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Handbook

Stream Sampling for Waste Load Allocation Applications

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Handbook

Stream Sampling for Waste Load Allocation Applications

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Abstract

This report discusses sampling requirements in support of waste load allocation studies in rivers and streams. Two approaches to waste load allocation are addressed: the chemical-specific approach and the whole effluent approach. Numerical or analytical toxicant fate models are used to implement the chemical-specific approach. Modeling requirements and sampling guidelines are delineated for this method.

For the whole effluent approach, the method is first summarized and then instream dye study requirements are presented. The report concludes with example applications of the chemical-specific approach for conventional and toxic pollutants.

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Chapter 1
Introduction

1.1 Background

The United States Environmental Protection Agency's Monitoring and Data Support Division is presently developing guidance manuals that describe approaches for allocating waste loads in rivers and streams, lakes and impoundments, and estuaries. The pollutants addressed in the manuals are biochemical oxygen demand/dissolved oxygen, nutrients, and toxic substances (ammonia, organics, and metals). Other manuals in the series present related topics, such as how to select the critical conditions for the waste load allocation (WLA) (e.g., the appropriate stream flow). Table 1-1 summarizes the documents.

Water quality simulation models are often used for WLA purposes. These models must adequately predict water body responses to different waste loads when large financial expenditures are at stake. Consequently, where feasible, models should be calibrated and verified prior to allocating waste loads. Sufficient historical data to accomplish these objectives are often lacking and of the wrong type, and additional data should be collected. Water quality specialists, therefore, have to decide what data are missing and their importance, and then design surveys to gather any required information. This handbook is intended to guide specialists through these steps for waste load allocations in rivers and streams. Both the chemical specific and whole effluent approaches to WLA are discussed.

This handbook can be used in conjunction with Book II, Rivers and Streams, with Book VI, Design Conditions, and with appropriate sections of Book VIII, Screening Manual. Book V, The Technical Support Document for Water Quality-based Toxics Control, will be useful as well (See Table 1-1).

Because the river water quality model QUAL-II (1,2) and its followup QUAL-2E (3) is widely used for WLA applications and is supported by the USEPA's Center for Water Quality Modeling, example stream survey designs for this particular model are included in this handbook. Stream survey guidance for the toxicant models TOXIWASP (4) and MICHRIV (5) are provided as well. Users of other models will find much of the guidance applicable to their models because of similarities in model requirements.

1.2 Purposes of Handbook

The primary purpose of this handbook is to help water quality specialists design stream surveys to support modeling applications for waste load allocations. The planner is guided through the data collection process so that models used for WLA can be calibrated, verified, and applied to the critical design conditions. Field sampling requirements of the whole effluent approach to waste load allocation are also addressed.

This handbook does not discuss a number of facets of stream sampling where significant reference materials already exist. These areas include:

- equipment requirements
- personnel requirements
- collection of samples
- determination of stream geometrical and flow characteristics
- laboratory analytical techniques.

The Appendix summarizes the appropriate literature in these categories. The references are primarily from the U.S. Geological Survey's Water Resource Investigation series, the U.S. Fish and Wildlife's Instream Flow Information series, and from the U.S. Environmental Protection Agency.

This handbook also recognizes that waterborne viruses are pollutants which produce definite health effects. However, these pathogens cannot be considered in the wasteload allocation process which are involved only with parameters that have established water quality criteria.

The second purpose of this handbook is to show how models can be used to help design stream surveys. Since the models will eventually be used to predict the allowable waste loads, they can be set up and applied before the stream surveys are finished. This will assist planners in examining the available data, allow preliminary sensitivity analyses to be made, and thereby help identify the most needed data. Stream surveys can then focus on the collection of such data, and de-emphasize data that are less important or previously well characterized.

The third purpose of this handbook is to educate field personnel on the relationship between sampling requirements and modeling requirements. Field

Table 1-1. Waste Load Allocation Guidance Documents

Waste Load Allocation Guidance	
Book I	*General Guidance*
Book II	*Streams & Rivers*
	BOD/DO
	Nutrients/Eutrophication
	Toxic Substances
	Simplified Methods for POTWs
Book III.	*Estuaries*
	BOD/DO
	Nutrients/Eutrophication
	Toxic Substances
Book IV.	*Lakes & Impoundments*
	BOD/DO
	Nutrients/Eutrophication
	Toxic Substances
Book V.	*Technical Support Document for*
	Water Quality-Based Toxics Control
Book VI.	*Design Conditions*
	Design Flow
	Design Temperature
	Design pH
	Design Effluent Flow
	Design Rate Constants
Book VII.	*Permit Averaging*
Book VIII.	*Screening Manual*
	BOD/DO
	Toxic Organics
	Toxic Metals
	Nutrients/Eutrophication
Book IX.	*Innovative Waste Load Allocations*

*Available from Monitoring and Data Support Division, USEPA (WH553), Washington, D.C. 20460. See latest Monitoring and Waste Load Allocation status report for completion dates for these documents.

personnel may sometimes question why historical data are not adequate, why specially designed surveys are often required to generate the data, and why certain sampling locations and parameters are selected. By understanding the factors that go into the selection process, field personnel are likely to perform their tasks more effectively. When unforeseen field conditions dictate a change in sampling strategy, there is a better basis for deciding how to modify the sampling program design.

1.3 Overview of Approach

Figure 1-1 summarizes the approach to stream survey design discussed in this handbook. Two parallel approaches are possible: the chemical specific approach and the whole effluent approach.

The chemical specific approach is selected if the pollutants to be allocated are conventional pollutants, or if toxic pollutants are to be allocated on a toxicant-by-toxicant basis. For example, if BOD/DO and copper are to be allocated, then QUAL-2E and MICHRIV might be the water quality models selected for the allocation.

Sampling periods to collect data for model calibration and verification are then selected. *Model calibration* refers to the process of adjusting model parameters so predictions acceptably match field data. Calibration often requires that some of the input data, particularly rate constants (e.g., BOD decay rate) be adjusted within realistic limits to provide better agreement between observations and predictions. *Model verification* is a comparison of model predictions against an independent set of field data. A model or model component is verified when predictions and observations agree without having to arbitrarily adjust model coefficients.

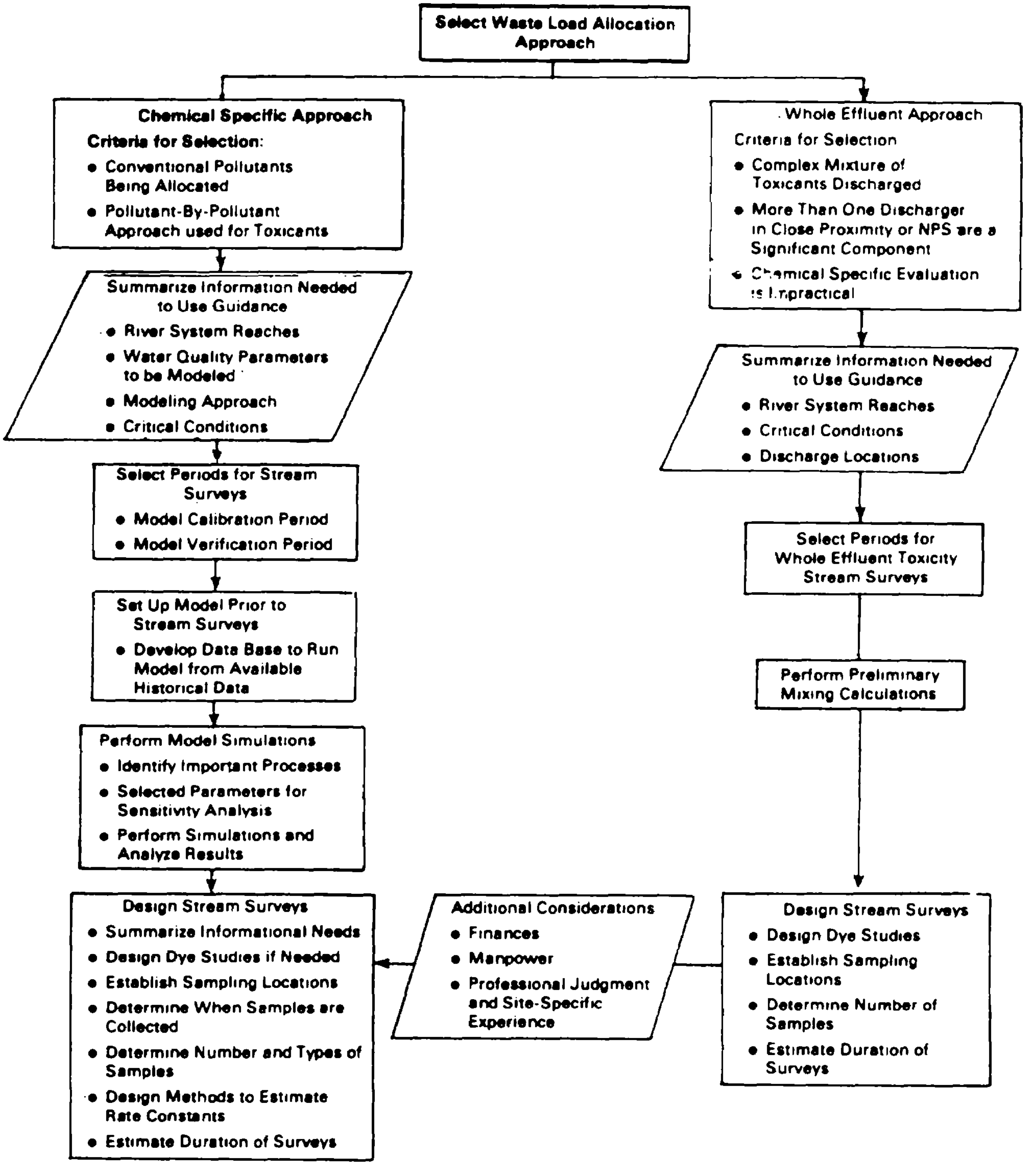
Stream surveys used to calibrate and verify models are typically intensive *synoptic surveys*. These are surveys that are usually completed within a week or so, and are intended to provide a definition of river responses to a specific set of loadings.

Since the models or calculation methods to be used in the WLA process will eventually be adapted to the river systems where sampling is to be conducted, model adaptation to the system should be completed prior to sampling. The models are used to simulate the parameters to be allocated and at the conditions expected to be encountered during the surveys (based on the best information available prior to sampling). This will encourage the specialist to examine the available data, determine what is missing, and to estimate values of the missing data. Then, by performing sensitivity analyses (i.e., by varying parameters and observing the effect on model outputs), the specialist can establish which data are more likely to influence model predictions and thus establish sampling frequencies and location. Locations where water quality conditions change most rapidly and where water quality standards are not expected to be achieved are the critical areas to find and sample.

Stream survey design for model calibration and verification can then be rationally executed with informational needs fairly well defined. Often, dye studies are needed to accurately estimate pollutant travel time through the river. Travel time reflects the average velocity over distance, and can be quite different from the velocity measured by a current meter at a cross section, especially if the river cross section changes from location to location. Normally, travel time studies are conducted at more than one stream flow so that travel times can be estimated at the critical flow.

Sampling locations are established considering accessibility, historical locations, critical points of maximum or minimum concentration, and other locations where water quality standards are expected to be violated. Other considerations include intervals between samples (smaller intervals are typically used where stream response is most rapid) and point source sampling. Sampling just below a point source is risky because of the likelihood of obtaining un-

Figure 1-1. Summary of stream survey design consideration for chemical specific approach and whole effluent approach to waste load allocation.



representative samples (point source discharges may not rapidly mix with stream flow), and often a mass-balance calculation using the point source and a location just upstream is preferable. Where the pollutant sources cannot be adequately measured, a downstream sample will be necessary to back calculate the load from nonpoint source (NPS) pollution, agricultural runoff, or point sources that cannot be adequately measured.

Special consideration is required for rate constant determinations. Typically, rate constants, such as the reaeration rate coefficient, are not directly measured but are determined through a series of indirect measurements, or are based on model calibrations. Field determinations of rate coefficients can be costly, and the specialist should justify the need prior to recommending this aspect of the field study.

Stream survey design and implementation must be tempered by factors such as financial resources and man-power limitations and should be conducted during critical conditions if at all possible. The judgement and experience of water quality specialists who are not necessarily modelers but who have considerable experience with the natural waters of interest must also be weighed. The importance of the data that are to be collected can help to guide and prioritize sampling program activities. All environmental monitoring tasks performed under EPA sponsorship must also be conducted under an approved Q.A. project plan following guidance provided by the EPA. Quality assurance is especially important when sample number is limited due to other project considerations.

The second approach to WLA of toxicants is called the *whole effluent approach*. Streams that receive complex or multiple effluent discharges may present a complicated sampling problem. All potential pollutants in complex wastes may not be identified nor their interactions assessed. In turn, pollutant bioavailability may be difficult to measure. The EPA has recently evaluated and validated this approach for setting discharge limits based on effluent toxicity (6,7).

For this approach, total toxicity in a river is treated conservatively. Under certain circumstances, an effective decay rate can be estimated based on toxicity decrease over distance below an outfall (6). Traditional chemical-specific toxicant models are not required for this approach.

The whole effluent approach may be used alone or in many cases in conjunction with the chemical specific approach to WLA. As pointed out in EPA policy, both approaches will be needed in many cases. In this manner it may be possible to develop a more complete evaluation of instream effluent effects. The primary objective of field sampling in support of the whole effluent toxicity approach is to determine mixing characteristics of the effluent in the stream or river and to determine whether toxicity is decreasing due to decay processes.

Every effort should be made to visit the proposed sampling locations during a brief field reconnaissance before executing the stream surveys for model calibration/verification. This will help to establish the accessibility of the selected locations, or to decide if for any other reason a sampling location change should be made.

Chapter 2
Sampling Requirements for Waste Load Allocation Modeling

2.1 Model-Independent Considerations

Sampling requirements for water quality modeling depend to some extent on the particular model or calculation procedure being used. This in turn depends on the type of problem being studied and the level of detail required in the modeling analysis. Models can range in detail from dilution models or simple Streeter-Phelps type models of dissolved oxygen to complicated models of stream ecosystems which include many interacting processes and variables, for example, oxygen dynamics, nutrient cycles, and algal and zooplankton dynamics. The major distinctions between different models are the specific parameters and processes modeled, the equations used to describe each process, the numerical techniques used to solve the equations, and whether the models are dynamic or steady-state.

However, in spite of these differences, all models share many common features. As a result, many sampling considerations are the same regardless of the specific model or the particular WLA problem being addressed. These model-independent considerations are discussed in this section. Sampling considerations specific to particular types of problems and specific models are discussed in the following sections.

2.1.1 Stream Geometry Data

All models require essentially the same types of information to define the geometric characteristics of the stream. Stream systems are divided into a series of reaches for model analysis, with each reach described by a specific set of channel geometry (i.e., cross-sectional dimensions) and flow characteristics (i.e., flow rates, depths, and velocities or time of travel). Reaches are defined between all major tributary junctions and flow diversions, or whenever stream geometry, hydraulic conditions, or biochemical processes (i.e., sediment oxygen demand) within the stream are expected to change significantly. The models assume that these conditions are uniform within each reach.

Each reach is in turn divided into a series of model segments or computational elements in order to provide spatial variation for the water quality analysis (Figures 2-1 and 2-2). Each segment is represented by a grid point in the model where all water quality variables are computed. The number and size of the segments depends on the spatial resolution desired. Enough detail should be provided to characterize anticipated spatial variation in water quality due to different pollutant sources, dissolved oxygen sags, and other significant processes within the stream. In general, the model grid must have a much higher resolution than the sampling network for computational reasons. For example, Figure 2-3 shows the effects of varying the grid resolution on dissolved oxygen predictions. The low resolution grid flattens out the dissolved oxygen sag curve due to the effects of numerical mixing in the model. Although 10 sampling locations are more than adequate to define the dissolved oxygen profile in the field, the use of only 10 computational nodes in the model results in inaccurate predictions.

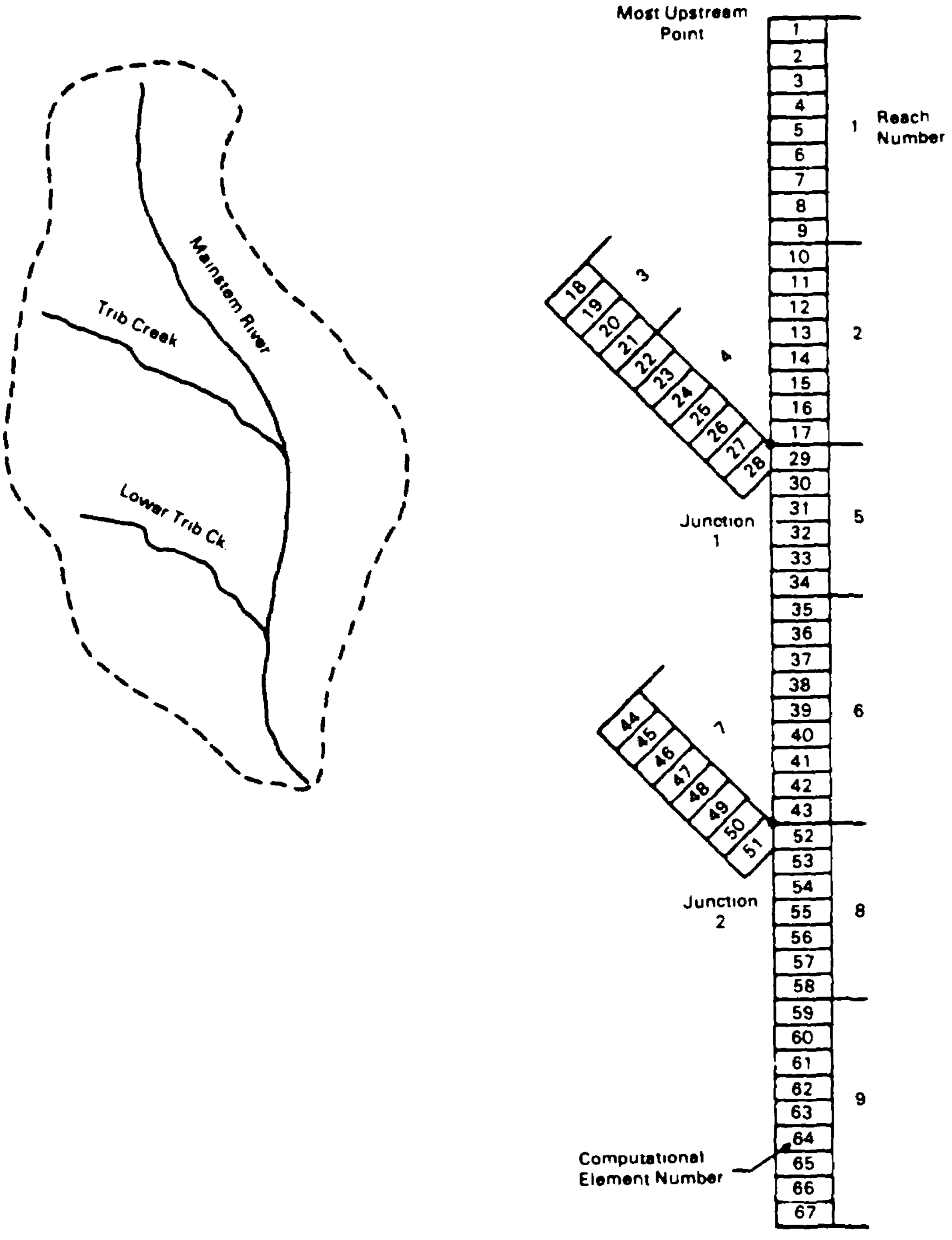
Channel geometry data are used to define the stream configurations and segment characteristics, regardless of the particular model being used. This includes both hand calculation methods and computerized modeling techniques. Additional types of geometry data may also be necessary depending on the hydrologic algorithm used to route the flows through the system. The basic types of data required for each reach include:

1. segment or reach length
2. variation of channel width and cross-sectional area with depth
3. bottom slope (or bed elevations)
4. variation of wetted perimeter or hydraulic radius with depth
5. bottom roughness coefficient (Manning's n).

Variation of water depth with flow is also important, but will be discussed later in the hydraulic data section. All of the above parameters are typically assumed constant for all model segments within a defined reach.

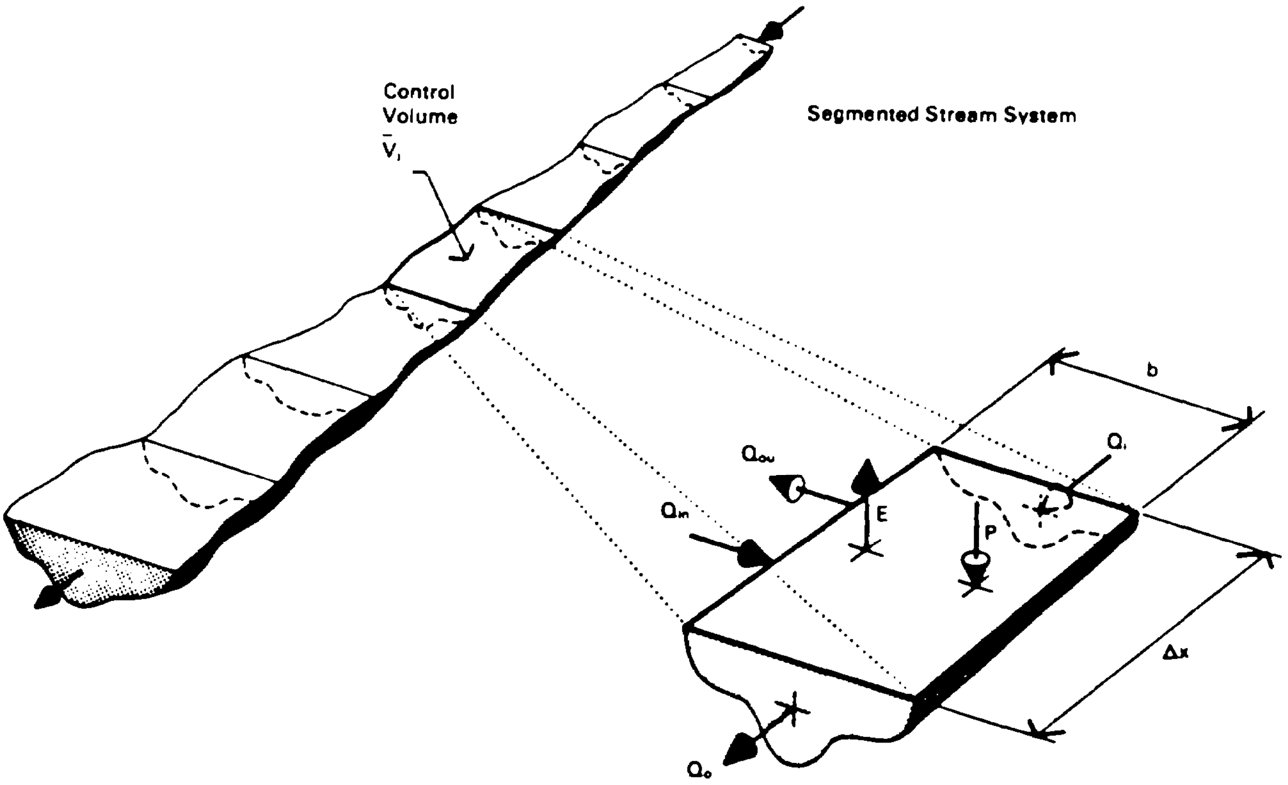
Length and average slope over long distances can be determined from topographic maps, while the other variables usually require field surveys. The first two

Figure 2-1. Example stream network showing reaches and computational elements (1,2,3)



data types, length and cross-sectional area, are fundamental to any modeling study. The remaining information may or may not be required, depending on the type of hydraulic computations used in the model. For example, if stage-flow relationships are used to describe the hydraulics (e.g., QUAL-2E, and SSAM IV (8), then only lengths and cross-sectional areas are required to fully define transport through the system. However, if Manning's equation (e.g., option in QUAL-2E) or the St. Venant equations (e.g.,

Figure 2-2. Physical representation of a stream by model segments (adapted from (10)).



RECEIV-II (9), and WQRRS (10) are used to route the flow, then the additional information (items 3 through 5 above) will be necessary for the hydraulic computations.

Many models internally compute the cross-sectional area as a function of depth based on idealized representations of the channel shape. For example, if a trapezoidal channel is assumed, only the bottom width and side slopes need to be specified. For a rectangular channel, only the width is needed.

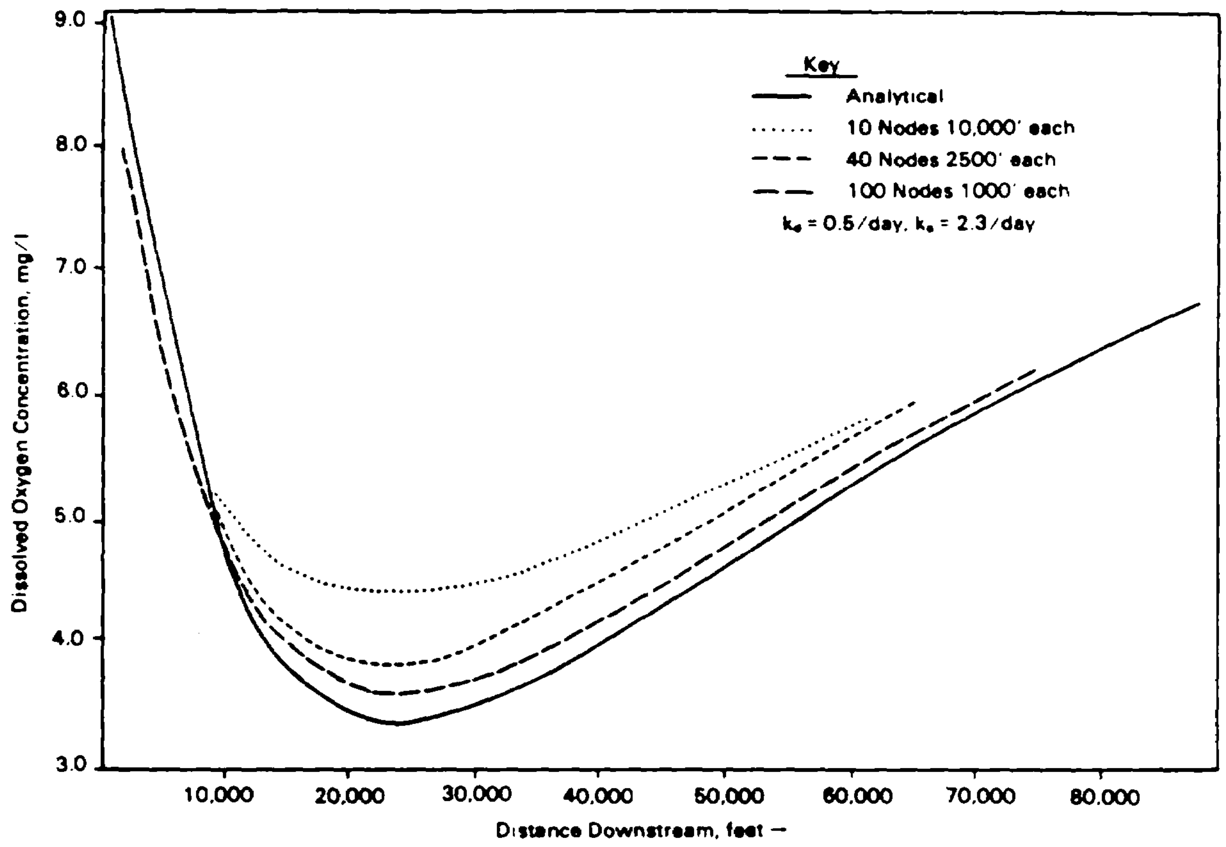
The level of detail required in describing the stream geometry depends on the amount of variability in the system. For streams which have uniform slopes and cross-sections over the study area, only a few transects will be necessary. However, in areas where the channel geometry varies widely, the stream should be divided into a series of representative reaches, and enough transects measured along each reach to adequately characterize the geometry. Three to five cross-sections could be measured along each reach, and the results could be averaged to define the reach characteristics for the model. As a minimum, one representative cross-section should be measured in each reach. Some pool and riffle streams may require dye studies and measurement of as many cross sections as possible to obtain adequate stream geometry.

2.1.2 Hydraulic Data

Hydraulic data are needed to define the velocities, flows, and water depths for the transport calculations that are used to describe how pollutants move down stream. Enough data are necessary to characterize the hydraulic regime throughout the study area. This includes the flows at the upstream boundaries of all channels, as well as all significant tributary inflows, lateral inflows (from groundwater or runoff), flow diversions, return flows and stage at some locations. In a general analysis, waste flows which represent a significant portion (i.e., greater than 5 to 10 percent) of the total stream flow should also be included in the hydraulic analysis. Enough flow sources should be characterized so that 90 to 95 percent of the total stream flow is accounted for in the analysis.

While the upstream boundary flows, tributary flows, and diversion flows can be measured directly, lateral

Figure 2-3. Effects of grid resolution on predicted dissolved oxygen profiles using an explicit finite difference solution scheme



inflows from ground water or runoff must be estimated from differences in measured flows at different locations along the stream channel.

Many models allow the specification of stage-flow relationships for each channel reach in the system. This requires the simultaneous measurement of water depth and flow for a series of flows over the range of interest. While a minimum of two values are necessary to construct a stage-flow rating curve, three or more values are desired for more accurate relationships. If possible, the flows measured should cover the range of conditions to be addressed in the WLA analysis. For a preliminary analysis it may be possible to estimate the relationship between d, A, V and Q at gauging stations. However, these stations are rarely representative of long reaches because these stations are located at control points in a stream where a unique relationship exists between stage and Q.

Stage-flow curves are constructed by plotting depth versus flow on log log paper since depth and flow can be related by an exponential equation of the form:

$$d = a_1 Q^{b_1} \qquad (2\text{-}1)$$

where d = water depth
Q = flow
a_1 = coefficient of stage-flow relationship
b_1 = exponent of stage-flow relationship

The coefficient a_1 and exponent b_1 of Equation (2-1) are determined from the intercept and slope of the log-log plot (Figure 2-4). Similar relationships can be developed for cross-sectional area and velocity as functions of flow:

$$A = a_2 Q^{b_2} \qquad (2\text{-}2)$$

$$V = a_3 Q^{b_3} \qquad (2\text{-}3)$$

where A = cross-sectional area
U = velocity
a_2 = coefficient for cross-sectional area vs. flow relationship
b_2 = exponent for cross-sectional area vs. flow relationship
a_3 = coefficient for velocity vs. flow relationship
b_3 = exponent for velocity vs. flow relationship

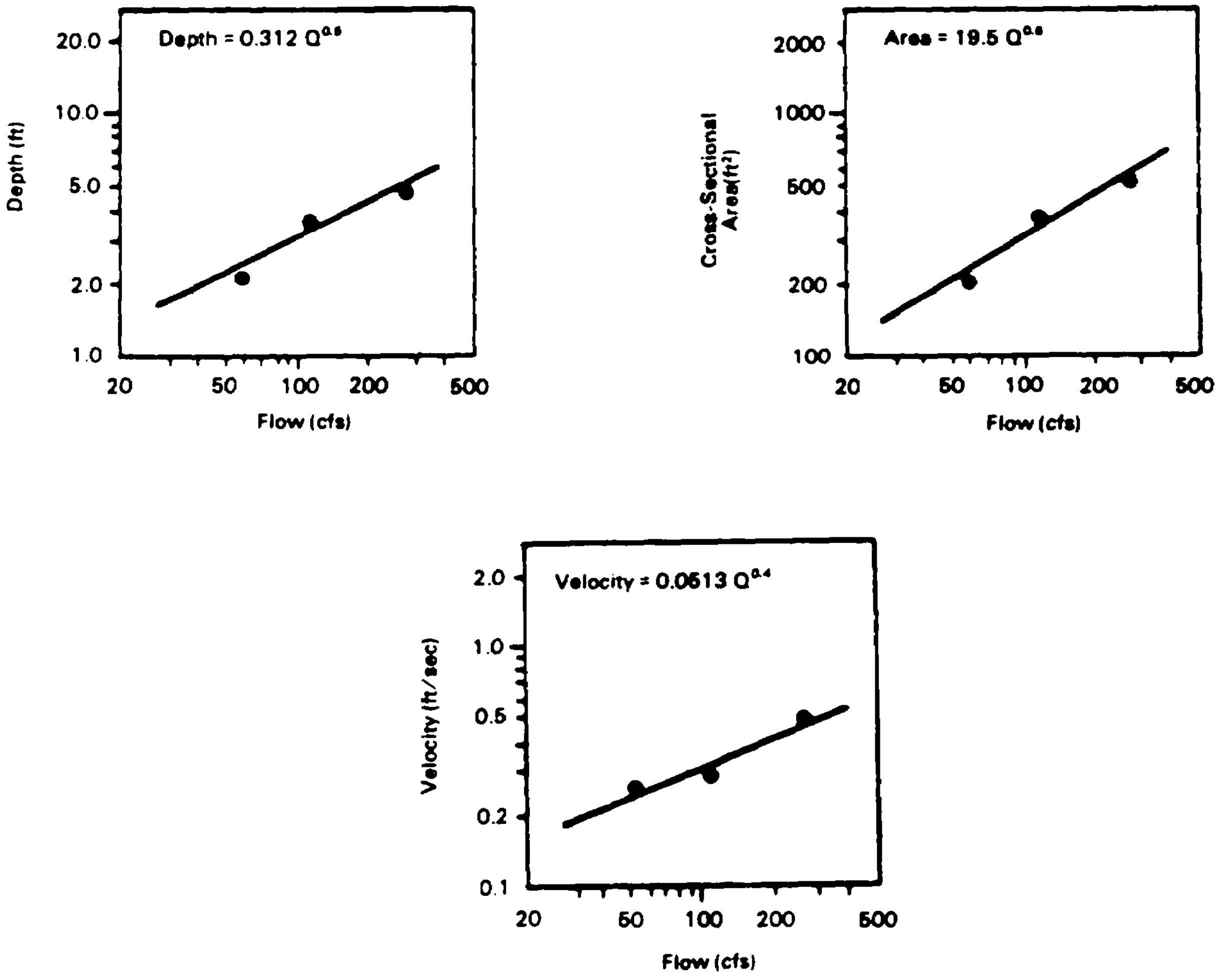
Cross-sectional area as a function of depth is obtained from the channel geometry data, and velocity is computed from the flow continuity equation ($U = Q/A$). These data are plotted against flow on log-log paper to determine the values of the coefficients and exponents in Equations (2-2) and (2-3) (Figure 2-4). These parameters are required as input to certain stream water quality models. There are considerable geometry data available from: 1) USGS, especially new gauging stations, 2) COE near reservoirs and proposed reservoirs (also from Bureau of Reclamation, TVA, Bonneville Power), 3) FEMA flood insurance studies, 4) National Weather Service forecasting centers. In areas where stream bed varies with time, it is important to use the most recent geometry data.

Both the stream geometry and flow information are critical to the transport calculations. When the stream geometry varies widely within reaches and is difficult to characterize in detail, or when lateral inflows are not well defined (for example, because access problems limit measurement), it is often useful to supplement the hydrologic and geometric data with travel time studies using tracer techniques, typically with rhodamine WT dye. This information can be used to adjust the geometry or flow data so that model transport calculations match the results of the dye study. This calibrates the transport portion of the water quality model by defining the geometry or flow data to produce the net transport observed in the field.

2.1.3 Meteorological Data

Because temperature influences dissolved oxygen saturation and the rates of almost all of the chemical and biological processes occurring in streams, many water quality models include options for simulating temperature. Meteorological data are necessary to perform the heat budget computations in these models. Heat transfer at the air-water interface depends on several processes including short-wave solar radiation, long-wave atmospheric radiation,

Figure 2-4. Derivation of cross-sectional area vs. flow and velocity relationships from stage-flow data (from (11)).



long-wave back radiation, convective heat exchange, and evaporative heat loss. Most models compute each of these processes separately and add them together to give the net heat flux at the water surface. The alternative method is the equilibrium temperature approach in which all of the above processes are combined into two parameters: the equilibrium temperature and the surface heat exchange coefficient, both of which vary dynamically with the meteorological conditions. In fact, the equilibrium temperature formulation is essentially equivalent to the linearized version of the total heat budget which is used in most water quality models, including QUAL-2E.

The basic types of meteorological data required are essentially the same regardless of the particular model being used:

1. solar radiation
2. cloud cover
3. air temperature
4. relative humidity (or wet bulb temperature or dew point temperature)
5. wind speed
6. atmospheric pressure.

Many models compute incident solar radiation internally in the model as a function of latitude, longitude, day of the year, time of the day, and atmospheric scattering and absorption of light due to dust. Cloud cover data are then required to compute the amount of solar radiation reaching the water surface. The alternative approach used in other models is to input measured solar radiation directly. In mountainous areas, canyons, or in areas where riparian vegetation is dense, additional reduction in solar radiation due to topographic and vegetation shading should be included in the model. This is handled by an additional shading coefficient, by detailed formulations which compute the shading dynamically (12), or by inputing net solar radiation values which include these effects.

The five meteorological variables listed above can often be obtained from nearby weather stations. Most NOAA class A stations have monthly averages of these variables available. Long term monthly averages of these parameters based on several years of historical data are also available in the "Climatic Atlas" published by the National Oceanographic and Atmospheric Administration (13). More detailed records of meteorological data at 3-hour intervals can often be obtained on magnetic tape from the National Climatic Data Center, Federal Building, Asheville, North Carolina 28801 (phone (704) 259-0682).

Existing weather stations are usually adequate when studying larger rivers, streams near weather stations, or when water temperature and volatilization are not critical components of the model study. In other cases, temporary weather stations can be set up. A single station is generally sufficient. However, in areas where solar radiation, atmospheric pressure and temperature varies over the length of a river (greater than 1000 feet in elevation), it may be desirable to set up two stations, one near the upstream boundary and one near the downstream boundary of the study reach.

2.1.4 Water Quality Data

Given the semi-empirical nature of water quality models, water quality data are necessary to setup, calibrate, and verify any water quality model. Input data are needed for all parameters which will be simulated. For models like QUAL-2E that simulate conventional pollutants, this may include temperature, dissolved oxygen, carbonaceous BOD, phosphorus, nitrogen (ammonia, nitrite, and nitrate), coliforms, chlorophyll *a* or phytoplankton dry weight biomass, and conservative constituents such as total dissolved solids. Some models also include additional constituents such as total inorganic carbon, alkalinity, pH, inorganic suspended solids, suspended organic detritus, periphyton, zooplankton, and benthic organisms. Toxic fate models require data for the specific chemicals under investigation.

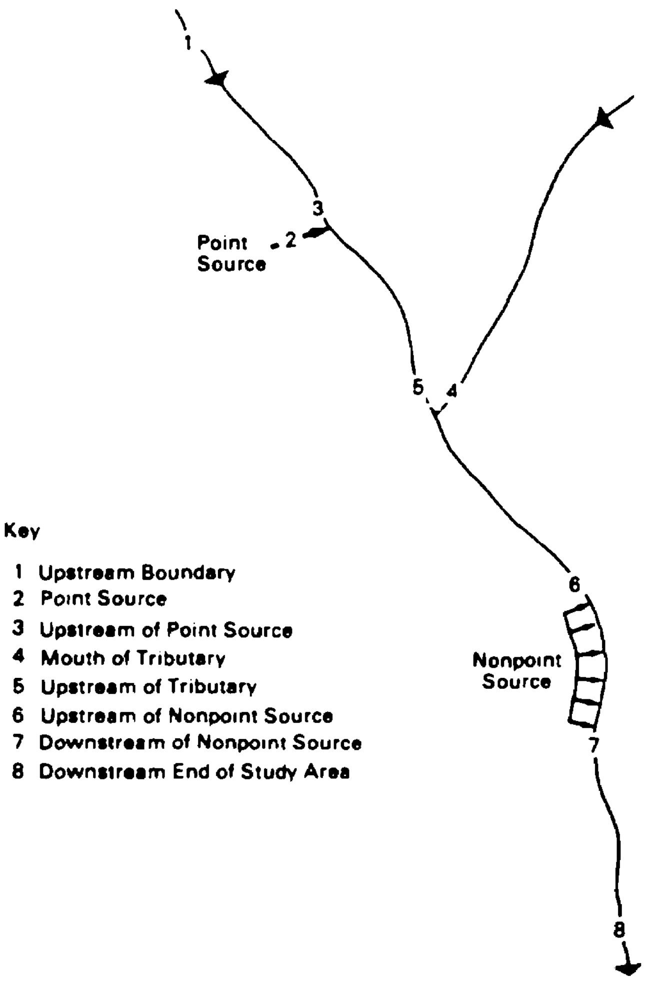
It is only necessary to collect data for the particular constituents and processes which are being evaluated, plus any other variables which significantly affect these constituents. For example, if coliforms are not of interest, there is no need to collect data for them even though they may be included in the model since they do not influence the other constituents. Any arbitrary value could be assigned to coliforms, or they could be set equal to zero when running the model. Some models (e.g., QUAL-2E), DOSAG3 (14), RECEIV-II, WQRRS (14), SSAM IV (8), HSPF (15) include options which allow the user to "switch off" many of the model constituents when running the model. This bypasses the computations for parameters which are of no importance in a particular application.

This section discusses some of the water quality sampling considerations which are basic to all WLA studies. Sampling considerations which pertain to particular types of problems (e.g., DO/BOD analyses) will be discussed later.

2.1.4.1 Sampling Locations

After an initial estimate of the constituents and parameters which must be sampled in a modeling study, it is necessary to determine where, when, and how often the samples should be taken. The *minimal* instream sampling effort should include the following locations (Figure 2-5):

Figure 2-5. **Recommended locations for a minimal sampling program.**



1. Upstream end (headwater) of each stream reach and tributary being modeled.
2. Mouths of all significant tributaries which are not included in the model grid, just above their entrances to the main stream.
3. Effluent samples of all significant point sources before they enter the stream.
4. Upstream and downstream ends of stream sections where nonpoint sources are expected to be significant.
5. Downstream end of the study area.

Water quality data are needed at the upstream extremities of all channels in the modeled stream system in order to define the upstream boundary conditions (i.e., flows and concentrations) for the computations. The model starts with these boundary conditions and routes the water along the channels, simulating all of the chemical, biological, and physical processes which act to change the concentrations of the various constituents. The water quality samples at the upstream boundaries also define the background concentrations in the study area before additional pollutant loads are added to the stream.

For tributaries which are not explicitly included in the model grid, water quality data are needed just above their mouths in order to define tributary loading rates for all constituents. However, if the flow contributions and mass loadings of tributaries are insignificant in comparison to the main channel flows and mass fluxes (i.e., less than 5 percent), they can usually be omitted from the analysis. Loadings due to tributaries which are included as part of the model grid are computed internally in the model based on the specified upstream boundary concentrations at the head of the tributary and the simulated water quality changes between the tributary headwater and confluence with the main stream.

In addition to instream concentrations, effluent data are needed to characterize pollutant loadings due to all significant point source discharges. These data can be obtained from the dischargers, NPDES permit holders, and federal, state, and local government regulatory agencies. However, it is most desirable to collect point source data during the survey, as historical data bases may not be indicative of survey loads.

In areas where significant nonpoint source loadings are known to exist, both the flow rate and constituent concentrations should be measured in the stream just above and below the area of the loading. If this area is not so large that other water quality changes are likely to occur during the travel time through the area, it is reasonable to assume that the changes in concentrations are due to the nonpoint sources and to use these differences as a basis for estimating the loads.

Water quality data should be collected at the downstream end of the study area for calibration and verification. While a single downstream station is the minimum requirement for short stream sections with no major tributaries, additional sampling stations are desirable to provide more spatial data for calibrating and verifying the model. Logical locations for additional stations are biologically sensitive areas, areas where water quality standards may be violated, areas just above major tributaries or point source loadings, and areas where stream changes may significantly cause changes in kinetics. The latter locations allow independent calibration of stream sections between each tributary or discharge based primarily on biochemical processes within the stream without the complication of water quality changes associated with major inflows or discharges. Water quality below tributary junctions or waste discharges can be directly computed based on data above the junction or discharge site and the tributary or point source loading rates using simple flow weighted mixing computations:

$$C_b = \frac{Q_s C_s + Q_1 C_1}{Q_s + Q_1} \qquad (2\text{-}4)$$

where C_b = average concentration below tributary or discharge

C_s = concentration in stream above the tributary or discharge

C_1 = concentration in tributary or discharge

Q_s = stream flow above the tributary or discharge

Q_1 = tributary or discharge flow rate

These values can then be used as upstream boundary conditions to calibrate the next section of the stream. Since most stream models are one-dimensional, water quality is assumed to be well mixed and uniform over each cross-section of the stream. Therefore, samples taken immediately downstream of a discharge or tributary would probably not match conditions in the model unless they were taken far enough downstream for complete cross-sectional mixing to occur (Figure 2-6) (see Section 3.4 for a method to estimate the distance for complete mixing). If a stream branches into two separate channels moving downstream, it is also useful to include a sampling station at the head of the branch to define upstream conditions in each reach.

In addition to the above sampling locations which are based on the stream system configuration and waste discharge locations, it is desirable to include more stations where significant water quality gradients are expected, for example, dissolved oxygen sags below waste discharges. These stations provide data to calibrate and verify the ability of the model to predict important water quality variations. The appropriate locations for these additional stations are often difficult to determine in advance. Simplified screening calculations or preliminary model runs can often be useful in locating these stations. Guidance for determining these locations will be discussed in later sections where sampling considerations for specific types of water quality problems are discussed.

2.1.4.2 Sampling Time and Frequency

If possible, water quality sampling should be conducted during periods similar to the critical design conditions which will be used in the WLA analyses. These generally represent some type of "worst case" situation, such as summer minimum flow and maximum temperature conditions. The procedure for determining these conditions is described in Book VI (Design Conditions) of the waste load allocation guidance. The selected design conditions will probably represent an extreme event such as a 7-day, 10-year low flow (${}_7Q_{10}$) which occurs on the average every 10 years. Direct sampling of such conditions may not be possible and although similar flows may occur averaging shorter periods (e.g., 1 or 2 days) each year the sampling period may not be sufficiently long to accomplish all of the program goals. Therefore, the sampling program should be conducted at times most likely to approach these conditions when the same water quality processes are important.

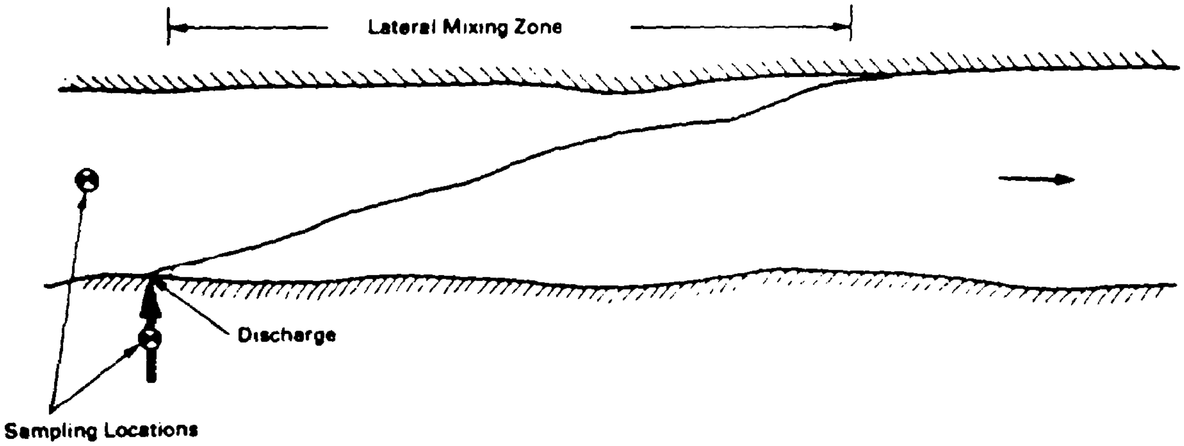
In addition to the calibration data, another set of water quality samples should be collected under different flow and water quality conditions for purposes of model validation. If several flow or water quality conditions will be evaluated in the WLA analyses, the calibration and validation samples should be collected at times which will bracket the conditions of the analyses.

The duration and frequency of water quality sampling depends to a large extent on whether a steady-state or a dynamic model will be used. Because they are easier to apply and require less data, steady-state models are generally used in WLA analyses. Steady-state models compute water quality conditions assuming everything remains constant through time. This includes:

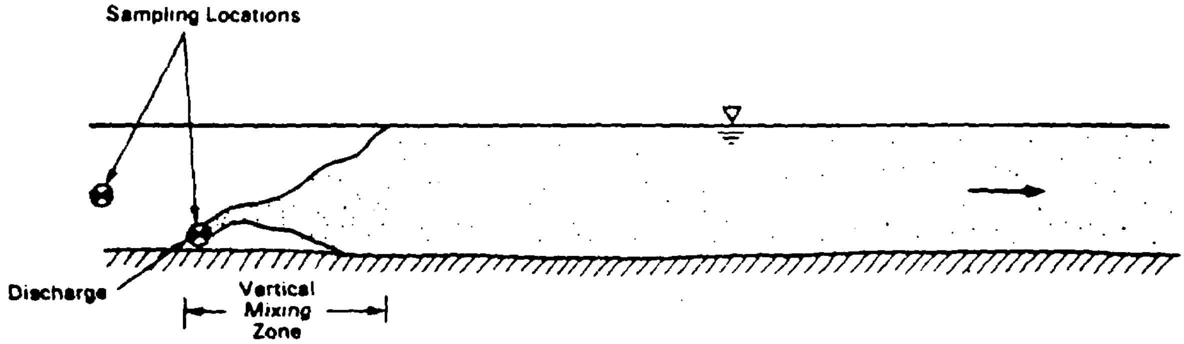
- flows and stream geometry (depths, widths, etc.)
- meteorological conditions
- temperature and quality of the water entering the up-stream boundary of the reach being modeled (upstream boundary conditions)
- temperature, quality, and flow rates of all tributaries
- temperature, quality, and flow rates of all nonpoint and point source loadings
- rates of all physical, chemical, and biological processes occurring in the stream.

Steady-state models simulate spatial (downstream) variations in the above factors, but not temporal changes. These models are appropriate for predicting water quality conditions at different locations in the stream when the above conditions do not change significantly with time. Since the travel time through an impacted stream reach is generally on the order of days, it is reasonable to assume that hydrologic and meteorologic conditions can remain fairly constant over this period and to apply a steady-state model. Seasonal variations can be analyzed by repeatedly running the model for different scenarios, for example monthly average conditions, monthly extreme conditions, etc. The major limitations of steady-state models are that they do not account for continuous flow variations or transient events such as storms or toxic spills, and that they do not directly simulate the

Figure 2-6. **Recommended sampling locations at point sources.**



(a)
Aerial View of River



(b)
Side View of River

diurnal dynamics of temperature and oxygen. Some quasi steady-state models are available which simulate these latter effects (e.g., 16,17,3).

Since steady-state models assume conditions remain constant with time, it is important to conduct the sampling program during a period when this assumption is valid. Synoptic surveys (e.g., sampling all stations over 1 to 2 days) should be conducted to the extent possible so that water quality conditions at different locations are not affected significantly by changes in the weather or variations in the waste discharges. However, since temperature varies diurnally and temperature influences the process rates of most biological and chemical reactions, some variability will be inevitable in the sampling results. If diurnal variations are important (for example, in some dissolved oxygen problems where algal activity is significant), then a 24-hour survey should be conducted for at least one station (preferably the station at the DO sag) and usually more. Short-term intensive surveys (diurnal measurements over 2 or 3 days) are recommended in all water quality studies, since this will provide enough data for sample variability (e.g., variances, confidence intervals, etc.) to be estimated.

The alternative approach to steady-state modeling is dynamic modeling. Dynamic models simulate streams in the same basic manner as steady-state models (i.e., they route water downstream and compute the physical, chemical, and biological processes occurring in the stream and the resulting changes in the water quality parameters). However, in addition, dynamic models compute the continuous changes which occur over time due to variations in stream flows, upstream water quality and temperature, tributary inflows, nonpoint and point source loadings, meteorology, and processes occurring within the stream. In dynamic modeling, all of the factors which are assumed constant for a steady-state analysis are free to vary continuously with time. This allows an analysis of diurnal variations in temperature and water quality, as well as continuous prediction of daily variations or even seasonal variations in water quality.

Dynamic model studies generally require much more detailed sampling programs than steady-state studies. Enough data must be collected to define the temporal variations in water quality throughout the simulation period at the upstream ends of all stream channels and the major pollutant loadings so that the model boundary conditions can be specified. Since dynamic models are used to study transient events such as combined sewer overflows during storms, toxic spills, and diurnal variations in temperature or dissolved oxygen, the duration and frequency of the sampling should be commensurate with the duration of the event plus the travel time through the study area. For toxic spills, one travel time plus the time for the trailing edge to pass is necessary to track the toxicant through the system. For storm runoff problems, the duration of the storm runoff should also be added to the sampling period since the pollutant loadings and stream hydrologic response will vary throughout the storm runoff period. For diurnal studies of temperature or dissolved oxygen, sampling at specified intervals (1 or 2 hours, for example) should be conducted over at least 24 hours.

Long-term dynamic simulations of seasonal variations in stream water quality may be impractical. Where seasonal variation is of interest, the general practice is to run a steady-state model or a dynamic model (with short term simulations) several times for different sets of conditions that represent the full spectrum of conditions expected over the period of interest. Enough data should be collected to characterize the seasonal variations, and to provide adequate data for calibrating and verifying the model. If possible, enough data should be collected to cover the full range of conditions of the model analysis. As a minimum, this should include conditions at both extremes of the seasonal range, as well as a few intermediate conditions (e.g., monthly averages).

2.1.4.3 Use of Models in Designing Sampling Programs

Models can be very effective tools in the design of sampling programs. This includes both computerized models and simple hand calculation techniques. Since sampling resources are generally limited, it is important to locate the stations in places that will provide the most information. Preliminary model calculations can be used to determine the best locations for sampling, as well as the critical times for sampling if dynamic analyses are being performed.

For example, when analyzing dissolved oxygen problems in streams with several discharges, more of the sampling effort should be allocated to areas where water quality standards are most likely to be violated (Figure 2-7). Also, areas where large water quality gradients exist should be sampled more thoroughly. These areas can be determined with Streeter-Phelps type calculations or simplified computer models. Processes or waste loadings which are not significant can then be omitted from these preliminary analyses (particularly if hand calculations are being used). Simple mixing calculations can be used to help determine which waste sources are significant. Mixing zone calculations can also be made to estimate the distance required for complete mixing of the waste water with the stream, and to estimate concentrations within the mixing zone. Rate coefficients and model parameters can be estimated from literature values (18,19,20) before site specific measurements are available. For important parameters such as the BOD decay rate (K_d), sensitivity analyses can be performed to evaluate the effects of different K_d values on the location of the DO sag. These analyses should provide enough information so that sampling stations can be located on the critical portion of the sag curve.

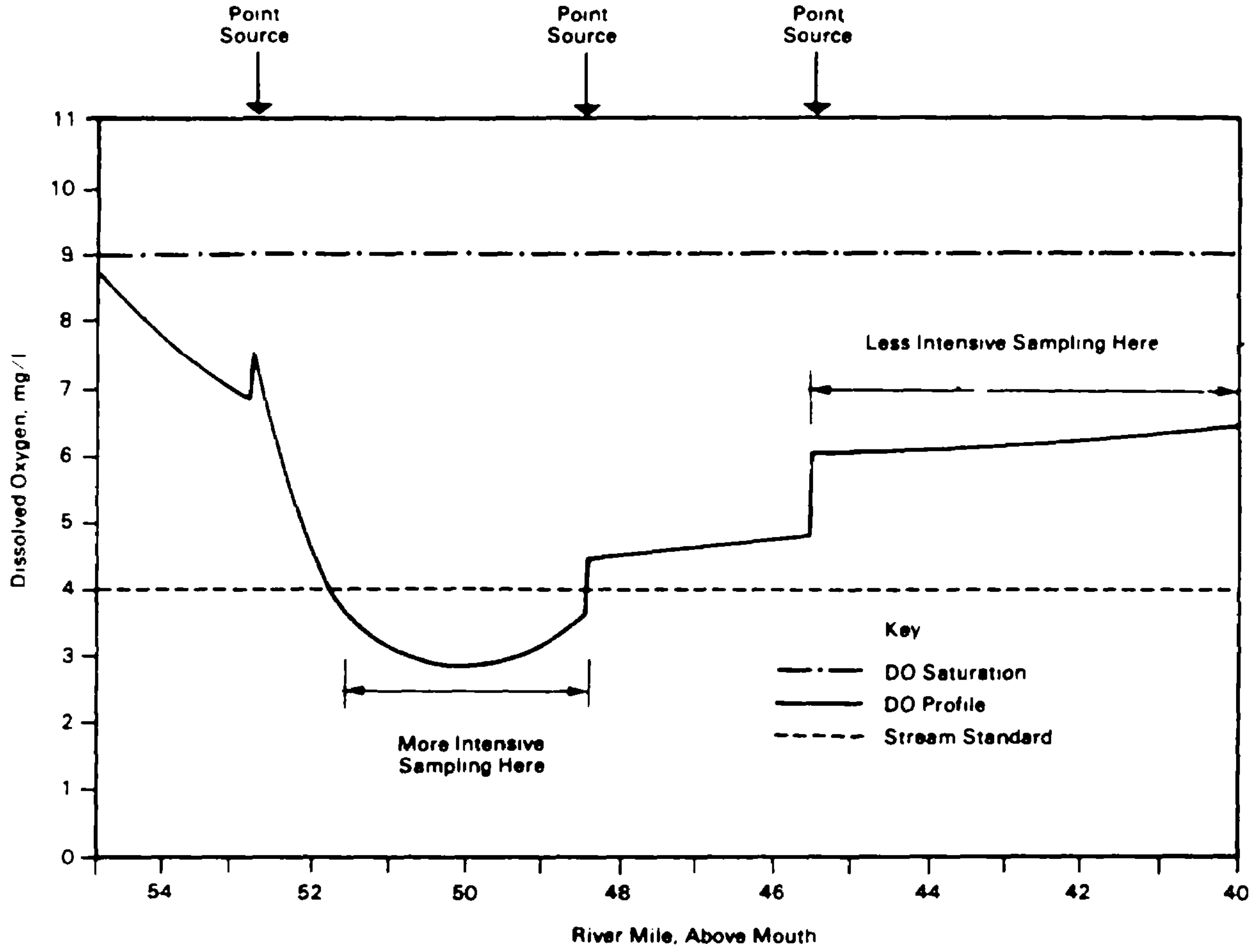
2.1.5 Plug Flow Sampling

Plug flow sampling is a type of instream sampling where a particular parcel of water is followed as it moves downstream, and samples of water quality are taken from the same parcel of water at different locations. Typically a dye (e.g., rhodamine WT) is injected into the river and is used to determine when to sample at selected downstream locations. Passage of the peak dye concentration indicates when to sample. Centroid-to-centroid measurements (rather than peak-to-peak measurements) are not used because centroids are not readily determinable in the field.

Plug flow sampling is particularly useful for rate constant determinations. Suppose, for example, that waste loading to a river segment is highly time variable. By sampling a particular slug of water as it moves downstream, the effects of time variability in waste loading can be eliminated.

Accessibility to the stream or river at multiple locations is necessary to implement plug flow sampling. For larger rivers, a boat may be appropriate to

Figure 2-7 Allocation of sampling effort based on preliminary analyses.



move from location to location, while for smaller streams, land transportation may be easier.

Before samples are collected, the dye should be well-mixed across the river. Section 3.2 provides guidelines on the distance required. For large rivers, complete mixing can take many miles, and plug flow sampling would be inappropriate.

It is not always necessary, or even desirable, for the dye to be injected at the upstream boundary of the segment under investigation. The dye can be injected at some distance further upstream so that when the dye reaches the segment boundary, it has attained its one-dimensional profile. If the upstream boundary is a wastewater treatment plant, the effluent from the plant is sampled at the time the peak dye concentration passes the plant, and subsequent samples are taken at selected downstream locations when the peak dye concentration passes those locations. Travel times between locations are calculated to determine stream velocities. Two methods for Lagrangian sampling are: 1) find peak every 2 hours or so by moving boat, or 2) await arrival of peak at predesignated sites.

2.2 Sampling Requirements for Conventional Pollutants

2.2.1 General Modeling Approaches

Most waste load allocations in streams focus on dissolved oxygen. Dissolved oxygen dynamics depend on the interactions of several constituents and processes. The constituents include dissolved oxygen, carbonaceous BOD, nitrogenous BOD (ammonia and nitrite), temperature, and in some cases phytoplankton, periphyton, and aquatic plants. The major processes include (Figure 2-8):

- Reaeration
- CBOD decay
- CBOD settling
- Sediment oxygen demand
- Nitrification
- Photosynthesis
- Respiration

These constituents and processes are typically modeled by a set of coupled mass balance equations such as:

Dissolved Oxygen

$$\frac{dO_2}{dt} = K_a(O_{sat} - O_2) - K_d L - \frac{K_{SOD}}{h} - \alpha_1 K_{N1} NH_3$$

$$-\alpha_2 K_{N2} NO_2 + (\alpha_3 \mu - \alpha_4 r) A \qquad (2\text{-}5)$$

Carbonaceous BOD

$$\frac{dL}{dt} = - K_d L - K_s L = - K_r L \qquad (2\text{-}6)$$

Nitrogen Forms

$$\frac{dNH_3}{dt} = - K_{N1} NH_3 + (\alpha_5 r - \alpha_6 \mu) A + \frac{K_{BEN}}{h} \qquad (2\text{-}7)$$

$$\frac{dNO_2}{dt} = - K_{N2} NO_2 + K_{N1} NH_3 \qquad (2\text{-}8)$$

$$\frac{dNO_3}{dt} = K_{N2} NO_2 - \alpha_7 \mu A \qquad (2\text{-}9)$$

Algae

$$\frac{dA}{dt} = (\mu - r - \frac{V_s}{h}) A \qquad (2\text{-}10)$$

For identification of coefficients for these equations, see p. 2-34.

The above equations are simplified in that they do not include the pollutant loading or transport (advection and dispersion) terms. All of the process rates are temperature dependent. In addition, algal growth depends on light, phosphorus, and other nutrients, so other equations may be coupled to the dissolved oxygen equation in an indirect way. Michaelis-Menten type saturation kinetics are typically used to compute nutrient limitation effects on algal growth, and often light limitation as well. Other saturation relationships (21) are also used for light limitation.

Periphyton and aquatic plants are rarely included in water quality models because of the difficulty in predicting these parameters. When they are, they are modeled by equations analogous to those used for algae (Equation (2-10)), except that the settling term is replaced by a sloughing or nonpredatory mortality term.

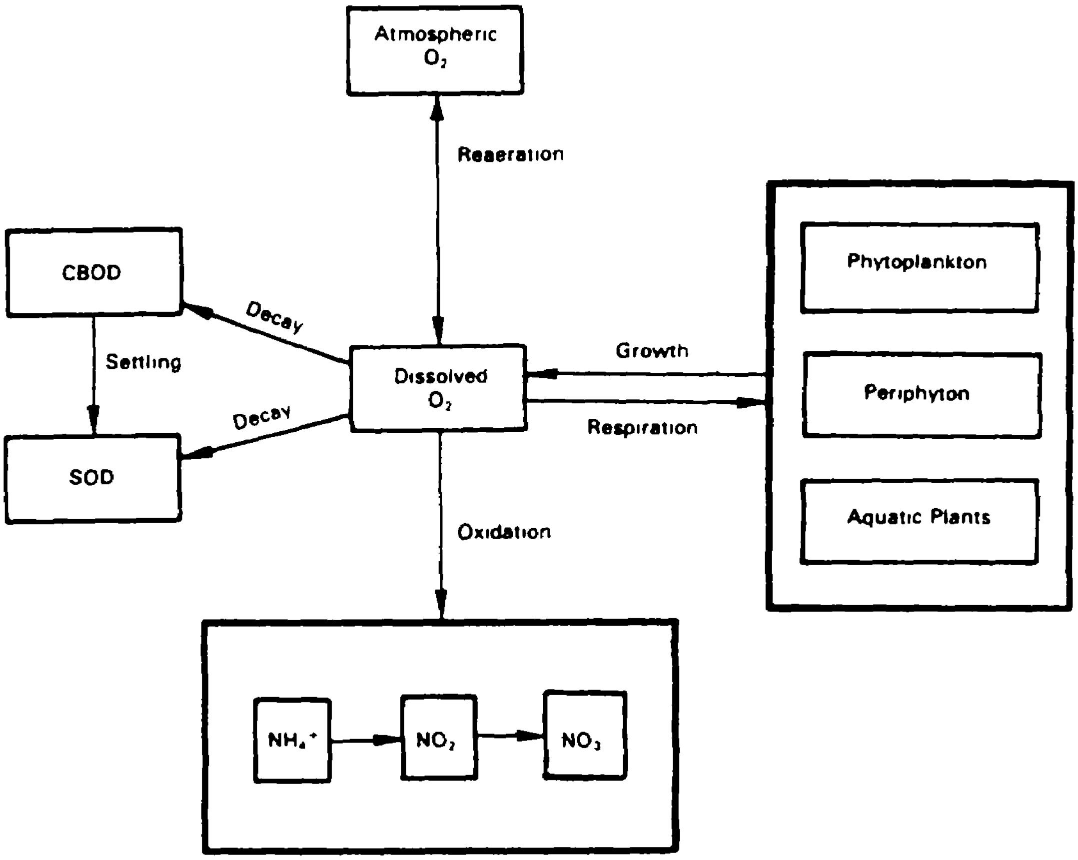
The above equations give the general framework which forms the basis of all dissolved oxygen models. However, many models use a simplified framework which ignores or combines some of the processes. For example, in systems where photosynthesis and respiration are not important, the corresponding terms and equations can be left out of the analysis (e.g., DOSAG1 [22], and SNSIM [23]). Simple models and hand calculation techniques often lump the nitrogen cycle into a single nitrogenous BOD equation analogous to Equation (2-6) (e.g., DOSAG1, SNSIM), or else combine the nitrogenous and carbonaceous BOD into a single constituent representing total BOD (24). In the latter case, only the first three terms of Equation (2-5) and a total BOD equation analogous to Equation (2-6) are left in the model.

Even when the nitrogen cycle is not lumped into a BOD equation, models differ in the number of stages included in the cycle. The complete sequence should include hydrolysis of organic nitrogen to ammonia and oxidation of ammonia to nitrite and nitrite to nitrate. However, most models do not even include organic nitrogen as a separate constituent (e.g., QUAL-II, DOSAG3, WQRRS). However, QUAL-2E does have organic nitrogen and organic phosphorus capability. Many models also leave out nitrite so that ammonia is oxidized directly to nitrate in the model equations (e.g., SSAM IV). As a result, some of the constituents and process rates may take on a different meaning since they represent two or more constituents and corresponding decay processes combined.

In addition to dissolved oxygen analyses, other conventional pollutant problems such as ammonia toxicity and eutrophication are sometimes important in waste load allocations.

Ammonia toxicity is due to the un-ionized form of ammonia. The un-ionized fraction of total ammonia increases with pH and temperature. Figure 2-9 shows this relationship. Most currently available water quality models do not simulate un-ionized ammonia

Figure 2-8. Processes affecting dissolved oxygen.



or pH. Therefore, waste load allocations which involve ammonia toxicity must usually be based on total ammonia simulations using equations such as (2-7) through (2-10) above in combination with field measurements of pH and temperature. Un-ionized ammonia concentration can be calculated from model-projected total ammonia and a relationship such as shown in Figure 2-9.

Eutrophication analyses require models which simulate nutrient and algal dynamics. Phosphorus and nitrogen are generally the only nutrients considered. The major processes include algal uptake, algal excretion, sediment release, and nitrification. The mass balance equations for the nitrogen cycle and algae were given above in Equations (2-7) through (2-10). The only additional equation required is a mass balance for orthophosphate, which is typically expressed as:

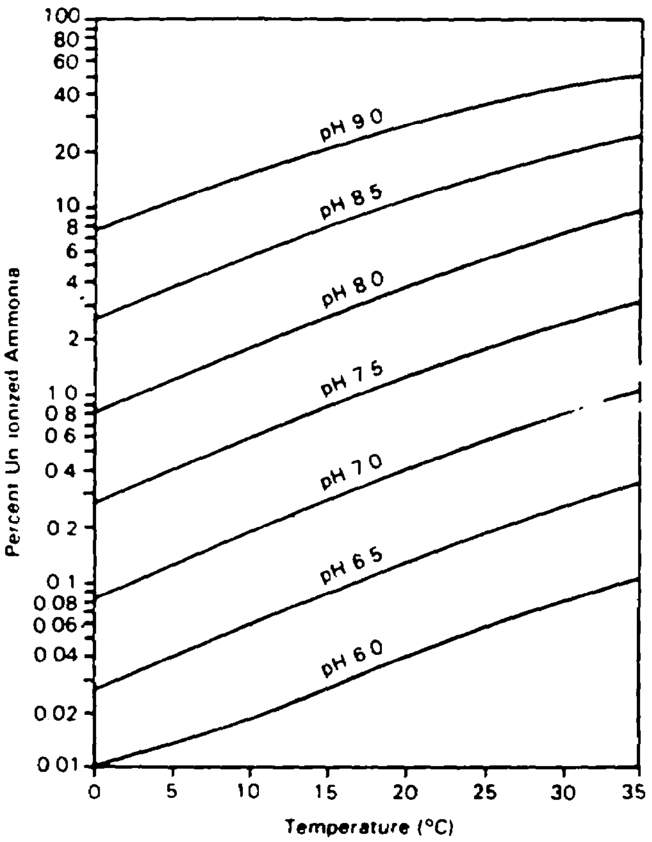
$$\frac{dPO_4}{dt} = (\alpha_8 r - \alpha_8 \mu) A + \frac{K_{SEP}}{h} \qquad (2\text{-}11)$$

2.2.2 Model Data Requirements

This section summarizes the data requirements for the different types of models used to allocate conventional pollutants. The modeling approaches range from simple hand-calculation techniques to complex computer models. Dissolved oxygen analyses using Streeter-Phelps type hand-calculations are probably the most commonly used techniques in waste load allocation analyses. Simplified methods are limited for eutrophication analyses since several constituents with complex interactions are involved. However, a few hand-calculation techniques for predicting algal concentrations and their effects on dissolved oxygen are described in Chapter 2 of Book II of the WLA guidance documents (see Table 1-1). Table 2-1 summarizes the data requirements for the various hand-calculation methods available.

The models QUAL-II, NCASI (26), and QUAL-2E are probably the most widely used computer model for predicting the effects of conventional pollutants in

Figure 2-9 **Effect of pH and temperature on un-ionized ammonia (From (25)).**



streams. The data requirements for QUAL-2E are, in general, the same as most other stream models, except models such as DOSAG1 which are restricted to simple dissolved oxygen analyses and therefore require less data. QUAL-2E simulates the following constitutents:

- Dissolved oxygen
- Biochemical oxygen demand
- Temperature
- Algae as chlorophyll *a*
- Organic nitrogen
- Ammonia
- Nitrite
- Nitrate
- Organic phosphorus
- Dissolved phosphorus
- Coliforms
- Arbitrary nonconservative constituent
- Three conservative constituents.

The model equations and process formulations are in general identical to those discussed in Equations (2-5) to (2-11) for dissolved oxygen, nutrients, and phytoplankton. Figure 2-10 shows the interactions of the various constituents, and Table 2-2 lists the processes which are simulated for each constituent. Table 2-3 compares QUAL-2E with other models commonly used in WLA analyses with respect to the constituents simulated.

Table 2-4 summarizes the input data requirements for QUAL-2E. Note that many of the process rates can vary with each reach. This feature is useful since waste characteristics may vary between different discharges, resulting in differences in the BOD decay rates and nitrification rates at different locations in the stream. Other process rates such as sediment oxygen demand, phytoplankton settling rates, and reaeration rates may also vary with distance, since these are affected by the hydraulic characteristics of the stream.

QUAL-2E is capable of running in either a steady-state or a quasi-dynamic mode. The dynamic option is used primarily for simulating diurnal variations in dissolved oxygen and temperature since the stream flows, point source loadings, and nonpoint source loadings cannot be varied during the simulation. Only the constituent concentrations at the upstream boundaries, the meteorological conditions, and the resulting water quality response are free to change.

Table 2-5 compares the general features of QUAL-2E with other computer models used in waste load allocation analyses. DOSAG1 and SNSIM are limited to steady-state DO/BOD analyses, while QUAL-2E and RECEIV-II can be used for eutrophication analyses as well as dissolved oxygen analyses. QUAL-2E and RECEIV-II both simulate the effects of photosynthesis, respiration, and temperature on diurnal variations of dissolved oxygen. RECEIV-II is truly dynamic since it simulates continuous temporal variations in stream hydraulics and waste loadings. QUAL-2E assumes these features remain constant, but allows the meteorology and water quality conditions downstream of the upstream boundaries to vary.

2.2.3 Sampling Guidelines

2.2.3.1 Constituents Sampled

The specific constituents which must be sampled, as well as the sampling frequency, depend to some extent on the particular modeling framework which will be used in the waste load allocation analysis. The selected model should include all of the processes which are significant in the stream being analyzed, without the unnecessary complexity of processes which are insignificant. A few preliminary measurements may be useful to define which processes are important.

Table 2-1. Data Requirements for Hand-Calculation Techniques Described in WLA Guidance Documents and Screening Manual (27) For Analysis of Conventional Pollutants

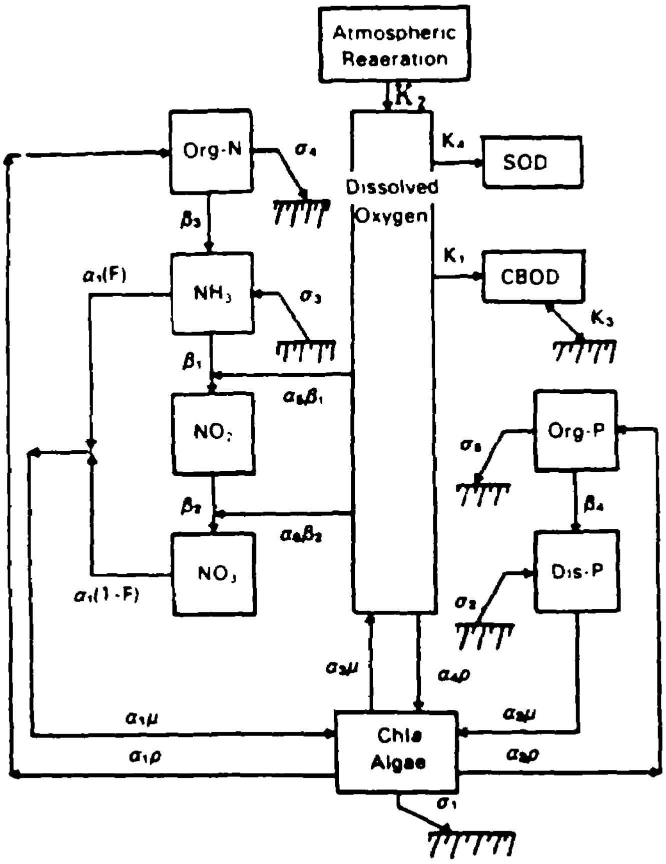
Data Requirements	Streeter-Phelps DO Analyses[a]	NH_3 Toxicity Calculations[b]	Algal Predictions Without Nutrient Limitation[c]	Algal Predictions With Nutrient Limitation[c]	Algal Effects on Daily Average DO[c]	Algal Effects on Diurnal DO[c]
Hydraulic and Geometry Data						
Flow rates[d]	X	X	X	X	X	X
Velocity	X	X	X	X	X	X
Depth	X	X	X	X	X	X
Cross-sectional area	X	X	X	X	X	X
Reach length	X	X	X	X	X	X
Constitutent Concentrations[e]						
DO	X					
CBOD, NBOD	X					
NH_3		X				
Temperature	X	X	X	X	X	X
Inorganic [illegible]			X	X	X	X
Inorganic [illegible]			X	X	X	X
Chlorophyll a			X[f]	X	X	X
pH		X				
DO/BOD Parameters						
Reaeration rate coefficient	X				X	X
Sediment oxygen demand	X					
CBOD decay rate	X					
CBOD removal rate	X					
NBOD decay rate	X					
NH_3 oxidation rate		X				
Oxygen per unit chlorophyll *a*					X	X
Algal oxygen production rate	X					
Algal oxygen respiration rate	X					
Phytoplankton Parameters						
Maximum growth rate			X	X	X	X
Respiration rate			X	X	X	X
Settling velocity			X	X	X	X
Saturating light intensity			X	X	X	X
Phosphorus half-saturation constant				X	X	X
Nitrogen half-saturation constant				X	X	X
Phosphorus to chlorophyll ratio			X	X	X	X
Nitrogen to chlorophyll ratio			X	X	X	X
Light Parameters						
Daily solar radiation			X	X	X	X
Photoperiod			X	X	X	X
Light extinction coefficient			X	X	X	X

[a] Streeter-Phelps DO calculations are described in Chapter 1 of Book II of the WLA guidance documents (Table 1-1) and the Screening Manual (27).
[b] Ammonia toxicity calculations are described in Chapter 1 of Book II of the WLA guidance documents.
[c] Algal predictions and their effects on DO are discussed in Chapter 2 of Book II of the WLA guidance documents.
[d] Flow rates are needed for the river and all point sources at various points to define nonpoint flow.
[e] Constituent concentrations are needed at the upstream boundary and all point sources.
[f] Chlorophyll *a* concentrations are also needed at the downstream end of the reach to estimate net growth rates.

The absolute minimum sampling requirements for all dissolved oxygen studies should include dissolved oxygen, temperature, carbonaceous BOD, and total Kjeldahl nitrogen (measure of nitrogenous BOD), since these are fundamental to any dissolved oxygen analysis. BOD is typically measured as 5-day BOD (BOD_5). However, a few measurements of long-term or ultimate BOD (BOD_{20}) are also necessary to establish the BOD_{20}/BOD_5 ratio since ultimate BOD is simulated in the models. If a model which considers only a total BOD component is selected, the analyst should be aware that nitrogenous BOD and carbonaceous BOD decay at different rates, which will cause both the composition of the remaining BOD and the net decay rate to change as the waste moves downstream. Therefore, the total BOD approach should only be used in situations where the nitrogenous components of the waste sources are known to be unimportant (e.g., less than 10 percent of the total BOD).

In addition to total Kjeldahl nitrogen (TKN), ammonia and nitrate (or nitrite plus nitrate) should be measured in both dissolved oxygen and eutrophication studies for models which simulate the nitrogen cycle. Even if they are not modeled, ammonia, nitrate, and nitrite

Figure 2-10. Major constituent interactions in QUAL-2E (3)



data are useful for estimating the nitrogenous BOD decay rate or ammonia oxidation rate as discussed below in Section 2.2.3.2. Ammonia, pH, and temperature must be measured in all studies involving ammonia toxicity. In streams where algae activity is significant, diurnal variations in pH as much as 1.5 units per day may occur. The potential effect of pH variation on ammonia toxicity should be taken into effect when designing a sampling program.

For models which simulate algae, concentrations of algal dry weight biomass or chlorophyll a should be measured. Orthophosphate concentrations and light extinction coefficients (or Secchi depths) will also be needed in addition to nitrate, ammonia, and temperature for the algal growth computations in both

Table 2-2. Processes Simulated in Qual-2E

- Dissolved Oxygen
  - Reaeration
  - BOD decay
  - Ammonia oxidation
  - Nitrite oxidation
  - Sediment oxygen demand
  - Photosynthetic oxygen production
  - Algal respiration
  - Advection
  - Dispersion
- Carbonaceous BOD
  - Decay
  - Settling
  - Advection
  - Dispersion
- Organic Nitrogen
  - Hydrolizes to Ammonia
- Ammonia Nitrogen
  - Ammonia oxidation
  - Algal uptake
  - Algal respiration
  - Sediment release
  - Advection
  - Dispersion
- Nitrite Nitrogen
  - Ammonia oxidation
  - Nitrite oxidation
  - Advection
  - Dispersion
- Nitrate Nitrogen
  - Nitrite oxidation
  - Algal uptake
  - Advection
  - Dispersion
- Organic Phosphorus
  - Transforms to Dissolved Phosphorus
- Phosphate Phosphorus
  - Algal uptake
  - Algal respiration
  - Sediment release
  - Advection
  - Dispersion
- Phytoplankton
  - Growth
  - Respiration
  - Settling
  - Advection
  - Dispersion
- Coliform Bacteria
  - Die-off
  - Advection
  - Dispersion
- Temperature
  - Short wave solar radiation
  - Atmospheric long wave radiation
  - Back radiation
  - Evaporative heat loss
  - Conduction with atmosphere
  - Advection
  - Dispersion
- Arbitrary Conservative Constitutent
  - Advection
  - Disperion
- Arbitrary Nonconservative Constituent
  - First-order decay
  - Advection
  - Dispersion

Table 2-3. Non-Toxic Constituents Included in Stream Models

		Water Quality Variables																			
Model Name	Reference	DO	CBOD or Total BOD	NBOD	SOD	Temp	Tot P	Org P	PO_4	Tot N	Org N	NH_3	NO_2	NO_3	Carbon	Algae or Chl-*a*	Zoo-plankton	pH	Alk	TDS	Coliform Bacteria
WQAM	(27)	X	X	X	X	X	X		X	X										X	X
DOSAG1	(22)	X	X	X		X**															
DOSAG3	(14)	X	X	X*	X	X**			X			X	X	X		X				X	X
SNSIM	(23)	X	X	X	X	X**															
QUAL-II	(1,2)	X	X	X*	X	X			X			X	X	X		X				X	X
QUAL-IIe	(3)	X	X	X*	X	X			X			X	X	X		X				X	X
RECEIV-II	(9)	X	X	X*	X	X**	X		X	X	X	X	X	X		X				X	X
WASP	(28)	X	X	X*	X	X**		X	X		X	X		X	X	X	X	X	X	X	
AESOP	(29)	X	X	X*	X	X**		X	X		X	X		X	X	X	X	X	X	X	
HSPF	(15)	X	X	X*	X	X			X			X	X	X	X	X		X	X	X	X
HAR03	(30)	X	X			X**															
FEDBAK03	(31)	X	X			X**															
MIT-DNM		X	X	X*							X	X	X	X		X	X			X	X
EXPLORE-1	(32)	X	X	X*	X	X**		X	X		X	X	X	X	X	X	X				
WQRRS	(10)	X	X	X*	X	X			X			X	X	X	X	X	X	X	X	X	X·

*NBOD simulated as nitrification of ammonia

**Temperature specified by model users

Table 2-4. Model Input Parameters for Qual-2E

Input Parameter	Variable by Reach	Variable with Time
Dissolved Oxygen Parameters		
Reaeration rate coefficients	Yes	
O_2 consumption per unit NH_3 oxidation		
O_2 consumption per unit NO_2 oxidation		
O_2 production per unit photosynthesis		
O_2 consumption per unit respiration		
Sediment oxygen demand	Yes	
Carbonaceous BOD Parameters		
CBOD decay rate	Yes	
CBOD settling rate	Yes	
Organic Nitrogen		
Hydrolize to ammonia	Yes	
Ammonia Parameters		
Ammonia oxidation rate	Yes	
Benthic source rate	Yes	
Nitrite Parameters		
Nitrite oxidation rate	Yes	
Nitrate Parameters		
None		
Organic Phosphorus		
Transformed to diss. p	Yes	
Phosphate Parameters		
Benthic source rate	Yes	
Phytoplankton Parameters		
Maximum growth rate		
Respiration rate		
Settling rate	Yes	
Nitrogen half-saturation constant		
Phosphorus half-saturation constant		
Light half-saturation constant		
Light extinction coefficient	Yes	
Ratio of chlorophyll *a* to algal biomass	Yes	
Nitrogen fraction of algal biomass		
Phosphorus fraction of algal biomass		
Coliform Parameters		
Die-off rate	Yes	

Input Parameter	Variable by Reach	Variable with Time
Nonconservative Constituent Parameters		
Decay rate		
Meteorological Data		
Solar radiation		Yes
Cloud cover		Yes
Dry bulb temperature		Yes
Wet bulb temperature		Yes
Wind speed		Yes
Barometric pressure		Yes
Elevation		
Dust attenuation coefficient		
Evaporation coefficients		
Stream Geometry Data		
Corss-sectional area vs. depth	Yes	
Reach lengths	Yes	
Hydraulic Data (Stage-Flow Curve Option)		
Coefficient for stage-flow equation	Yes	
Exponent for stage-flow equation	Yes	
Coefficient for velocity-flow equation	Yes	
Exponent for velocity-flow equation	Yes	
Hydraulic Data (Manning's Equation Option)		
Manning's n	Yes	
Bottom width of channel	Yes	
Side slopes of channel	Yes	
Channel slope	Yes	
Flow Data		
Upstream boundaries	Yes	
Tributary inflows	Yes	
Point sources	Yes	
Nonpoint sources	Yes	
Diversions	Yes	
Constituent Concentrations		
Initial conditions	Yes	
Upstream boundaries		Yes
Tributary inflows	Yes	
Point sources	Yes	
Nonpoint sources	Yes	

dissolved oxygen and eutrophication analyses. Some dissolved oxygen models include the effects of algal photosynthesis and respiration without actually simulating algae (e.g., 16,17). This can be done in many cases by using photosynthesis and respiration fluxes obtained from light-dark bottle measurements, or by measuring the diurnal DO variations and superimposing them on the daily average concentrations predicted in the model, typically assuming a sinusoidal relationship.

Table 2-5. **Comparison of Qual-II With Other Conventional Pollutant Models Used in Waste Load Allocations (Adapted from (11).**

Model	Temporal Variability		Variable Loading Rates	Types of Loads	Spatial Dimensions	Water Body	Water Quality Parameters Modeled	Processes Simulated	
	Water Quality	Hydraulics						Chemical/Biological	Physical
DOSAG-I	Steady-state	Steady-state	No	multiple point sources	1-D	stream network	DO, CBOD, NBOD, conservative	1st-order decay of NBOD, CBOD, coupled DO	dilution, advection, reaeration
SNSIM	Steady-state	Steady-state	No	multiple point sources & nonpoint sources	1-D	stream network	DO, CBOD, NBOD, conservative	1st-order decay of NBOD, CBOD, coupled DO, benthic demand (s), photosynthesis (s)	dilution advection, reaeration
QUAL-II	Steady-state or Dynamic	Steady-state	No	multiple point sources & nonpoint sources	1-D	strean network	DO, CBOD, temperature, ammonia, nitrate, nitrite, algae, phosphate, coliforms, nonconservative subetances, three conservative substances	1st-order decay of NBOD, CBOD, coupled DO, benthic demand (s), CBOD settling (s), nutrient-algal cycle	dilution, advection, reaeration, heat balance
RECEIV-II	Dynamic	Dynamic	Yes	multiple point sources	1-D or 2-D	stream network or well-mixed estuary	DO, CBOD, ammonia, nitrate, nitrite, total nitrogen, phosphate, coliforms, algae, salinity, one metal ion	1st-order decay of CBOD, coupled DO, benthic demand (s), CBOD settling (s), nutrient-algal cycle	dilution, advection, reaeration

(s) = specified

2.2.3.2 Field Data Used to Estimate Model Coefficients

Besides sampling for the constituents to be simulated, additional measurements may be necessary to help quantify the various coefficients and parameters included in the model equations. Coefficient values can be obtained in four ways, 1) direct measurement, 2) estimation from field data, 3) literature values, and 4) model calibration. Model calibration is usually required regardless of the selected approach. However, coefficients which tend to be site specific or which can take on a wide range of values should either be measured directly or estimated from field samples. This could include the following parameters:

- Carbonaceous BOD decay rate
- Carbonaceous BOD settling rate
- Ammonia oxidation rate (nitrogenous BOD decay rate)
- Sediment oxygen demand.

Carbonaceous BOD decay and settling rates can be estimated from field data by plotting CBOD measurements versus travel time on semi-log paper. The decay rates are estimated from the slopes of the lines (Figure 2-11). Slope calculations should be limited to reaches where tributaries are negligible. In situations where CBOD settling is important, a two-stage curve usually results, with a steep slope on the first part and a more gradual slope on the second part (Figure 2-12). The first part of the curve gives the total removal rate when both settling and decay are significant (K_r), while the second part generally represents CBOD decay after most of the settling has taken place (K_d). The settling rate (K_s) can then be estimated from the difference between K_r and K_d. Carbonaceous BOD decay rates can also be measured in the laboratory using nitrogen inhibited tests or calculated by other techniques (33), but the above approach is generally preferred since it reflects the actual conditions measured in the field.

Figure 2-11. **Example computation of total BOD removal rate, K_r, based on BOD measurements.**

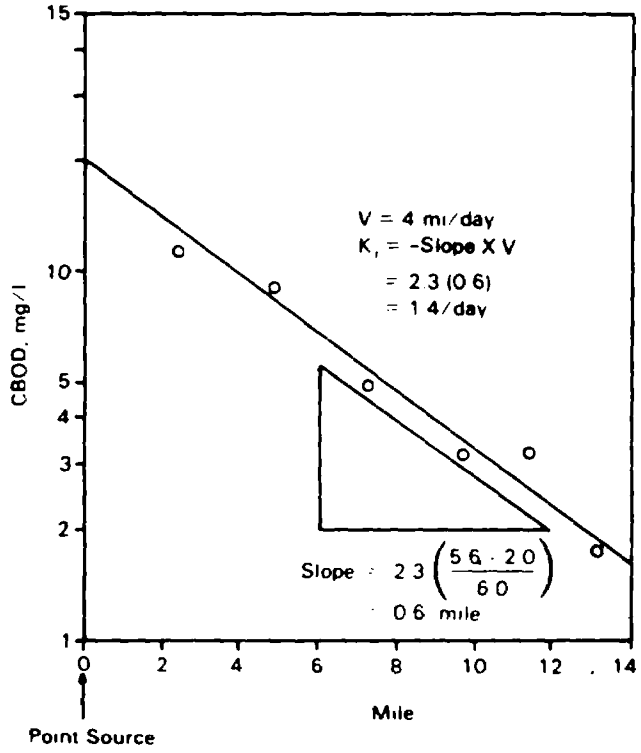
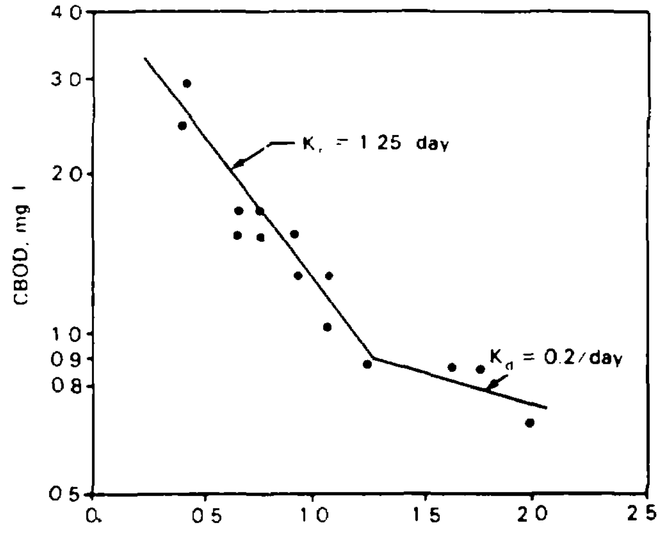


Figure 2-12. Procedure for estimating K_d and K_r from BOD measurements



Ammonia oxidation (or nitrogenous BOD decay) rate coefficients can also be estimated from field data using the same graphical technique. Total Kjeldahl nitrogen (TKN) rather than ammonia is generally plotted, since TKN includes both hydrolyzable organic nitrogen and ammonia, both of which will ultimately be oxidized to nitrate. Unfortunately, ammonia concentrations are influenced by algal uptake and respiration in addition to oxidation, so these processes may affect the slope of the curve. Similar plots of nitrate versus travel time can be used to provide a second estimate of the ammonia oxidation rate, but nitrate is also influenced by algal uptake. Unlike CBOD, most water quality models do not include separate components for settleable and non-settleable NBOD. If the model does include separate formulations for NBOD settling and decay, the settling rate can be estimated using the procedure above.

Sediment oxygen demand (SOD) should be measured in situ in situations where it is a significant component of the oxygen budget. This is most likely to occur in shallow streams where the organic content of the sediments is high. The significance of SOD can be evaluated by comparing it to the carbonaceous BOD and nitrogenous BOD fluxes. For example, SOD can be neglected if:

$$\frac{K_{SOD}}{h} \ll K_d L \qquad (2\text{-}12)$$

and

$$\frac{K_{SOD}}{h} \ll K_{N1} NH_3 \qquad (2\text{-}13)$$

Measurements should be taken both upstream and downstream of the waste discharges, since the background SOD will probably be lower than the SOD in the area impacted by the discharge.

In addition to the above model parameters which are determined primarily from the results of field sampling surveys, several other rate coefficients can be measured in the field. For example, stream reaeration rates can be measured using tracer techniques (34,35,36,37,38). However, the usual procedure is to select an appropriate reaeration rate formula e.g., (39,40,41) and compute the reaeration rate as a function of the hydraulic characteristics of the stream. Most computer models provide several options for the reaeration rate equation, since many of the equations are applicable only over certain ranges of depth and velocity e.g., QUAL-2E, DOSAG3, RECEIV-II, and WQRRS.

*As mentioned above, algal photosynthesis and respi*ration rates can be measured using light-dark bottle techniques. However, it is usually more convenient to estimate these rates by model calibration using field measurements of diurnal variations in dissolved oxygen and spatial and temporal variations in algal concentrations.

Table 2-6 summarizes the methods typically used to determine the values of each model parameter in Equations (2-5) through (2-11).

2.2.3.3 Sampling Locations

The general model-independent sampling locations discussed in Section 2.1.4.1 (i.e., upstream boundaries, tributaries, point and nonpoint sources, etc.) are the minimum sampling requirements for all conventional pollutant studies. In addition, enough stations should be sampled to characterize the shape of the dissolved oxygen profile below each major waste source in dissolved oxygen studies. A minimum of five or six stations are necessary to define the shape of a typical DO sag, assuming the location and extent of the sag curve are known in advance. Since this is rarely the case, a few more stations (2 or 3) should generally be included so that at least one station is near the dissolved oxygen minimum. It is important to sample this region since this will be the area where water quality standards are likely to be violated. Where violations exist, more intensive sampling should be conducted in the sag region to determine the extent of the violations (Figure 2-7). In general, more sampling effort should be allocated to those waste discharges which have the most impact on the stream. These can be determined by comparing the mass fluxes of CBOD and NBOD with the corresponding ambient fluxes in the stream. In many *cases, the DO sags from different discharges will* overlap, reducing the total number of sampling locations required.

Table 2-6. Methods for Determining Coefficient Values in Dissolved Oxygen and Eutrophication Models

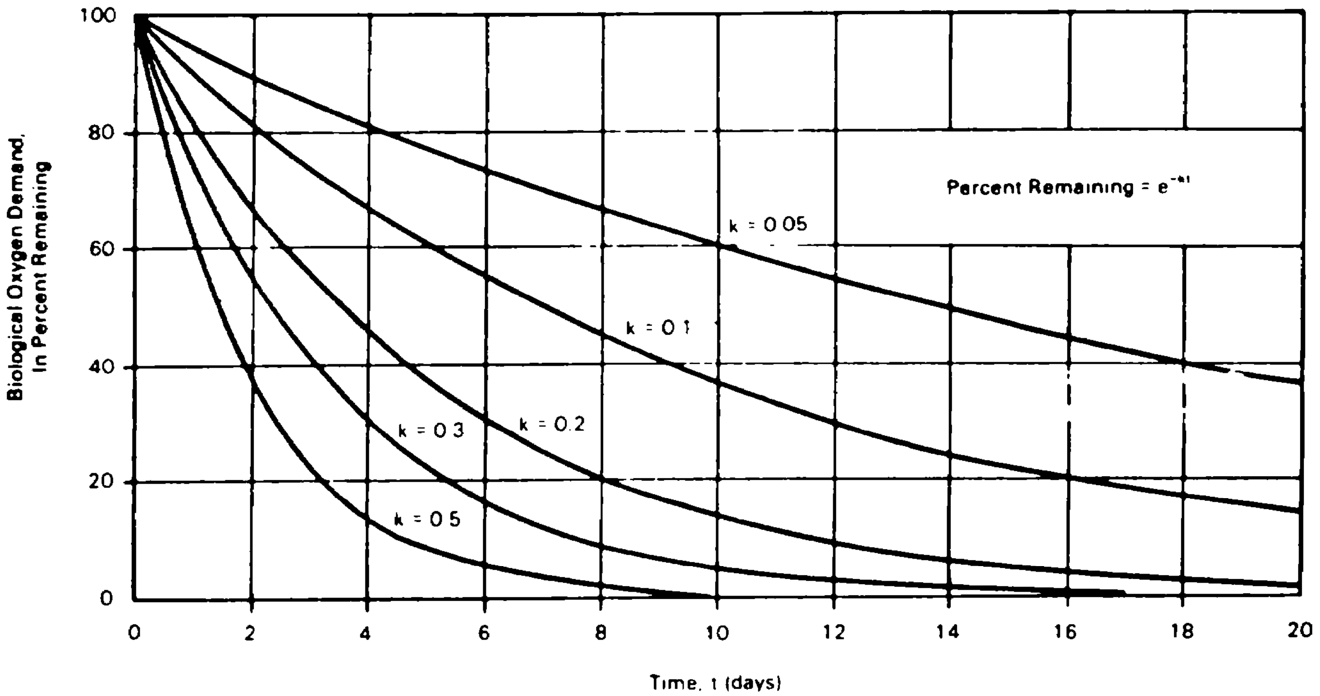
Model Parameter	Symbol	Method of Determination
Dissolved Oxygen Parameters		
Reaeration rate coefficients	K_a	Compute as a function of depth and velocity using an appropriate formula, or measure in field using tracer techniques.
O_2 consumption per unit NH_3 oxidation	α_1	Constant fixed by biochemical stoichiometry.
O_2 consumption per unit NO_2 oxidation	α_2	Constant fixed by chemical stoichiometry.
O_2 production per unit photosynthesis	α_3	Literature values, model calibration and measurement by light to dark bottles and chambers.
O_2 consumption per unit respiration	α_4	Literature values and model calibration.
Sediment oxygen demand	K_{SOD}	In situ measurement and model calibration.
Carbonaceous BOD Parameters		
CBOD decay rate	K_d	Plot CBOD measurements on semi-log paper or measure in laboratory.
CBOD settling rate	K_s	Plot CBOD measurements on semi-log paper and estimate from steep part of curve.
Ammonia Parameters		
Ammonia oxidation rate	K_{N1}	Plot TKN measurements and $NO_3 + NO_2$ measurements on semi-log paper.
Benthic source rate	K_{BEN}	Model calibration.
Nitrite Parameters		
Nitrite oxidation rate	K_{N2}	Use literature values and calibration, since this rate is much faster than the ammonia oxidation rate.
Phosphate Parameters		
Benthic source rate	K_{BEP}	Model calibration.
Phytoplankton Parameters		
Growth rate	μ	Literature values and model calibration, or measure in field using light-dark bottle techniques.
Respiration rate	r	Literature values and model calibration, or measure in field using light-dark bottle techniques.
Settling rate	V_s	Literature values and model calibration.
Nitrogen fraction of algal biomass	$\alpha_5, \alpha_6, \alpha_7$	Literature values and model calibration or laboratory determinations from field samples.
Phosphorus fraction of algal biomass	α_8, α_9	Literature values and model calibration or laboratory determinations from field samples.
Half-saturation constants for nutrients	K_n, K_p	Literature values and model calibration.
Saturating light intensity or half-saturation constant for light	I_s or K_L	Literature values and model calibration.

Note: Literature values for model coefficients are available in ref. (18, 19, 20)

As discussed in previous sections, simplified Streeter-Phelps calculations or preliminary model runs may be useful estimating the location of the DO sag prior to sampling. The total length of the sag region can also be estimated by considering the BOD decay rate along with the travel times and stream velocities below the discharge (Figure 2-13), since BOD decay is generally the major process removing oxygen from the stream. However, this latter information does not provide any information on the location of the DO minimum.

All of the major water quality parameters of interest (DO, CBOD, TKN, NH_3, NO_3, PO_4, temperature, pH, etc.) should be measured at each station in the sampling network. Some constituents, however, may be unimportant at certain locations, i.e., BOD in the area of recovery (past the sag point). Algal measurements may not be necessary at all stations in areas where the sampling grid is close, for example, if intensive sampling is conducted in the critical region of the DO sag, since algal concentrations should not change significantly over small distances. Sediment-related processes such as SOD only need to be measured at a few locations. These locations do not have to coincide with the locations of the other water quality samples. Rather, they should be located in areas which will characterize the differences in sediment characteristics throughout the study area. Typical locations would be downstream of a major discharge to define the SOD in areas where significant settling of BOD occurs, and a site away from the

Figure 2-13. BOD decay times for various decay rates (From (11)).



influence of the discharge to characterize the background SOD. Figure 2-14 shows an example of the sampling locations for a typical dissolved oxygen analysis.

2.2.3.3.b Sediment Oxygen Demand Measurement Strategy

The selection of sampling locations for SOD measurement is not usually quantitatively addressed by water quality modelers. The first step is to determine which stream reaches should be selected for SOD measurement, and then outline a strategy for determining the measurement frequency for the selected reaches.

In developing a strategy for SOD measurement, it is logical to assume that those factors important in establishing model reaches or segments are also relevant to selecting SOD measurement sites. The more important of these factors are:

- Geometric—depth, width
- Hydraulic—velocity, slope, flow, bottom roughness
- Water Quality—location of: point sources, nonpoint sources runoff, abrupt changes (large gradients) in DO/BOD concentrations, tributaries, dams and impoundments.

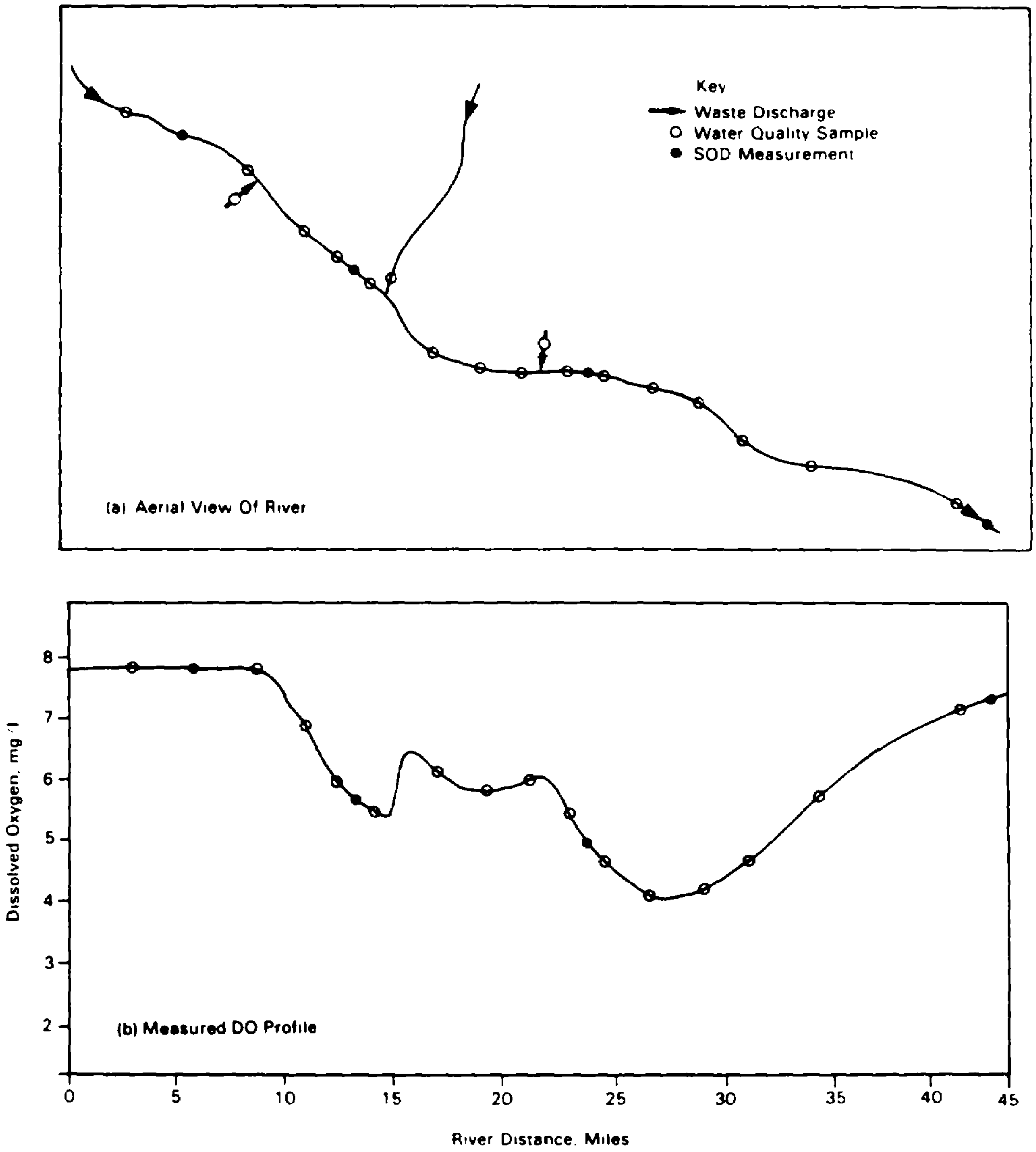
The most important factor for SOD is likely to be the location of abrupt changes in DO/BOD concentrations.

In the absence of historical water quality information, it is best to assume for planning purposes that SOD should be measured in each model reach. This recommendation is particularly important in rivers and streams where significant DO deficits occur. In these cases, it is important that the modeler obtain sufficient data to independently account for the effects of point sources and SOD on water quality. Lumping instream BOD decay for example, with SOD is not good modeling practice and should be avoided in models used for waste load allocation.

As a practical matter, however, this recommendation is difficult to implement completely due to a number of financial constraints imposed during modeling studies. For these situations, it is recommended that the partially calibrated model be used to determine which stream reaches (segments) are critical in terms of DO concentration. SOD measurements can then be concentrated in these areas.

The modeler should also be aware that the sensitivity of DO to SOD (and other model mechanisms) can change significantly when forecasts are made at the 7Q10 flow (or other worst case conditions). Typically, the model is calibrated with water quality data collected at flows higher than the 7Q10 flow. It is possible in this case that the DO sensitivity to SOD is low, and the modeler might elect to reduce the number of SOD measurements accordingly. This action becomes inappropriate if the stream DO sensitivity to SOD increases at the longer travel times usually associated with the $_7Q_{10}$ flow.

Figure 2-14 Example sampling network for a dissolved oxygen analysis



Once critical reaches are defined, several considerations that should be addressed by the modeler include: measurement technique, measurement precision, and measurement frequency.

Although it is not the purpose of this handbook to review SOD measurement, it is important to note that there is a controversy regarding the accuracy of appropriate laboratory based procedures when compared to preferred in-situ methods (18,42). There is growing evidence, however, that laboratory based procedures can be used as a reliable surrogate for in-situ measurements (18). These data would further suggest that basin specific correlations of laboratory SODs with in-situ SODs are credible alternatives to extensive in-situ measurements. In this case, the modeler would collect the data to develop the correlation at one location and then rely upon the less expensive laboratory technique for remaining stream segments. This option would be especially advantageous for large basins with similar sediment characteristics throughout.

There is some data available for SOD measurement precision for both in-situ and laboratory methods (42,43,44,45). To a large degree, the precision is a function of the experience of the field crew or laboratory analyst. For in-situ work with an experienced crew, a precision defined by the coefficients of variation of multiple measurements could be as high as ±40%. With additional field experience, the precision should consistently improve to the ±20% range. Laboratory precision is usually better than in-situ precision and as a rule in the range ±10% to ±20%. It is recommended that measurement crews pay close attention to measurement precision in model studies used for wasteload allocation. Five duplicate measurements at one location prior to extensive SOD work throughout the basin are advisable to define this potentially important factor for model calibration. Reference (16) presents guidance for both laboratory and in-situ SOD methods.

Since most water quality models require that SOD be specified as a single value per reach, the input value must be an average for the entire reach. For large, slow moving rivers a minimum of 2 to 3 measurements per reach is recommended and should include both mid-channel and shallower stream bank areas. One measurement per reach may be appropriate for small, shallow streams if bottom conditions are consistent within each cross-section. Visual observations of the streambed should provide the modeler with a basis for this judgment. For all streams, however, duplication of at least 10% of all SOD measurements is recommended for quality assurance purposes.

The final point to consider is that SOD may vary with season. This observation is particularly relevant to some estuarine and impoundments dominated by algal activity and/or oxidation of organic and inorganic nutrients by benthal microorganisms, both of which may occur seasonally. The modeler should thus be aware of this potential concern and structure the SOD measurement times accordingly.

2.2.3.4 Sampling Time and Frequency

The general model-independent sampling concerns discussed in Section 2.1.4.2 are directly applicable in conventional pollutant studies. Most WLA analyses use steady-state models, except in some cases where diurnal variations in oxygen are important or when long term eutrophication analyses are necessary. The analyses are typically conducted for a low flow condition with a high summer temperature since dissolved oxygen problems are usually most severe under these conditions. Procedures for selecting the appropriate flow and temperature conditions are described in Book VI ("Design Conditions") of the WLA guidance documents (see Table 1-1). The sampling program should be conducted during the time of the year that most closely approaches the conditions to be used in the analysis. Samples should be collected during a period when weather, waste loading, and stream flows are expected to remain approximately constant. If possible, a short-term intensive survey should be conducted in which several samples are collected at each station at different times of the day over a period of 2 or 3 days. This approach provides enough data to accurately define the average DO profile, as well as the variability in the profile (Figure 2-15).

Diurnal variations in dissolved oxygen can be important in streams when phytoplankton, periphyton, or aquatic plant densities are high, or in streams which have large diurnal variations in temperature (5°C or more). In the first case, the DO variations are due to photosynthesis and respiration, while in the second case the variations are due primarily to the effects of temperature on DO saturation. Photosynthesis and respiration produce maximum DO concentrations in late afternoon and minimum concentrations in early morning. Temperature variations result in essentially the opposite effects, minimum DO levels in mid afternoon and maximum levels at dawn. Figure 2-16 shows examples of two rivers in which these effects cause diurnal variations of about 2 or 3 mg/l. These could be significant if the background levels were close to the water quality standards.

If diurnal variations are important, a dynamic model or a quasi steady-state model which simulates these effects should be used in the WLA analysis. Preliminary sampling over a 24-hour period at a few stations should first be conducted to determine if diurnal effects are significant. The significance of the variations depends on the context of the problem. For example, if the daily average DO concentration is around 5 mg/l or less, then a diurnal variation of less than 1 mg/l could be very important with respect to meeting water quality standards, while if the average DO concentration is around 10 mg/l, then diurnal variations of 2 or 3 mg/l may not matter. However, these latter variations would be important if future projected waste loads were being analyzed since these loads could lower the ambient DO levels in the stream to a point where a 2 to 3 mg/l diurnal fluctuation could violate standards. If preliminary sampling indicates diurnal variations are important, then the sampling program should include 24-hour sampling for dissolved oxygen and temperature at all of the key stations. As a minimum, these would include the upstream boundary, *all major tributaries*, and a few stations near the low points of the major DO sags. If there is reason to suspect that the significant diurnal variations in characteristics of the waste

Figure 2-15. Results of a short-term intensive survey to establish the dissolved oxygen profile (modified from Clarence J. Velz, *Applied Stream Sanitation*, copright © 1984 by John Wiley & Sons, Inc.).[47]

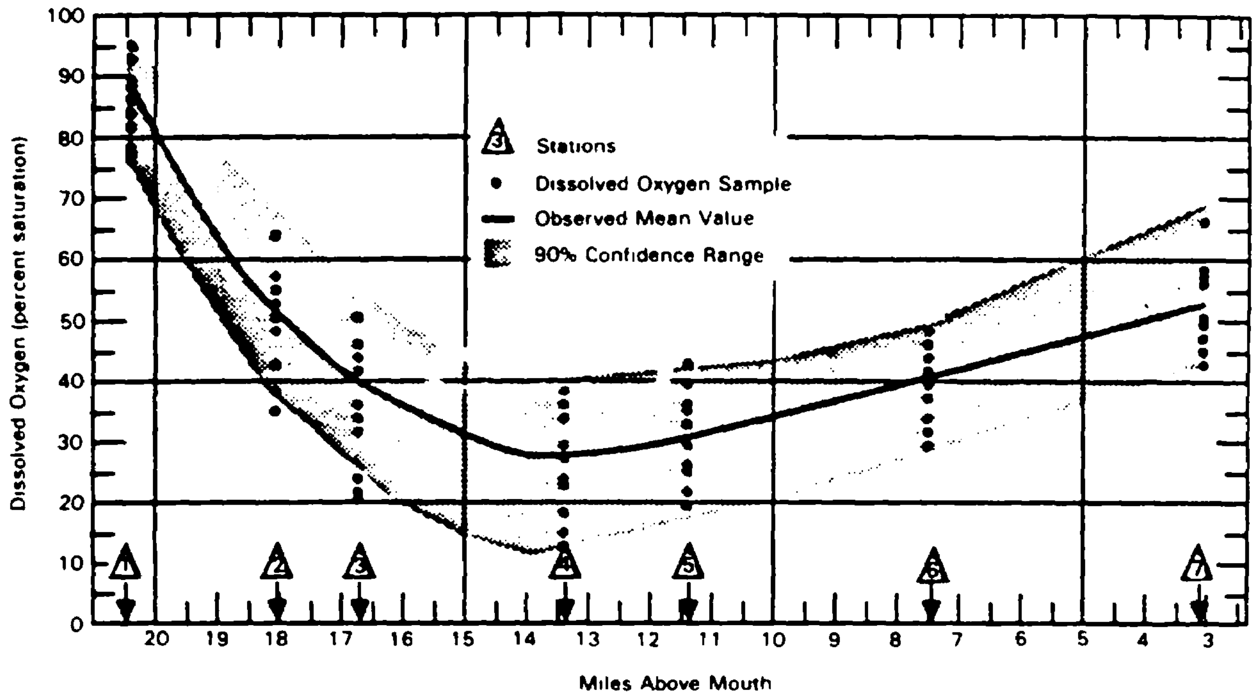
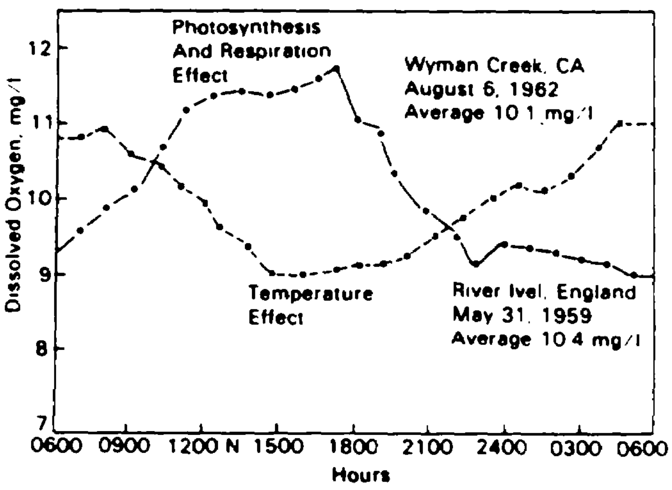


Figure 2-16. Daily dissolved oxygen variation in two streams (From [27]).

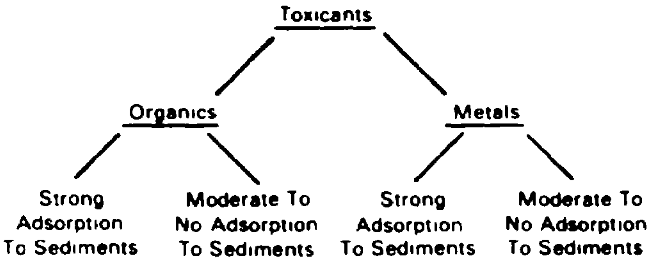


discharges will occur, then the discharges should be sampled. These locations satisfy the minimum requirements of defining the boundary and loading conditions plus a few calibration stations in the critical portions of the DO sags. However, additional stations would also be desirable, for example, upstream of the tributaries and waste discharges, and at several locations along the major DO sags. As with the other data, two sets of sampling data are required, one for calibration and one for verification. The diurnal sampling should be conducted at the same time or as close as possible to the rest of the water quality sampling.

2.3 Sampling Requirements for Toxic Pollutants

2.3.1 Introduction

Thousands of toxic pollutants are discharged into rivers across the United States. The toxicants can arbitrarily be grouped in many different ways (e.g., by use, by quantity produced, by volatility, or by molecular structure). For design of stream surveys, the following categorization is convenient:



Sampling requirements are generally more intensive when toxicants adsorb to suspended and bottom sediments because data are needed to quantify such interactions. Since not all toxicants adsorb to sediments, however, the assumption should not automatically be made that sediment-toxicant interactions must be quantified in stream surveys. Such an assumption can lead to needless expenditures. For example, many metals can be transported largely as dissolved species if river water pH is low (e.g., 6.0 to 6.5), and if suspended solids concentrations are also low (e.g., 0 to 25 mg/l). These conditions pertain in many rivers in the Northeast and Southeast during moderate to low flow periods.

Also, many of the organic toxicants are transported predominantly in dissolved form at low suspended solids concentrations. Adsorption of organics can be evaluated using the following expression:

$$C/C_T = \frac{1}{1 + K_p \cdot S \cdot 10^{-6}} \qquad (2\text{-}14)$$

where C/C_T = fraction of organic toxicant in dissolved form, dimensionless
K_p = partition coefficient, 1/kg = $0.6 . f_c . K_{ow}$ [See (27)] for details and values of K_{ow}
S = suspended solids concentration, mg/l
f_c = fraction by weight of organic carbon on suspended sediments (typically 0.01 - 0.10)
k_{ow} = octanol-water partition coefficient

For conditions when C/C_T approaches unity (e.g., ≥0.9), adsorption is unimportant, and pollutant-sediment interactions can be neglected. For example, suppose $f_c = 0.03$, $K_{ow} = 50$, and $S = 25$ mg/l. Then

$$C/C_T = \frac{1}{1 + 0.6 \cdot 0.03 \cdot 50 \cdot 25 \cdot 10^{-6}} = 0.9999$$

and adsorption is negligible.

Equation (2-14) has been used with limited success for metals as well as organics. However, the partition coefficient K_p is usually taken as site-specific for metals and local data for pH, suspended sediments and other WQ paramters are needed to reliably use this approach.

The fate of organic toxicants can be controlled by processes in addition to adsorption such as photolysis, biodegradation, hydrolysis and volatilization. Surprisingly, however, the fate of many organic toxicants are often dominated by a *single process*. For example, the following organics are commonly discharged into rivers, and are also commonly found at Superfund sites:

- Trichloroethylene (TCE)
- Toluene
- Benzene
- PCBs
- Chloroform
- Tetrachloroethylene.

Volatilization probably controls the fate of five of the toxicants, while adsorption is most important for the remaining one (PCBs). The volatilization rate constant as shown in (27) can be found from:

$$k_v = \left(\frac{32}{MW}\right)^{1/4} k_2 \qquad (2\text{-}15)$$

where k_v = volatilization rate
k_2 = reaeration rate of dissolved oxygen
MW = molecular weight of the organic compound that is volatilizing

Consider, for example, TCE (MW = 131) in a stream where the atmospheric reaeration rate is 2.0/day. The volatilization rate is:

$$k_v = \left(\frac{32}{131}\right)^{1/4} 2 = 1.4/\text{day}$$

Other processes (hydrolysis, photolysis, biodegradation) are insignificant compared to the volatilization rate. Further TCE has a low K_{ow} so that adsorption can also be neglected. Consequently, the atmospheric reaeration rate is the major process that must be quantified to predict the fate of TCE in streams. This example illustrates that simple approaches can be used to allocate waste loads for some toxicants, and that instream data requirements may not be prohibitively expensive.

When multiple processes mutually influence the fate of toxicants, stream surveys cannot always be easily designed to segregate out the significance of each process. However, the composite rate constant can be found in the same manner as for the BOD decay rate by plotting toxicant concentration versus distance (See Section 2.2). Transformation rates for toxicants are usually determined from theoretical relationships, or in the laboratory, and the sum of the rate constants can then be compared to the instream composite rate. Only under special circumstances can the individual transformation processes be found from a stream survey (see the example problem in Section 3.2, for example) or by resorting to more elaborate approaches (Hern *et al.*, 1983).

2.3.2 Model Data Requirements

This section summarizes data requirements for methods that can be used to to determine the amount of toxicants that can be assimilated. The methods range from simple to complex:

- screening techniques for organic toxicants and metals
- the MICHRIV model, a steady-state computer model for metals and organic toxicants
- the TOXIWASP model, a dynamic computer model for toxic organics

Tables 2-7 through 2-10 summarize the data requirements for each approach. The first two tables show data requirements for screening techniques. The requirements in those two tables have been further subdivided as shown below:

Metals	Organics
• dilution only is considered	• dilution only is considered
• dilution and adsorption are considered	• dilution and adsorption are considered
• dilution, adsorption, and interactions with streambed are considered	• dilution, adsorption, and decay are considered (often volatilization, dilution, and adsorption are the most important)
• dilution, adsorption, interactions with streambed, and speciation are considered	

Depending on the specific situation and resources available, the analyst can select an appropriate level of complexity, and collect data accordingly. The screening methods are most applicable when one or two sources of toxicants are present, when hydraulics are simple, and when fate processes are easily quantified.

The data requirements of MICHRIV (Table 2-9) are similar to the most complex level of screening analysis. However because MICHRIV is a computer model, multiple waste sources and spatially variable parameters are more easily accommodated. The data required for metals and organics are indicated separately, and those associated with adsorption are shown with an asterisk (*).

The data requirements for TOXIWASP (Table 2-10) are presented in a very summarized format. Data requirements are greater than for the previous approaches. The analyst should consult the TOXIWASP user manual (4) for specific details.

TOXIWASP is designed explicitly for organic toxicants (and not metals) and requires more technical exper-

Table 2-7. Summary of Data Requirements for Screening Approach for Metals in Rivers (27)

Data	Calculation Methodology Where Data are Used*	Remarks
Hydraulic Data		
1. Rivers:		
• River flow rate, Q	D, R, S, L	An accurate estimation of flow rate is very important because of dilution considerations. Measure or obtain from USGS gage.
• Cross-sectional area, A	D, R, S	
• Water depth, h	D, R, S, L	The average water depth is cross-sectional area divided by surface width.
• Reach lengths, x	R, S	
• Stream velocity, U	R, S	The required velocity is distance divided by travel time. It can be approximated by Q/A only when A is representative of the reach being studied.
2. Lakes:		
• Hydraulic residence time, T	L	Hydraulic residence times of lakes can vary seasonally as the flow rates through the lakes change.
• Mean depth, H	L	Lake residence times and depths are used to predict settling of absorbed metals in lakes.
Source data		
1. Background		
• Metal concentrations, C_T	D, R, S, L	Background concentrations should generally not be set to zero without justification.
• Boundary flow rates, Q_u	D, R, S, L	
• Boundary suspended solids, S_u	D, R, S, L	One important reason for determining suspended solids concentrations is to determine the dissolved concentration, C, of metals, based on C_T, S, and K_p. However, if C is known along with C_T and S, this information can be used to find K_p.
• Silt, clay fraction of suspended solids	L	
• Locations	D, R, S, L	
2. Point Sources		
• Locations	D, R, S, L	
• Flow rate, Q_w	D, R, S, L	
• Metal concentration, C_{T_w}	D, R, S, L	
• Suspended solids, S_w	D, R, S, L	

Table 2-7. (Continued)

Data	Calculation Methodology Where Data are Used*	Remarks
Bed Data		
• Depth of contamination		For the screening analysis, the depth of contamination is most useful during a period of prolonged scour when metal is being input into the water column from the bed.
• Porosity of sediments, n		
• Density of solids in sediments (e.g., 2.7 for sand), μ_s		
• Metal concentration in bed during prolonged scour period, C_{T2}		
Derived Parameters		
• Partition coefficient, K_p	All	The partition coefficient is a very important parameter. Site-specific determination is preferable.
• Settling velocity, w_s	S, L	This parameter is derived based on suspended solids vs. distance profile.
• Resuspension velocity, w_{rs}	R	This parameter is derived based on suspended solids vs. distance profile.
Equilibrium Modeling		
Water quality characterization of river:	E	Equilibrium modeling is required only if predominant metal species and estimated solubility controls are needed.
• pH		
• Suspended solids		
• Conductivity		
• Temperature		
• Hardness		Water quality criteria for many metals are keyed to hardness, and allowable concentrations increase with increasing hardness.
• Total organic carbon		
• Other major cations and anions		

*D - dilution (includes total dissolved and adsorbed phase concentration predictions)
R - dilution and resuspension
S - dilution and settling
L - lake
E - equilibrium modeling

Table 2-8. **Summary of Data Requirements for Screening Approach for Toxic Organics in Rivers (27)**

Data	Methodology Where Data are Used*	Remarks
River Hydraulic Data		
• Flow rate, Q	D, DA, DAK	An accurate estimate of flow rate is very imporant because of dilution, which for many organics is the most important process that influences their fate. Measure or obtain from USGS gage.
• Cross-sectional area, A	D, DA, DAK	
• Water depth, h	DAK	Water depth can influence rate processes such as volatilization and photolysis.
• Reach lengths, x	DAK	
• Stream velocity, U	DAK	U = Q/A should be used only where A is representative of the reach being analyzed. Otherwise dye tracers, measured from centroid to centroid of the dispersing dye is a better method of finding velocity (indirectly as distance divided by travel time).
Source Data		
1. Background		
• Toxicant concentrations	D, DA, DAK	Concentrations of organic toxicants may be negligible in areas not influenced by man.
• Boundary flow rates	D, DA, DAK	
• Boundary suspended solids	DA, DAK	Suspended solids are used to help determine the dissolved and adsorbed phase concentrations.
2. Point Sources		
• locations	D, DA, DAK	
• Flow rates, Qw	D, DA, DAK	
• Total toxicant concentration, C_T	D, DA, DAK	
• Suspended solids, Sw	DA, DAK	

Table 2-8. (Continued)

Data	Methodology Where Data are Used*	Remarks
Partition Coefficient and Rate Constant Data		Stream surveys can not always be easily designed to calculate rate constants or partition coefficients for toxic organics. A step-by-step procedure for calculating each rate constant and partition coefficient discussed here can be found in Mills *et al.* (in press). Input data needed to calculate rate constants and partition coefficients are identified here, and ranges of values for the data are found in (27, 49)
• Solid-liquid partition coefficients, K_p	DA, DAK	Data required: • K_{ow}, octanol-water partition coefficient (use literature, e.g., Leo *et al.*, 1971) • X_{oc}^{S}, organic carbon fraction of sand in suspension (typically 0.00-0.05) • X_{oc}^{f}, organic carbon fraction of silt-clay in suspension (typically 0.03-0.10).
• Acid-base speciation	DA, DAK	Data required: • pH of water • K_a or K_B, the association constant for the organic acid or base (from literature, e.g., (51))
• Volatilization rate	DAK	Data required: • Henry's Law Constant (from) literature, e.g., (52) • Stream depth • Reaeration rate for dissolved oxygen • Wind speed (only for toxicants with small Henry's Constant, e.g., $K_H \leq 10^{-5}$)
• Biodegradation rate	DAK	Typically, only an approximation of biodegradation rate is obtainable due to factors such as adaptability to stream environment
• Hydrolysis rate	DAK	Data required: • pH of river • Acid or base catalyzed hydrolysis rate constants (from literature, e.g., (53)) • Neutral hydrolysis rate (from literature e.g., (53))
• Photolysis rate	DAK	Data required: • Solar radiation • Water depth • Concentrations of light-attenuating substances (chlorophyll *a*, DOC, SS)

*D - dilution only (total organic in water column, sum of dissolved and adsorbed phases)
DA - dilution plus adsorption (to predict dissolved and adsorbed phases)
DAK - adsorption and rate processes both considered.

Table 2-9. **Michriv Model Data Requirements (5)**

Variable	Pollutant Category[1]	Remarks/Qualifications
Channel Data		
• River flow, Q	M, O	Measure or obtain from USGS gage.
• Velocity, U	M, O	Measure directly with time-of-passage dye study, (Ref. (54)) or compute from area and flow: U = Q/A.
• Cross section area, A	M, O	Compute from measured width and depth, or compute from velocity and flow.
• Reach length, x	M, O	Reaches determined by significant morphometric changes, tributaries, or point sources; measure from charts, confirm in field.
• Depth of water, h	M, O	Measure directly or compute from cross section area and measured width.

Table 2-9. (Continued)

Variable	Pollutant Category[1]	Remarks/Qualifications
Loading Data		
1. Upstream "Boundary" Concentration		Direct measurement of loading data is preferable for WLA modeling.
• Toxicant, Cu	M, O	
• Suspended solids, Sw	M*, O*	
2. Point Sources		
• Flow, Qw	M, O	
• Concentration toxicant, Cw	M, O	
• Concentration-suspended solids	M*, O*	
Bed and Particulate Data		
• Thickness of Active Sediment, H_2	M*, O*	Estimate from core samples, measuring vertical distribution of contaminants; or use typical published values. This parameter has no effect on steady state results unless significant decay occurs in the bed.
• Solids concentration in bed, m_2 Porosity, n Solids type Size distribution	M*, O*	Measure or estimate: m_2 = (particle density) (1-n)
• Settling Velocity, w_s	M*, O*	Estimate from particle-size distribution and stream turbulence coupled with published data or Stokes formula. Measure with sedeiment traps or in lab. Adjust by calibration.
• Resuspension velocity, w_{rs}	M*, O*	Calibrate to suspended solids data; estimate from theory.
• Partition coefficient, K_p	M*, O*	Calibrate from dissolved and particulate data. Otherwise, use literature values (5)
• Sediment diffusion, K_1	M, O	Use literature values (5)
Rate Constants and Related Data		
• Volatilization coefficient, k_v	O	Calculate from theory.
Reaeration coefficient, k_2	O	
Solubility, S	O	Use published data (49)
Vapor pressure, P	O	Use published data (49)
• Photolysis rate, k_p	O	Calculate from theory (27) or by Actinometer.
Chlorophyll *a*	O	
Diss. organic carbon	O	
Suspended solids	O	
Solar/UV radiation	O	
Near surface rate	O	Meausred by Actinometer at water surface, or in laboratory (49)
• Biolysis rate, k_b	O	
Cell count	O	
Chlorophyll *a*	O	
Hydrolysis rate pH	O	Laboratory experiment at different pH values or from published data (53)
Ancillary data: temperature	O	

[1]M = Metals; O = Organics. The asterisk (*) indicates the data are required only if adsorption to sediments is important.

Table 2-10. Summary of Input Data Required for TOXIWASP

Category	Data
Mass Exchange	• exchange coefficients • interfacial cross-sectional area • river segment lengths
Volumes	• volumes of segments
Flows	• flow between segments • flow routing information • piecewise linear approximation of time variable flows

Table 2-10. (Continued)

Category	Data
Boundary Condition	• boundary concentrations • piecewise linear approximation of time variable flows
Forcing Functions	• loading rates • piecewise linear approximation of time variable function
Parameters	• temepratrure vs time function • depth of compartments • water velocity • wind speed • bacterial population • biomass • reaeration rate • molar concentration of environmental oxidants • organic carbon content of fine sediments • percent [illegible] artments • pH • settling rates of fine sediments
Constants	• 66 constants required
Miscellaneous Time Functions	
Initial Conditions	• initial concentrations of concentrations, water temperature, etc.
Stability and Accuracy Criteria	

tise and resources than the approaches discussed previously. TOXIWASP may be an appropriate model to use for WLA when:

- waste loadings (and other boundary conditions) are highly variable over time
- the flow field is highly dynamic (e.g., during a storm)
- other significant parameters (e.g., water temperature) are time variable
- detailed sediment—water column interactions are required (for toxicants that adsorb strongly).

2.3.3 Sampling Guidelines

Profiles of toxicants in rivers, under most hydrologic conditions, often approach gradually curved lines, as shown by Figure 2-17. Exceptions occur in the vicinity of point sources where an abrupt increase or decrease in toxicant concentrations may occur. Because toxicant profiles do not exhibit "sag points" as do dissolved oxygen profiles, sampling stations can usually be more evenly distributed downstream of the source.

Distance between sampling locations can be estimated based on the relative change in toxicant concentration desired between the stations. Table 2-11 summarizes travel times required for various C/Co ratios (ratios of downstream to upstream concentrations) and decay rates. Travel times greater than approximately 2 days between locations are not recommended.

The travel times shown in Table 2-11 can be found by solving the following equation:

$$t = \frac{\ln (Co/C)}{k} \qquad (2\text{-}16)$$

where t = travel time between locations where the concentration changes from Co to C
k = first order decay rate, 1/day

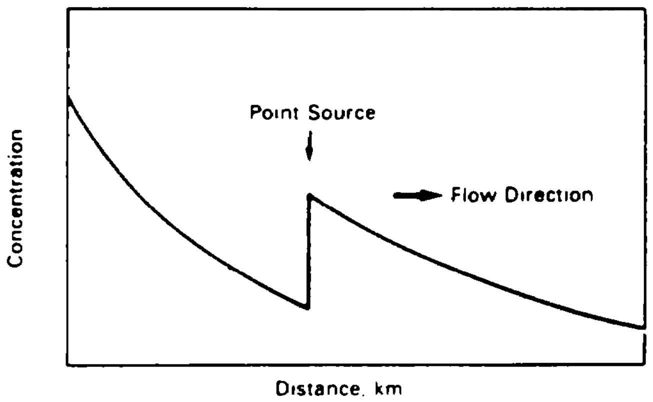
By selecting a C/Co ratio and an approximate decay rate, the analyst can determine the travel time interval between sampling locations. Given the travel time the equivalent distance between two sampling stations (x) is approximately

$$x = Ut \qquad (2\text{-}17)$$

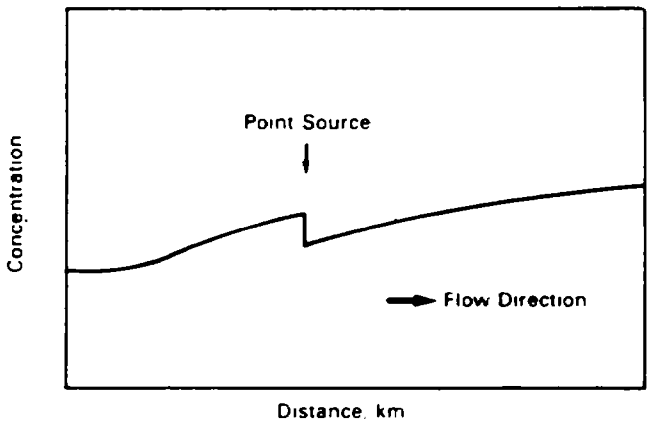
where U = stream velocity
t = travel time

For toxicants that are expected to act nearly conservatively, the distance increment is approximately controlled by the longest travel time between sampling points the water quality specialist is willing to tolerate, but generally this should be less than two days. For toxicants that decay rapidly, travel time between sampling points are on the order of 0.2 to 0.5 days for C/Co ratios of 0.5 to 0.7. This will generally correspond to intervals of 5 to 9 km (3 to 5 miles).

Figure 2-17 Typical concentration profiles of toxicants in rivers



(a) Toxicant Profile That Reflects Settling Or Decay



(b) Toxicant Profile That Reflects Scouring Of Contaminated Sediments

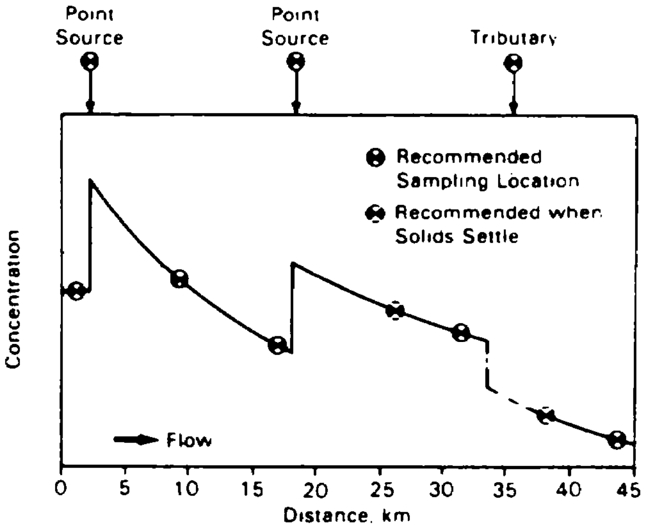
Table 2-11. Travel Times for Various C/Co Ratios Corresponding to Different Toxicant Decay Rates.

Travel Time (Days)

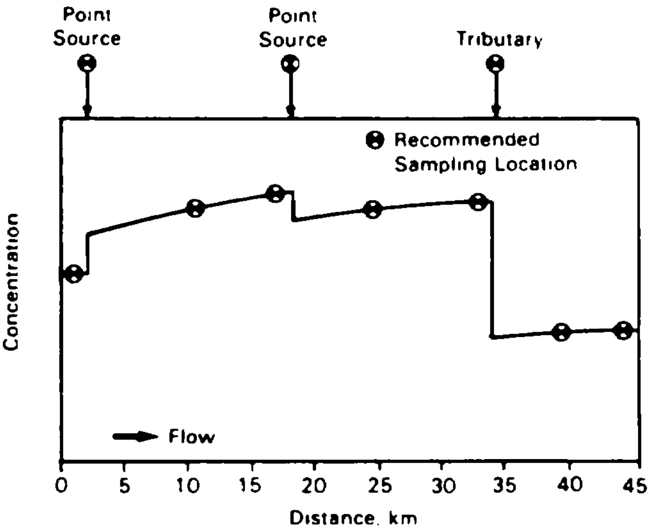
	k, (1/day)										
C/Co	0.05	0.1	0.2	0.3	0.4	0.5	0.6	0.8	1.0	1.5	2.0
0.9	2.1	1:0	0.5	0.4	0.3	0.2	0.2	0.1	0.1	0.07	0.05
0.8	-	2.2	1.1	0.7	0.6	0.4	0.4	0.3	0.2	0.1	0.1
0.7	-	-	1.8	1.2	0.9	0.7	0.6	0.4	0.4	0.2	0.2
0.6	-	-	2.6	1.7	1.3	1.0	0.9	0.6	0.5	0.3	0.3
0.5	-	-	-	2.3	1.7	1.4	1.2	0.9	0.7	0.5	0.3
0.4	-	-	-	-	2.0	1.6	1.5	1.1	0.9	0.6	0.5
0.3	-	-	-	-	-	-	2.0	1.5	1.2	0.8	0.6
0.2	-	-	-	-	-	-	-	2.0	1.6	1.1	0.8
0.1	-	-	-	-	-	-	-	-	2.3	1.5	1.1

Figure 2-18 shows profiles of toxicant concentrations in a river during two seasons of the year (a summer low flow period and a spring high flow period). During high flow it is assumed that the toxicant is scoured back into the water column to produce increasing concentrations with distance.

Figure 2-18 Sampling locations for toxicants during low flow and high flow period



(a) Typical Low Flow Profile



(b) Typical High Flow Profile

Also shown in Figure 2-18 are suggested sampling locations for a minimal sampling program. Sampling directly below point sources is not recommended. Instead, samples should be collected upstream and in the point source (the latter should include a measurement of the discharge flow rate). At least one sample per reach (between sources) is recommended; two or more samples in one reach help add a degree of certainty to the observed profile.

In short reaches on wide rivers, sampling should be conducted at several points laterally across a river if evidence (e.g., from a dye study) indicates that complete lateral mixing has not been attained. See Section 3.2 for general guidance on this subject. In one-dimensional models the predicted concentrations are cross-sectional averages, which can be significantly different from a single measured concentration if large lateral concentration gradients exist across the river.

When adsorption to suspended solids is important (e.g., $C/C_T < 0.9$), suspended solids profiles versus distance should be found to determine the significance of settling or scouring of sediments and adsorbed toxicants. Figure 2-19 shows example profiles of suspended solids during a low flow and high flow period, and can be used to help make this determination.

The settling rate (w_s) and resuspension rate (w_{rs}) of the solids are required for use in WLA modeling, and can be generated from the profiles. For settling of solids, w_s can be computed as:

$$w_s = \frac{-Hu}{x} \ln\left[\frac{SS(x)}{SS(0)}\right] \qquad (2\text{-}18)$$

where w_s = settling rate
h= stream depth
U= stream velocity
SS(0) = suspended solids concentrationat a reference location x = 0
SS(x) = suspended solids concentration at location x

Based on Figure 2-19(a), the approximate settling rate between km 50 and km 35 is:

$$w_s = \frac{0.5 \times 0.2}{30 \times 10^3} \ln\left(\frac{10}{4}\right) \times 86400 = 0.26 \text{ m/day}$$

where the depth (0.5 m) and velocity (0.2 m/sec) are taken from (5).

The resuspension velocity, w_{rs}, can be estimated as:

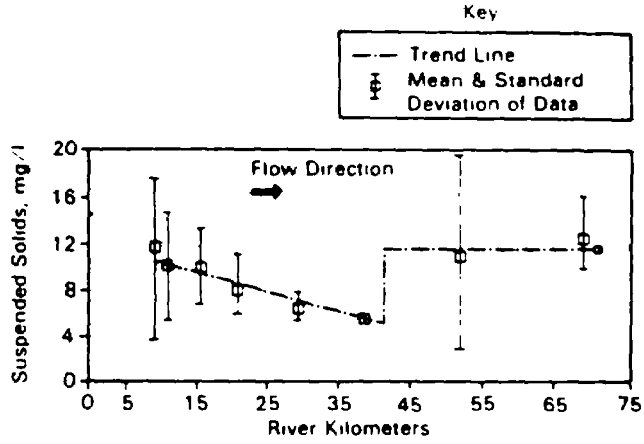
$$w_{rs} = \frac{UH\,\Delta SS}{m_2\,\Delta x \cdot 10^6} \qquad (2\text{-}19)$$

The term $\Delta SS/\Delta x$ is the change in suspended solids concentration over distance Δx and m_2 is the solids density in the bed. From Figure 2-19(b), the resuspension velocity is computed as:

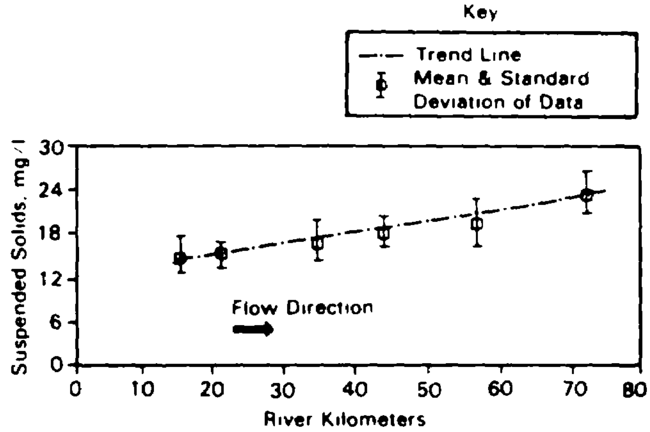
$$w_{rs} = \frac{1 \cdot 2 \cdot (25 - 12)}{0.2 \cdot 80 \cdot 10^3 \cdot 10^6}\ 86400 = 1.4 \cdot 10^{-4} \text{ m/day}$$

The data for velocity (1 m/sec), depth (2 m) and bedded sediment concentration (0.2 kg/l) are also from (5).

Figure 2-19. Typical suspended solids concentrations during (a) low flow and (b) high flow periods



(a) Suspended Solids, mg/l, During Low Flow Period



(b) Suspended Solids, mg/l, During High Flow Period

Equations 2-18 and 2-19 should be used cautiously since they give only the net settling rate and the net resuspension rate.

Note that the values for w_s and w_{rs} are specific to the flow regime at the time of sampling. Thus, these values can change between the calibration period, the verification period, and the wasteload allocation period.

Table 2-12 summarizes the topics presented in this section. Sampling requirements can be intensive if multiple fate processes, multiple point sources, sediment interactions, and time variability need to be evaluated. However, if steady-state conditions prevail, one well quantifiable process controls the fate of the toxicant being allocated, hydraulics are at steady state, and there is a single waste discharge, then stream survey requirements will be minimal.

Table 2-12. Summary of Sampling Guidelines for Toxicants

Seasonal Considerations

- Summer low flow conditions can result in high levels of toxicants in rivers. Even if toxicants tend to be highly adsorptive, downstream transport in solution can still be significant due to low suspended solids concentration. This period is often used for WLA analyses.

- High flow conditions can scour toxicants from streambeds and elevate total instream concentrations. This occurs only for highly adsorptive toxicants, and elevated loadings can be offset by dilution from high flow rates during periods of scour.

Waste Loading Considerations

- *Point Sources:* Any diurnal variations in loadings should be established. If loadings vary significantly TOXIWASP can be used for organics. Otherwise multiple simulations with steady state models should be considered.

- *Tributaries:* Sampling within tributaries is required if sources that are subject to allocation are located there. Otherwise, sampling at the mouth of the tributaries to establish boundary conditions is acceptable.

- *Upstream Boundary and Other Background Locations:* Background concentrations and flow rates are required at upstream boundaries on rivers and tributaries. Concentrations of background organic toxicants are ofen negligible. However, background metal concentrations can be significant.

Sampling Location Considerations

- Sample upstream of point sources.

- Typically sample at 1-2 locations per reach, with the stations located below the zone of complete lateral mixing.

- If samples are taken at locations where complete mixing of upstream point sources has not occurred, several samples across the width of the stream should be taken and averaged before comparing to one-dimensional model predictions.

- The maximum recommended travel time between sampling locations should be less than two days for toxicants that appear to be conservative.

- For toxicants with high decay rates, a spacing of 3-5 miles (5-8 km) between sampling stations is appropriate. This will vary depending upon travel time.

- For pollutants that adsorb significantly, depth-averaged suspended solids profiles should be determined for each season analyzed for the waste load allocation. Fairly close spacing of sampling stations is recommended (5-8 km).

Temporal Considerations

- Sampling at 3-4 hour intervals over a day may be required when:
  - source loadings are highly time variable.
  - the fates of the toxicants of concern are controlled by temperature dependent processes such as volatilization and water temperature fluctuate considerbly (e.g., 5-10°c or more over a 24 hour period).
  - photolysis (which depends on solar radiation) is an important process for the toxicant.

Rate Constant and Equilibrium Process Considerations

- Generally rate constants for toxicants are determined based on theoretical considerations. When multiple processes are operative, the processes may be difficult to segregate based on instream measurements alone. However, some supporting instream data are required (see Tables 2-2 and 2-3) nevertheless.

- The total rate constant for toxicants can be determined by plotting concentration vs. distance. Settling and scour are included in this approach.

- The total instream rate constant can be compared with the theoretical rate constants for validation.

- For metals, if speciation is to be predicted, major cations and anions, plus pH, is required. Ref (55) provides appropriate data for major rivers through the United States. MEXAMS is a computer model which will make these predictions for arsenic, cadmium, copper, lead, nickel, silver and zinc. On a screening level, the methods of (27) can be used for the same seven metals plus mercury and chromium.

Coefficients

where O_2 = dissolved oxygen concentration
O_{sat} = dissolved oxygen saturation concentration
L = carbonaceous BOD concentration
NH_3 = ammonia concentration
NO_2 = nitrite concentration
NO_3 = nitrate concentration
A = algal concentration
K_a = reaeration rate
K_d = carbonaceous BOD decay rate
K_s = carbonaceous BOD settling rate
K_r = total removal rate for carbonaceous BOD
K_{SOD} = sediment oxygen demand
h = water depth
K_{N1} = ammonia oxidation rate
K_{N2} = nitrite oxidation rate
K_{BEN} = benthic source rate for ammonia
μ = algal growth rate
r = algal respiration rate
V_s = algal settling velocity
α_1 = oxygen consumed per unit of ammonia oxidized
α_2 = oxygen consumed per unit of nitrite oxidized
α_3 = oxygen produced per unit of photosynthesis
α_4 = oxygen consumed per unit of respiration
α_5 = ammonia produced per unit of algal respiration
α_6 = ammonia uptake per unit of algal growth
α_7 = nitrate uptake per unit of algal growth

Chapter 3
Whole Effluent Approach

3.1 Overview

Guidelines have been established for the use of the whole effluent approach to waste load allocation (6). These guidelines are based on information concerning an effluent's chemical constituents and whether single or multiple effluents discharge into the stream. The whole effluent approach should be used if:

- effluent constituents are not well characterized
- known effluent constituents have not been evaluated as to potential effects on stream biota
- the mixture of effluent constituents may produce a complex (additive, antagonistic or synergistic) instream effect
- multiple dischargers may create complicated effluent mixtures instream

In the case of multiple dischargers, or nonpoint source pollution, it may not be possible to characterize the chemical constituents of each individual effluent. From the above considerations, it might be concluded that only whole effluent testing should be conducted in this situation. However, if any of the effluents has been characterized as containing chemicals with bioaccumulative, carcinogenic, teratogenic, or mutagenic potential, the USEPA suggests the use of an integrated approach where both chemical-specific analyses and whole effluent analyses are conducted. The chemical-specific approach is discussed in Section 2. In this section, the data requirements for whole effluent toxicity testing are addressed.

The whole effluent approach to waste load allocation involves testing of effluent toxicity as well as ambient toxicity testing in streams. Two tiers of effluent toxicity testing are defined. Tier 1 consists of screening methods and may be used to identify potential water quality impact situations. Where this potential impact is minimal, further evaluation is not required and the process can proceed directly to wasteload allocations. Tier 2 effluent testing is used to develop the data necessary to quantify potential effluent impacts. In some cases, effluent toxicity assessment may bypass the screening level and proceed directly to the Tier 2 analysis. This determination is made as the first step of the screening process. The overall process of effluent toxicity testing is presented in Figure 3-1.

Ambient toxicity testing is conducted to identify areas in the receiving waters where ambient toxicity exists. These procedures consist of exposing test organisms to receiving water samples and can be used to determine whether or not the effluent has a measurable toxicity after mixing and undergoing instream alteration/decay processes. An overview of ambient toxicity testing procedures is presented in Figure 3-2.

3.2 Tier 1 Effluent Testing—Screening

The first step of the screening process consists of determining the amount by which an individual effluent may be diluted by stream flow and mixing. Effluent dilution ratios (R) are calculated on the basis of average effluent flow and the critical low-flow conditions in the following manner:

$$R = \frac{Q_R}{Q_E} \qquad (3\text{-}1)$$

where Q_R =Stream critical low-flow defined by the state
Q_E = Average effluent flow.

The determination of effluent dilution under conditions of complete mixing requires information on the average effluent flow and the critical low-flow of the stream. Effluent flows can be obtained from plant operating records or NPDES permits. Stream critical low-flow is state-specified and may be based on a variety of water quality parameters. The critical low-flow typically selected is the $_7Q_{10}$. Stream flow data vailable from the USGS's WATSTOR data base.

The instream distance required for complete mixing of the effluent to be achieved must also be determined. This information is used to determine both the need for toxicity testing and the type of testing to be conducted as part of the Tier 1 screening procedure.

Waste water discharged into rivers does not instantaneously mix across the entire channel. Although vertical mixing occurs quickly, considerable distance is sometimes necessary for complete transverse mixing to occur (Figure 2-2). The following methods

Figure 3-1 Overview of effluent toxicity testing procedures

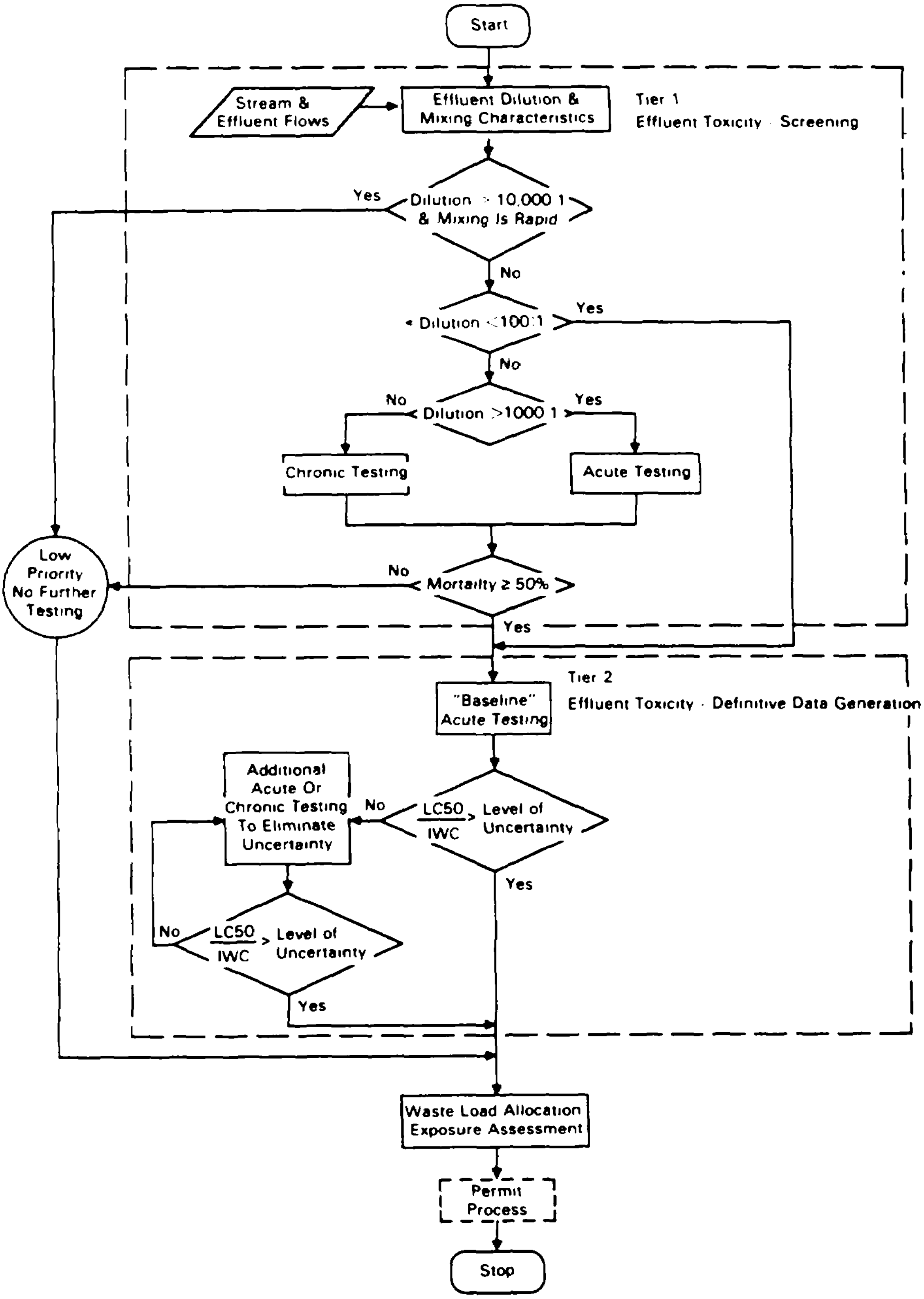
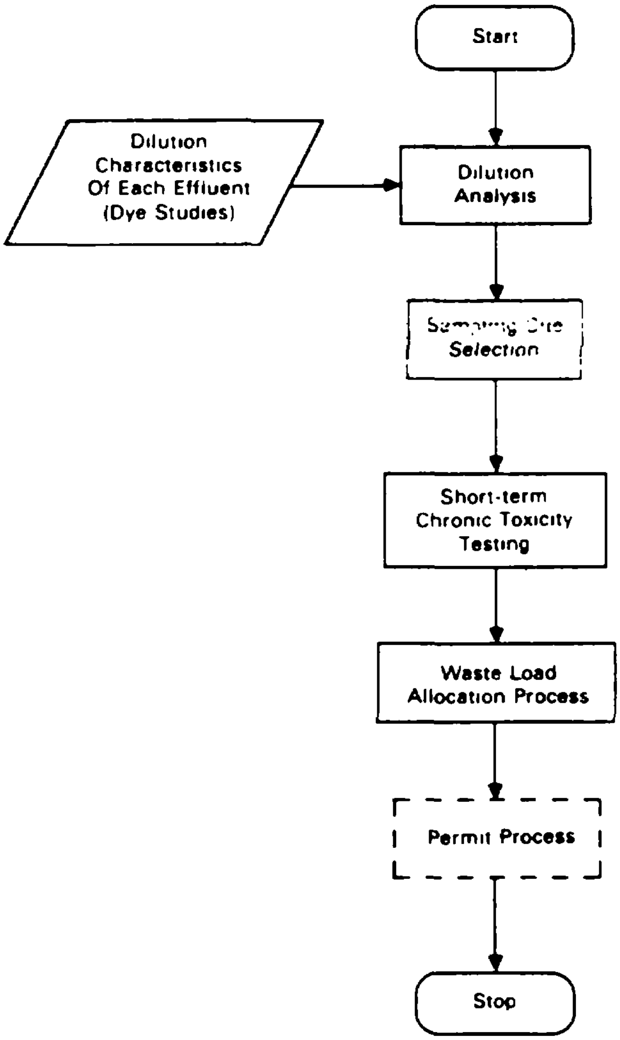


Figure 3-2. **Overview of ambient toxicity testing procedures.**



can be used to estimate mixing distances. The estimated mixing distances obtained using these methods can be used to determine the appropriate toxicity tests.

Distances below an outfall where complete vertical and lateral mixing are achieved can be estimated by the following expressions (6,56):

$$x_v = \begin{cases} 0.4\ h^2/\varepsilon_z, \text{ for a bottom discharge} \\ 0.1\ h^2/\varepsilon_z, \text{ for a mid-depth discharge} \end{cases} \qquad (3\text{-}2)$$

and

$$x_t = \begin{cases} 0.4\ w^2/\varepsilon_y, \text{ for a side discharge} \\ 0.1\ w^2/\varepsilon_y \text{ for a centerline discharge} \end{cases} \qquad (3\text{-}3)$$

where x_v = distance required for vertical mixing to be approximately 95 percent complete, feet
x_t = distance required for transverse mixing to be approximately 95 percent complete, feet
h = average river depth, feet
W = river width, feet
$\varepsilon_z, \varepsilon_y$ = mixing coefficients in vertical and transverse directions, respectively, ft^2/sec
U = stream velocity

The mixing coefficients ε_z and ε_y are typically expressed as:

$$\varepsilon_z = \beta h U_* \qquad (3\text{-}4)$$

and

$$\varepsilon_y = \alpha h U_* \qquad (3\text{-}5)$$

where U_* = $(ghS)^{1/2}$ = friction velocity, ft/sec
S = slope, ft/ft
β = 0.05-0.07, typically
α = 0.3-1.00, typically.

To help estimate x_v and x_t, Equations (3-2) and (3-3) are plotted in Figure 3-3. The distance to vertical mixing (Figure 3-3a) is plotted as a function of river depth for two different riverbed slopes. For river depths of 3 to 10 feet, x_v is typically between 10 to 300 feet. Even for very deep rivers, vertical mixing is typically accomplished within 500 feet. For most rivers, then, vertical mixing is completed quite rapidly.

For transverse mixing (Figure 3-3b), x_t is plotted against $W^2/h^{1.5}$, which indicates that river width and depth are both required to estimate x_t. Typical $W^1/h^{1.5}$ combinations are between 500 to 5000, so that x_t can vary from several hundred feet to many miles. For a river 100 feet wide and 3 feet deep, for example, the mixing distance is likely to be about 2 miles for a side discharge.

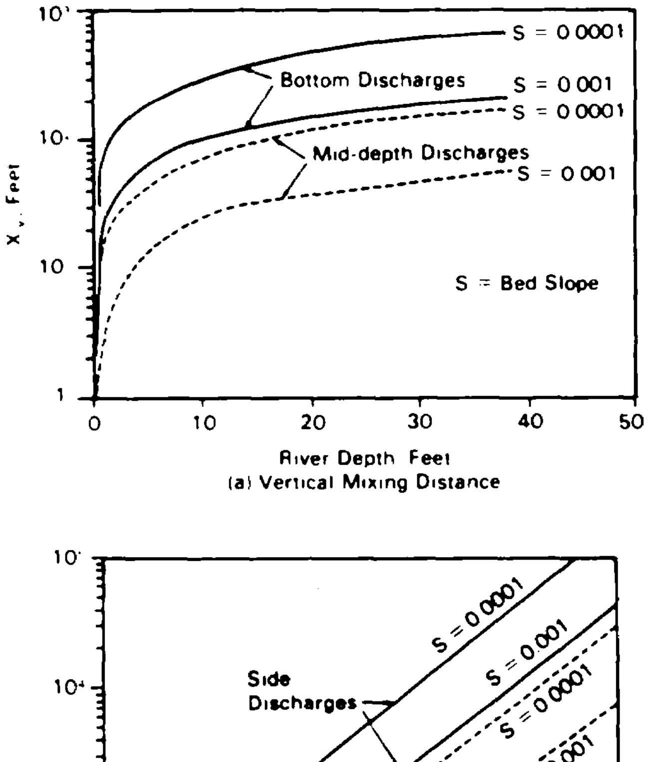
For particularly wide rivers, Equation 3-3 is likely to overestimate x_t, because other factors which enhance mixing are not considered in the equation. For wide rivers then, dye studies (see Section 3.4) are more likely needed to characterize the multi-dimensional aspects of mixing.

For the purposes of determining the appropriate screening test methods, four categories are defined based on the effluent dilution ratios (6):

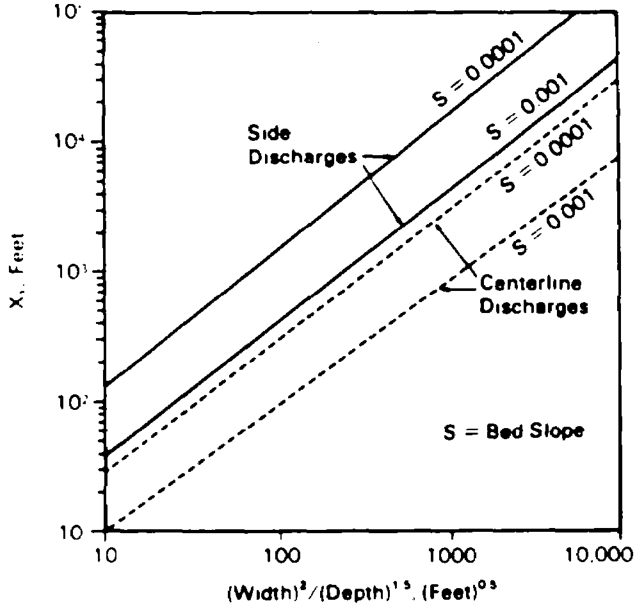
Category	Dilution Ratio
1	$R \geq 10000$
2	$1000 \leq R < 10000$
3	$100 \leq R < 1000$
4	$R < 100$

Each of these categories is evaluated differently within the whole effluent toxicity procedure (see Figure 3-1). If the effluent is diluted by a factor of greater than 10,000 to 1 and there is a reasonably rapid mix of the effluent outside of the zone of initial dilution in the receiving water, then no further evaluation is necessary. The effluent is assigned a low priority in the assessment of any potential toxic impacts on stream biota. If an effluent dilution is less than 100 to 1, then further screening is not conducted; definitive data generation, Tier 2 testing, is begun instead. Thus, the toxicity tests are conducted as part of the screening process only for dilution categories 2 and 3.

Figure 3-3. **Distance below point source discharges required for 95 percent vertical and transverse mixing.**



(a) Vertical Mixing Distance



(b) Transverse Mixing Distance

The decision concerning the type of toxicity testing to conduct as part of the screening procedure is based on the level of dilution achieved (refer to (6), page 18). If dilution is between 1,000 to 1 and 10,000 to 1 (dilution category 2) or a poorly mixed effluent plume is of concern, then acute toxicity tests should be conducted. If dilution is between 1,000 to 1 and 100 to 1 (dilution category 3), chronic toxicity tests are appropriate.

When either chronic or acute toxicity testing is performed, effluent samples must be collected. The selection of sample type (grab or composite) and time of collection should be based on information concerning variability of effluent characteristics. Guidance for effluent sampling as well as toxicity testing methods are provided elsewhere (6,57,58).

The evaluation criterion for the results derived by screening toxicity tests is based on the level of observed mortality. If mortality exceeds 50 percent in any sample, the potential for toxicity is assumed and Tier 2 toxicity testing is required. If less than 50 percent mortality is observed for all samples, the discharge should be given a low priority for further analysis.

3.3 Tier 2 Testing—Definitive Data Generation

Once screening has indicated the potential for toxic impact, further testing is conducted to determine whether or not the discharge causes unacceptable impact. Initially "baseline" acute toxicity testing is conducted using whole effluent and two species of test organisms. Then a simple relationship can be applied to determine whether to require more data (i.e., additional chronic and/or acute testing (see Figure 3-1) or whether to stop testing and begin the process of establishing permit conditions. The evaluation criterion for the results of the Tier 2 toxicity tests is given by the following formula:

$$\frac{\text{LC50}}{\text{IWC}} > \text{Level of Uncertainty}$$

where LC50 = concentration of effluent producing 50 percent mortality in toxicity tests
IWC = Instream Waste Concentration

The level of uncertainty is determined by a number of factors, e.g., effluent variability, species sensitivity variability and the type of toxicity test conducted. All of these factors are defined in (6). If it is determined that additional data are required, further testing, including acute or short-term chronic testing, may be required to reduce the level of uncertainty by eliminating the identified sources of variability in a stepwise manner.

Where more than one effluent is contributing to toxic impact, additional toxicity testing may be required. Additional testing is only required if the regulatory agency decides not to treat each effluent separately. If effluents are considered as portions of an interactive system, testing must be conducted to ascertain the potential for additive, antagonistic or persistent toxicity. Either chronic or acute toxicity testing may be necessary depending on whether the receiving water body is considered to be:

- "effluent-dominated" or
- "stream-dominated"

Guidelines for this determination have been developed and are shown in (6).

When multiple effluents affect a receiving-water system it is also necessary to determine the "relative" and "absolute" effects of each effluent. The appropriate procedure for conducting these effluent toxicity tests is described in the technical support document (6).

3.4 Ambient Toxicity Testing and Dye Studies

Ambient toxicity testing can be used to determine instream toxicity levels resulting from individual discharges. The same test organisms used in the tiered-testing procedures are exposed to receiving water samples collected from selected sampling stations above, at, and below the discharge point(s). Chronic toxicity tests are generally conducted since the primary concern following dilution of the effluent is the effect of chronic, lowdose exposures on the aquatic community.

The number and location of sampling stations should be based on a knowledge of the mixing characteristics of the effluent including the influence of other point and nonpoint sources. The best way to characterize the mixing and dispersion of the effluent is to conduct dye studies. The information developed in these studies can be used to determine which instream concentration isopleths correspond to concentrations used in the dilution series in effluent tests (see Sections 3.2 and 3.3), assuming the toxicants behave conservatively.

A widely used dye for this type of study is rhodamine WT in 20 percent solution. The dye can be purchased as a liquid so that mixing of powder and water is not required. Often the dye is not locally available, but can be purchased from its manufacturer, Crompton and Knowles Corporation, in Skokie, Illinois.

Rhodamine WT 20 percent solution has a specific weight of about 1.19. However, because of its high solubility it mixes rapidly with the river water and soon becomes neutrally buoyant. Consequently, mixing of the dye with solvents less dense than water (e.g., methanol) is not required.

The dye should be injected continuously into the effluent of the discharger so that it is completely mixed with the waste stream when it is discharged into the receiving water. The injection rate of the dye should remain constant over the duration of the study. Based on the expected study duration, the quantity of dye required can be estimated, and prepared beforehand. When possible, the effluent discharge rate should also be kept constant.

Some time is required before the dye isopleths attain their steady-state concentrations in the river. Figure 3-4 provides guidelines for distances of up to 10 miles below a discharge. Because of stream dispersion, the time exceeds the travel time to the location in question. For example, for a stream velocity of 0.3 fps and a distance of 3 miles, approximately 21 hours of continuous release is required to establish steady-state dye isopleths. The travel time is 15 hours and by then the dye has attained about 60 percent of its steady-state concentration, based on predictions from the advection-dispersion equation using a dispersion coefficient of 500 ft^2/sec.

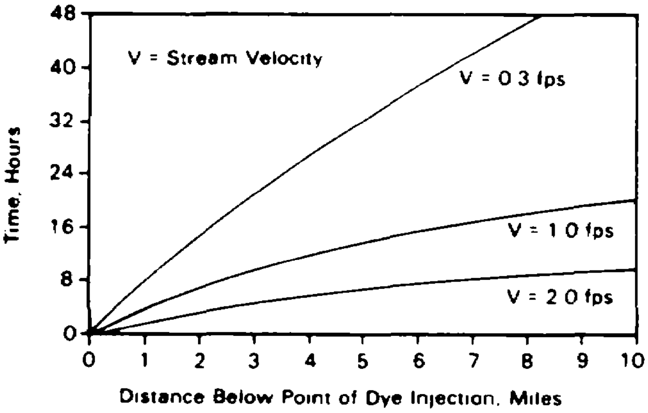


Figure 3-4. **Time required for a continuous release of dye to reach steady-state concentrations at selected locations below the point of discharge. Note: the curves are based on a solution to the advection-dispersion equation which is used to predict when dye concentrations are 95 percent of steady-state levels.**

Instream sampling should begin upstream of the outfall and progress downstream. Thus, sampling near the outfall can commence before downstream dye levels have attained steady state.

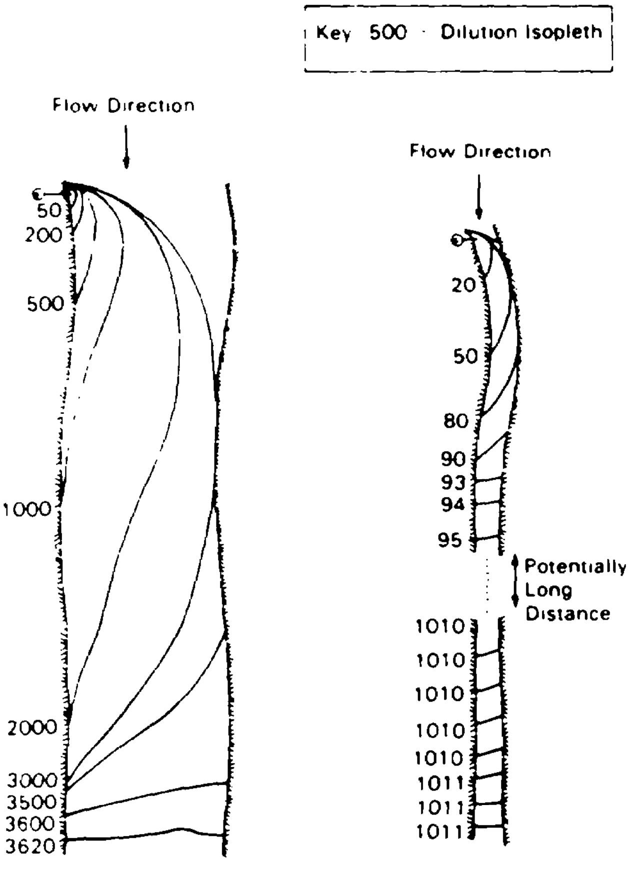
Typical background fluoresence in rivers is equivalent to about 0.1 µg/l as rhodamine WT, so dye concentrations should be above background levels, but also within levels calibrated for fluorometers (typically less than 200-300 µg/l). Consequently a dilution of

2000 or 3000 to 1 can normally be measured. If dilutions greater than this are required for the study, two separate continuous releases may be required, one using a higher effluent concentration so that dye concentration isopleths can be measured further downstream.

The dye injection rate should be selected so that the dye is not visible after it has begun to mix with the river water. The USGS plans dye studies so that concentrations do not exceed 10µg/l at water treatment plant intakes and other diversions. If the dye is visible, concentrations will be high enough so that instrument readings will be inaccurate and adverse public reaction may be generated as well.

Figure 3-5 shows example dye isopleths that might result from injection into wide and narrow rivers. For the wide river the two-dimensional profile can be maintained for large distances.

Figure 3-5 Dye isopleths in wide and narrow rivers.

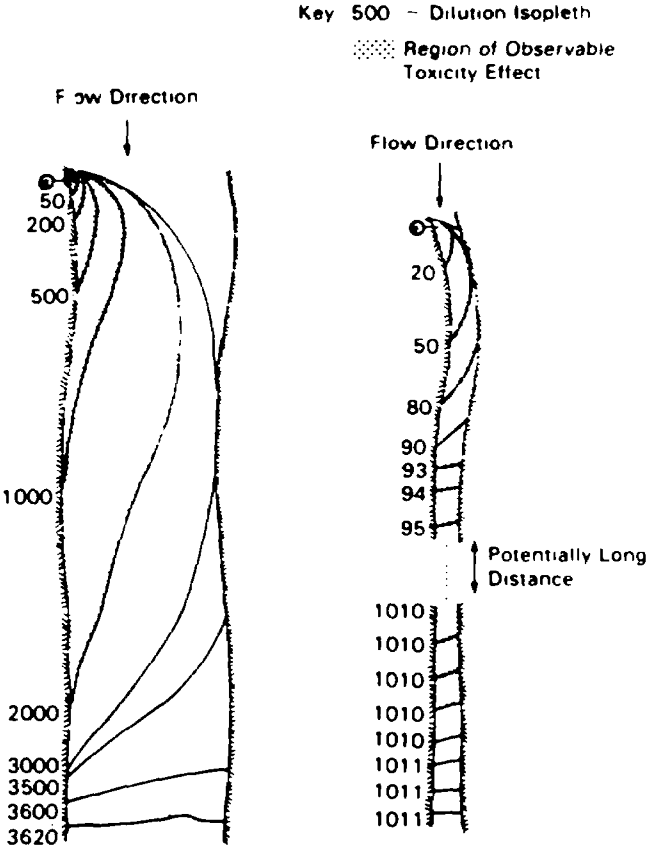


(a) Wide River

(b) Narrow River

Dye isopleths should be generated from the point of discharge to below the no observable effects level (NOEL) as determined from toxicity tests. Figure 3-6 shows example limits of observable toxicity. For the narrow river, the NOEL extends to a dilution of approximately 1010 to 1. Once complete mixing is attained the concentration isopleths change very slowly with distance. However the NOEL may have a distinct downstream location that indicates toxicity is decreasing for reasons other than dilution, as suggested in Figure 3-6b.

Figure 3-6. Regions of observable toxicity in wide and narrow rivers.



(a) Wide River

(b) Narrow River

Figure 3-7 illustrates a typical sampling network for narrow and wide rivers. Sampling of dye concentrations at a number of transects is required. For wide rivers, samples should be taken from 4 to 5 points on the transect. By putting the fluorometer in a boat and moving it across the river and starting on the side that the outfall is located, the lateral extent of the plume can be readily determined. In shallow rivers, a flat bottomed canoe can be used to move the fluorometer. On a wide river, sampling may be required only 100 feet or so below the outfall, even though the river may be 500 feet wide.

The fluorometer can be used to assist in selection of downstream transects. Generally, change in dye concentration (based on measurements taken on the same side of the river as the discharge) should not exceed a factor of three to four between adjacent transects so that detailed concentration isopleths can be generated.

The following formula can be used to estimate the number of required transects:

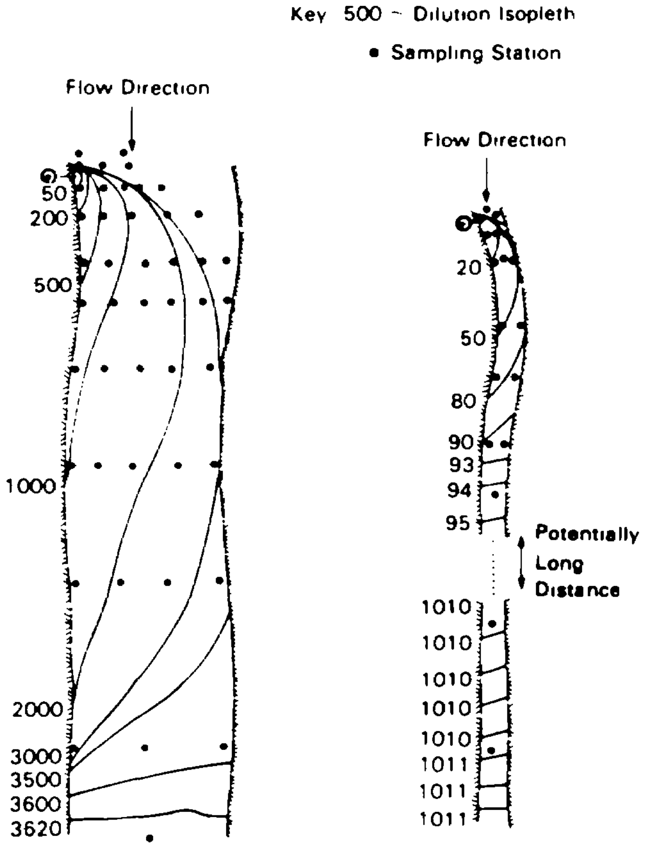
$$N = \frac{\log (Q_R/Q_W)}{\log R_F} \qquad (3\text{-}6)$$

where N = number of transects
Q_R = river flow rate
Q_W = point source flow rate
R_F = ratio of fluorometer readings between two adjacent transects, measured on the same side of the river as the discharge.

For example if $Q_R = 500$, $Q_W = 0.3$, and R_F is specified to be 2, then

$$N = \frac{\log \frac{500}{0.3}}{\log 2} = 10.7 = 11 \text{ transects}$$

Figure 3-7. **Example sampling locations in wide and narrow rivers.**



(a) Wide River (b) Narrow River

Once the dye readings along a transect are uniform (say less than 5 percent difference between readings) then complete transverse mixing has almost been attained, so one reading per transect is sufficient further downstream.

Sampling at multiple depths may be necessary just below the outfall. Since vertical mixing is rapid (see Figure 3-3), vertical profiles probably are not required at a large number of locations. The fluorometer itself is the best method of determining if sampling at multiple depths is required. To simplify this aspect of sampling, a preselected standard can be used, where, for example, samples 1 foot off the bottom are uniformly taken.

For multiple discharges, the dye studies and procedures outlined above are repeated separately for each discharge. The dye is injected in the downstream discharge first, and then at the next upstream discharge, and so on. This will prevent upstream dye from contaminating earlier surveys.

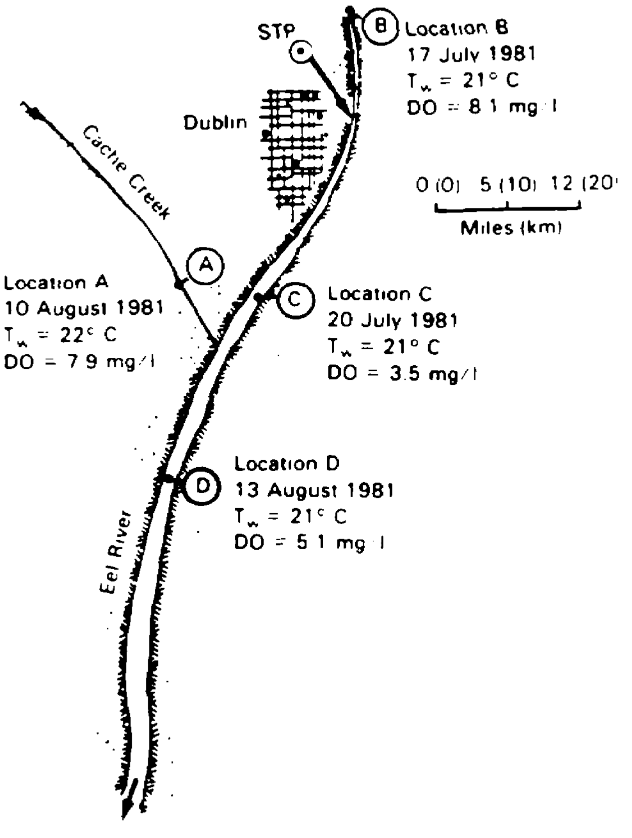
The delineation of effluent plume configurations using the results of the dye studies provides a basis for comparing instream effluent concentrations with the toxicity concentrations determined in Tier 1 and Tier 2 toxicity tests. Where dye study results indicate that effect-level concentrations are exceeded instream, ambient toxicity tests should be conducted. Receiving-water samples should be obtained from sampling locations within the potential impact zones to conduct static-renewal exposure tests. Sampling stations should be placed at instream locations which correspond to concentrations measured in the dilution series in the effluent tests. For example, where effluent testing shows the effluent NOEL is 10 percent, an instream station should be placed where dilution is estimated to create a 10 percent instream waste concentration. The results of the ambient toxicity testing can be used to evaluate the persistence of effluent toxicity and the decay rate of toxicity. This supplementary information is of value in setting waste load allocations.

Chapter 4
Example Application

4.1 Dissolved Oxygen

Figure 4-1 shows an 80 mile (130 km) stretch of the Eel River below the City of Dublin. Also shown on the figure are Cache Creek, the Dublin wastewater treatment plant, and historical water quality data collected during the summer of 1981. The data show that dissolved oxygen levels in the river have been as low as 3.5 mg/l. The dissolved oxygen standard is 6.0 mg/l, expressed as a daily average. The state has mandated that the municipality reduce their waste loadings to be in compliance with the water quality standard for dissolved oxygen. Consultants for the municipality have been retained to design a summer low flow survey so that data can be gathered for a dissolved oxygen model of the river.

Figure 4-1. **Eel River and environs showing summer of 1981 water quality results.**



Before deciding on their modeling approach, the consultants first review the historical data. Based on the data, they conclude that high loadings of CBOD and NBOD from the treatment plant are primarily the causes of the depressed dissolved oxygen levels. The data show that algal activity has been minimal and the river is large enough so that diurnal temperature changes are no more than 2 to 3°C. Based on their assessment of the problem, the consultants intend to use a steady-state approach to dissolved oxygen prediction, where the processes of CBOD, NBOD, sediment oxygen demand (SOD), and reaeration are simulated.

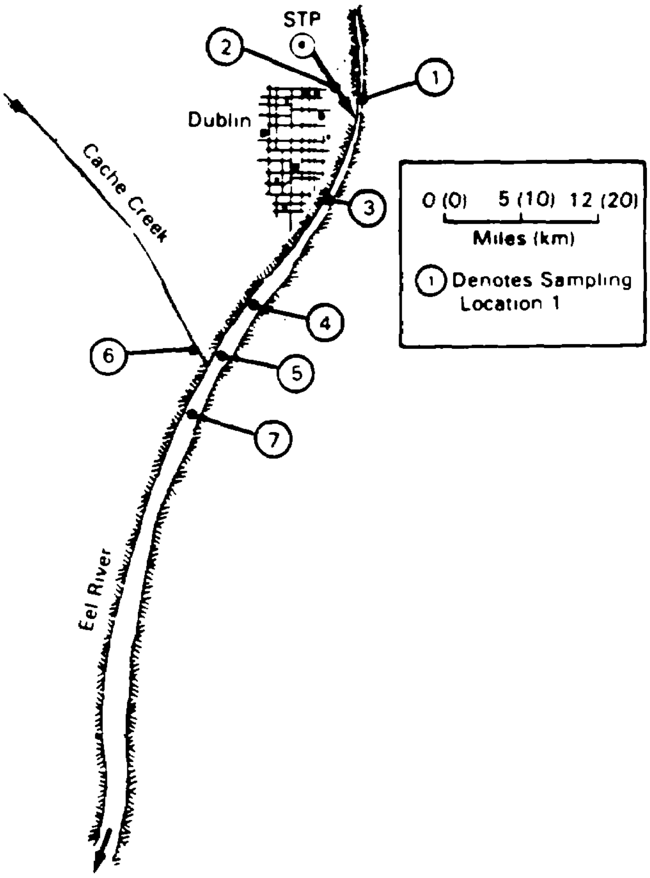
A $_{7}Q_{10}$ summer low flow is selected for the wasteload allocation period. A stream survey will be conducted during a summer low flow period to provide the necessary data to calibrate the model. The model will then be applied to simulate the $_{7}Q_{10}$ conditions. The sampling locations selected are shown in Figure 4-2. They include locations to characterize:

- background levels in the river above the treatment plant
- the treatment plant effluent and tributary
- the river just prior to mixing with the tributary
- intermediate locations in the river necessary to locate the dissolved oxygen sag and to determine the CBOD and NBOD profile
- water quality at the end of the reach

Based on historical data, and a preliminary model application, the minimum dissolved oxygen level is expected to occur near location 4. Locations 3, 4, and 5 will help to accurately establish the shape of the dissolved oxygen sag curve. Location 3 is far enough below the treatment plant that the effluent is expected to be well mixed before that location; consequently multiple samples across a section are not needed.

Table 4-1 summarizes the data that are to be collected. Diurnal variations of effluent loading (station 2) and of instream quality at stations 3 and 4 will be quantified. Diurnal variations are needed to predict daily average dissolved oxygen levels to compare with the state standard. Instream diurnal variations are expected to be due to wasteload variation, and not to temperature and algal effects.

Figure 4-2. Location of sampling stations on Eel River



Additionally, a plug flow sampling event will be conducted between stations 1 and 5 to help better estimate NBOD and CBOD decay rates. Diurnal loading variations are expected to make the range of CBOD and NBOD concentrations at specific locations quite large that accurate decay rates will be difficult to estimate otherwise.

In-situ sediment oxygen demand rates will be determined at stations 1, 3, and 7. Station 1 represents background conditions, station 3 is expected to show the influence of the treatment plant discharge, and station 7 is located in a recovery zone.

Because the river is fairly deep (4 ft or greater even during low flow), the consultants intend to use an historical reaeration rate expression characterized by a depth-velocity relationship. Specific tracer studies are not planned. The water temperature is expected to remain fairly constant over time, so that water temperature simulation techniques are not needed. Rather, water temperature effects will be considered indirectly in terms of temperature effects on rate constants and temperature effects on dissolved oxygen saturation. Consequently meteorological data are not needed.

The judgement and experience of the consultants and water quality specialists employed by the municipality have been combined to design this particular sampling program. Review of historical data, preliminary model applications to the river, and understanding the behavior of rate coefficients such as the reaeration rate constant, were all used to design the survey.

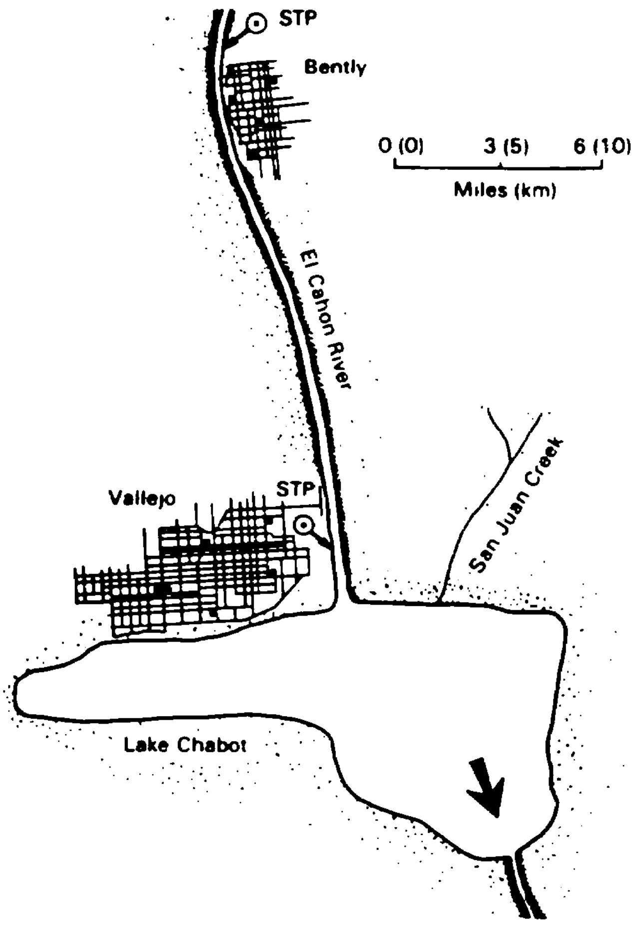
Table 4-1. Summary of Data to be Collected During Stream Survey for Dissolved Oxygen Waste Load Allocation

Sampling Station	Parameters	Frequency	Comments
1. Background station, Eel River above Dublin STP	• CBOD, NBOD, DO, Temperature • Flow	• 1 per day for 7 days • USGS gage	Station 1 is used to establish background level.
2. Effluent of Dublin STP	• CBOD, NBOD, DO, Temperature • Flow	• Every 3 hours for 7 days • Continuously	The diurnal variability is used to establish daily average loads, and to help explain time variability in BOD and DO at specified location downstream.
3. In Eel River 8 miles below Dublin STP	• CBOD, NBOD, DO, Temperature	• Every 3 hours for 24 hours, plus sample for plug flow analysis	Stations 3, 4, and 5 show the diurnal response to waste load variations. The plug flow sample is taken to correspond with the passage of the centroid of dye released at the treatment plant.
4. In Eel River 16 miles below Dublin STP	same as station 3	same as station 3	
5. In Eel River just above Cache Creek	same as station 3	same as station 3	
6. Mouth of Cache Creek	same as station 1	same as station 1	Single flow rate estimates at the beginning and end of survey will be sufficient if a continuous gage is not available.
7. In Eel River 4 miles below Cache Creek	same as station 3	same as station 1	Flow rates are not needed.

4.2 Organic Toxicant

Figure 4-3 shows two wastewater treatment plants that discharge to the El Cahon River, which flows into Lake Chabot. A limnological investigation has shown that surficial sediments of Lake Chabot are contaminated with the polycyclic aromatic hydrocarbon pyrene. Subsequent investigations in the river also revealed high concentrations of pyrene in the bed and occasional high pyrene concentrations in the water column as far upstream as the Bently sewage treatment plant. Sampling of the effluent from the Bently and Vallejo plants has confirmed that these two plants are sources of pyrene. To meet water quality standards, the state has decided that the loading of pyrene to the river is to be reduced and allocated between the two sources.

Figure 4-3. El Cahon River, Lake Chabot, and environs.



Prior to collecting supplemental stream data to use in the WLA analysis, the state first selects a modeling approach and a sampling period. Since historical data have indicated that pyrene levels have been highest during the low flow period, the state has selected both a $_7Q_{10}$ period (for chronic criteria) and a $_1Q_{10}$ period (for maximum criteria) to perform the WLA. This example problem, therefore, deals with sampling during a low flow period.

The state selects a dilution or mass balance approach to allocate pyrene from the Bently treatment plant. Above the Vallejo treatment plant, however, the state believes that pyrene concentration is not predictable by pure dilution alone, based on the presence of pyrene in the stream sediments.

The state decides to perform a preliminary analysis of the fate of pyrene in the river, and to use the computer model MICHRIV for the WLA (if needed) to simulate the transport and transformation of pyrene in the river between the two treatment plants. Table 4-2 summarizes data the state has collected on the fate of pyrene. The data show that hydrolysis is probably negligible, but that the biodegradation rate, while unknown, is likely to be significant. The volatilization rate is not shown in the table, but its importance can be determined from Henry's Constant:

$$K_H = \frac{P_s \cdot MW}{760 \cdot Sw} \qquad (4\text{-}1)$$

where P_s = saturation vapor pressure, torr
MW = molecular weight
Sw = solubility in water, mg/l

For pyrene,

$$K_H = \frac{(6.9 \cdot 10^{-7})(202)}{(760)(.140)} = 1.3 \cdot 10^{-6}\ \text{atm} \cdot \text{m}^3/\text{mole}$$

Table 4-2. Properties and Fate Processes for Pyrene (data are from (27) unless otherwise noted)

- Molecular weight = 202
- Octanol-water partition coefficient, $K_{ow} = 2 \cdot 10^6$
- Saturation vapor pressure (torr at 20°C), $P_s = 6 \cdot 9 \cdot 10^{-7}$
- Solubility (mg/l at 25°C), S_w = 140 μg/l
- Biodegradation rate (1/day): unknown but probably significant from (49)
- Hydrolysis rate (1/day): unknown, but probably negligible
- Near surface direct photolysis rate (1/day at a light intensity I_o = 2100 langleys/day), k_{do} = 24
- Wavelength of maximum light absorption (nm), λ^* = 330

This a very small K_H, and indicates that volatilization is negligible (probably between 0.01/day and 0.001/day based on the two-film theory of volatilization (27). The high octanol-water partition coefficient ($K_{ow} = 2 \times 10^6$) indicates that pyrene adsorbs to suspended and bedded sediments, and will settle out in the streambed along with solids that are deposited there, consistent with historical observations.

The near-surface direct photolysis rate is 24/day. The expected photolysis rate in the stream can be approximated by (6):

$$k_d = k_{do} \frac{DI}{D_o I_o} \left[\frac{1 - e^{-k(\lambda^*) Z}}{k(\lambda^*) Z} \right] \qquad (4\text{-}2)$$

where k_{do} = near surface rate, 1/day
I, I_o = intensity of radiation from sunlight and from laboratory source, respectively
D, D_o = distribution coefficients in river and in clear water, respectively
Z = water depth, m
$k(\lambda^*)$ = light attenuation in water at wavelength λ^*, 1/meter

The light attenuation term in Equation 4-2 can be estimated from Table 4-3, excerpted from Mills (26). For the El Cahon River during low flow conditions, the attenuation factor is on the order of 0.1 for water type C with depth of 1 m. Since I_o = 2100 langleys/day and I = 540 langleys/day,

$$k_d \sim (24)(.1) \frac{540}{2100} = 0.6/\text{day}$$

Table 4-3. **Range of $\frac{1-e^{K(\lambda^*)Z}}{K(\lambda^*)Z}$**

•(nm)	Water Type^a	Depth of Water (m) 1	2	3	5	10
300	A	0.9	0.8	0.8	0.6	0.4
	B	0.5	0.4	0.2	0.14	0.07
	C	0.1	0.06	0.04	0.03	0.01
	D	0.03	0.01	0.009	0.005	0.003
340	A	0.9	0.9	0.9	0.8	0.7
	B	0.7	0.5	0.4	0.2	0.1
	C	0.2	0.08	0.06	0.03	0.02
	D	0.04	0.02	0.01	0.007	0.004

^{a}Water Type	Chl a (mg/l)	DOC (mg/l)	SS (mg/l)
A	0.0	0.0	0.0
B	0.001 (oligotrophic, e.g., Lake Tahoe)	0.1	0.5
C	0.01 (eutrophic)	0.5	5.0
D	0.1 (highly eutrophic)	2.0	20.0

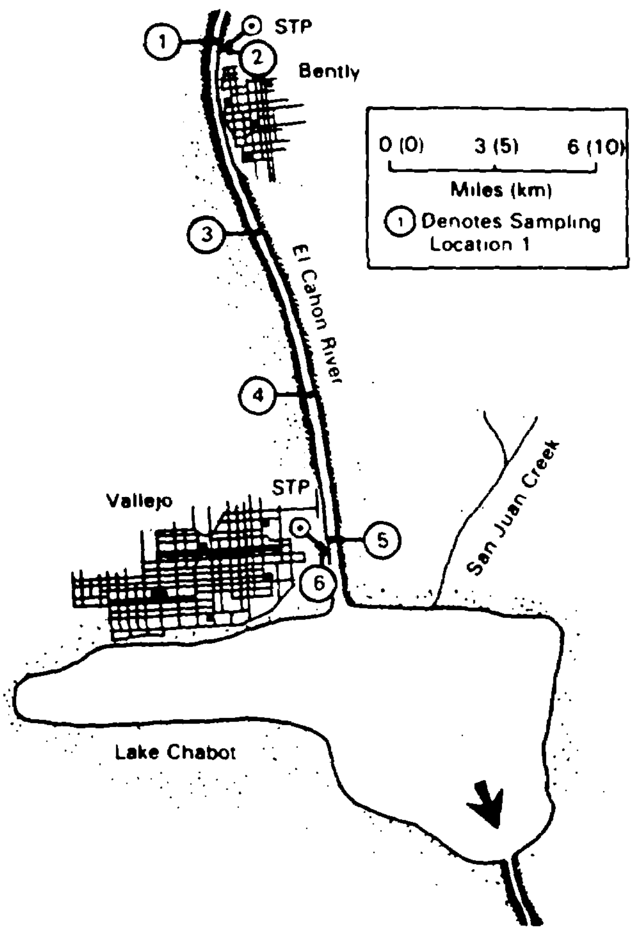
Hence, photolysis is an important process for pyrene. This can be compared to the volatilization rate of 0.01-0.001/day to show that volatilization is unimportant.

Based on this preliminary analysis and previous historical data, the state decides to determine the diurnal variation of pyrene discharged from each treatment plant and also the diurnal variation of concentrations in the river, the latter caused both by daily variations in loading and variations in the photolysis rate.

Additionally, because of the potential importance of biodegradation, the state decides to determine the biodegradation rate by a plug flow sampling event at night when photolysis is negligible. The biodegradation rate can be determined by a plot of pyrene concentration versus distance (the effects of settling, if important, also have to be accounted for). The state feels that for WLA purposes, it is important to quantify the individual processes affecting the fate of pyrene, so that model processes can be rationally adjusted for WLA conditions.

Table 4-4 summarizes the data the state intends to collect. Locations of sampling stations are shown in Figure 4-4. Four instream stations are chosen in addition to effluent sampling at the two treatment plants. No sampling stations are required below the Vallejo plant.

Figure 4-4. Location of sampling stations on El Cahon River.



The stations between the two point sources are selected based on an assumed travel time of about 0.7 days between stations (it is assumed that the state had previously determined travel times), and considering that pyrene may photolyze and biode-

Table 4-4. Summary of Data to be Collected During Stream Survey

Sampling Station	Parameters	Frequency	Comments
1. Background station in El Cahon River above Bently STP	• Suspended solids • Pyrene, total • Flow rate	• Three times during 7-day survey • Three times during 7-day survey • Continuously (USGS gage)	• Used to establish background levels • used to confirm that background pyrene concentrations are negligible
2. Effluent of Bently STP	• Suspended solids • Pyrene, total • Flow rate	• Every 3 hours for 7 days • Every 3 hours for 7 days • Continuously	• The frequency for suspended solids sampling can be relaxed if time variability of suspended solids is small, or if the suspended solids concentrations in the river are insensitive to effluent suspended solids.
3. In El Cahon river 6 mi (10 km) below Bently STP	• Suspended solids • Pyrene, total • Pyrene, dissolved • Water temperature • Cross-sectional area • Water depth	• Twice during 24-hour period • Every 3 hours for 24 hours • Twice during 24-hour period • Every 3 hours • Once • Once	• Samples for suspended solids and dissolved pyrene should be taken at the same time, and along with total pyrene, used to find the partition coefficient (See Table 2-1). • Suspended solids versus distance profiles should be used to analyze the importance of solids settling on total pyrene in the water column.
4. In El Cahon River 12 mi (20 km) below Bently STP	• Same as at Station 3, plus:		• If the state has the resources ch *a* and DOC can e found at station 3 as well.
	• Chlorophyll *a* • Dissloved organic carbon	• Twice during 24-hour period • Twice during 24-hour period	
5. In El Cahon River just below Vallejo STP	• Same as Station 3	• Same as Station 3	• Same as Station 3
6. Effluent of Vallejo STP	• Same as Station 2	• Same as Station 2	• Same as Station 2
Other:			
Plug flow sampling: between stations 3 and 4 (approximately), depending on the travel time corresponding to sunrise	• Dye • Total pyrene • Dissolved pyrene • Suspended solids	• Every two hours from sunset to sunrise beginning near Station 3	• The dye is injected into the El Cahon River near the Bently STP so than it is well mixed by the time it passes Station 3.

grade fairly rapidly. Based on the mixing characteristics of the river, it has been established that complete mixing of effluent and stream water is achieved upstream of station 3. Thus, the state does not need to take multiple samples laterally across a transect.

The state chooses to sample at three hour intervals, over a 24-hour period at stations 3, 4 and 5. Due to manpower limitations, the stations are sampled sequentially, beginning with station 3. The state is aware that this is not as desirable as sampling simultaneously at the three stations because of the time variability of the waste loadings. The effluent quantity and quality of the treatment plants are monitored for a period of one week, beginning the day before the instream sampling begins at station 3.

At the upstream boundary station, a nearby USGS gauge continuously records the flow. Because pyrene contamination has never been found in the river above the Bently treatment plant outfall, only three background grab samples are taken during the sampling period (one every two days).

Once sampling is completed at stations 3, 4 and 5, the plug-flow sampling event is begun. Dye is injected into the stream at the Bently treatment plant so that it is well-mixed at station 3 and arrives near sunset. The effluent loading of pyrene at the time of dye injection is recorded. Sampling for pyrene then begins at station 3 as the peak dye concentration passes. Samples are collected approximately every two hours based on passage of peak dye concentrations, and continues through the night. Suspended solids concentrations are also taken to see if settling of solids is significant. The state realizes that the plug-flow sampling event has to be carried out accurately in order to determine the decay rate, because of the time limitation (approx. 12 hours) before photolysis is again active.

Once the state has completed the seven day sampling program, enough information has been collected to analyze the fate of pyrene in the river, and to calibrate MICHRIV. The agency intends to run MICHRIV a number of times, with different loading rates to see how well the predictions match the envelope of instream concentrations observed at locations 3, 4 and 5.

Following model calibration, it is expected that the state will conduct a second survey for model verification. Different conditions will intentionally be chosen between the calibration and verification periods. For example, if the calibration survey were conducted under cloudy or rainy conditions when the solar radiation is suppressed by as much as 50 to 70 percent, the verification survey would be conducted under clear sky conditions.

Chapter 5
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Chapter 6
Appendix

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