronyms

gal/d, gallon per day
µg/g, microgram per gram
µg/kg, microgram per kilogram
µg/L, microgram per liter
mg/L, milligram per liter
mg/L as N, milligram of nitrogen per liter
pCi/L, picocuries per liter

AET-H, apparent effects threshold-high
AS, aquifer surveys
AVHRR, Advanced Very High Resolution Radiometer
CAS, Chemical Abstracts Service
CCREM, Canadian Council of Resources and Environmental Ministers
DWA, drinking-water aquifer
ER-M, effects range-median
FSV, factor summary value
GCMS, gas chromatography/mass spectroscopy
HA-L, lifetime health advisary
HPLC, high-pressure liquid chromatography
IBI, Index of Biotic Integrity
IJC, International Joint Commission
LUS, land-use studies
MCL, maximum contaminant level
NAWQA, National Water-Quality Assessment
NM, national median
PAH, polycyclic aromatic hydrocarbon
PCBs, polychlorinated biphenyls
PEL, probable effects level
PTD, mean point-to-tree distance for a reach, in meters
RD, relative density of riparian vegetation
RSD, risk specific dose
SGW, shallow ground water

SMCL, secondary maximum contaminant level
SQAL, sediment-quality advisory level
SQC, sediment-quality criterion
SVOC, semivolatile organic compound
USEPA, U.S. Environmental Protection Agency
USGS, U.S. Geological Survey
VOC, volatile organic compound
WQS, water quality score

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