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Office of Water Regulations
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Monitoring and Data Support
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Technical Guidance Manual for Performing Waste Load Allocations

Book II Streams and Rivers
Chapter 3 Toxic Substances

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

JUN 18 1984

MEMORANDUM

SUBJECT: Technical Guidance Manual for Performing Waste Load Allocations Book II, Streams and Rivers, Chapter 3, Toxic Substance Impacts

FROM: Steven Schatzow, Director
Office of Water Regulations and Standards (WH-551)

TO: Regional Water Division Directors
Regional Environmental Services Division Directors
Regional Wasteload Allocation Coordinators

Attached, for national use, is the final version of the Technical Guidance Manual for Performing Waste Load Allocations Book II, Streams and Rivers, Chapter 3, Toxic Substance Impacts. We are sending extra copies of this manual to the Regional Wasteload Allocation Coordinators for distribution to the States to use in conducting wasteload allocations.

If you have any questions or comments or desire additional information please contact Tim S. Stuart, Chief, Monitoring Branch, Monitoring and Data Support Division (WH-553) on (FTS) 382-7074.

Attachment

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TECHNICAL GUIDANCE MANUAL FOR

PERFORMING WASTE LOAD ALLOCATIONS

BOOK II STREAMS AND RIVERS
CHAPTER 3 TOXIC SUBSTANCES

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SECTION 1.0

INTRODUCTION

This document addresses methods for predicting concentrations of individual constituents resulting from pollutant loads to the aquatic environment. Within the context of the waste load allocation (WLA) process, the methods predict the ambient concentrations expected to result from existing or projected pollutant loadings. By relating the predicted concentrations to ecosystem or human health effects levels, an appropriate level of pollution abatement can be specified, tailored to protection of the environment of a specific site.

As the focus of the material is the prediction of ambient concentrations, it will not address all facets of the allowable load determination. In order to use predictions effectively, it is also necessary to establish (a) a target for allowable concentrations, and (b) a target frequency for not exceeding the allowable concentrations. Data on the former are contained in the Water Quality Criteria documents; data on the latter are sparse. Neither subject is within the scope of this volume.

The organization intended for the first four volumes of the complete manual is shown in Table 1.1. In order to reduce redundancy, material discussed in Book II, Chapter 1 (BOD, dissolved oxygen and ammonia) is not repeated here. In particular, it is assumed that the reader is familiar with the concepts of advection and dispersion, variations of depth and velocity with flow, first order reaction rates, surface transfer of oxygen, and steady-state versus time-variable analyses. This document is intended for use in conjunction with chemical data references such as Mabey et al. (1982) and Callahan et al. (1979).

Table 1.1 ORGANIZATION OF GUIDANCE MANUAL FOR PERFORMING OF WASTE LOAD ALLOCATIONS

BOOK I	GENERAL GUIDANCE (Discussion of overall WLA process, procedures, considerations)
BOOK II	STREAMS AND RIVERS
	Chapter 1 - BOD/Dissolved Oxygen Impacts and Ammonia Toxicity Chapter 2 - Nutrient/Eutrophication Impacts Chapter 3 - Toxic Substances Impacts
BOOK III	ESTUARIES
	Chapter 1 - BOD/Dissolved Oxygen Impacts Chapter 2 - Nutrient/Eutrophication Impacts Chapter 3 - Toxic Substances Impacts
BOOK IV	LAKES, RESERVOIRS, IMPOUNDMENTS
	Chapter 1 - BOD/Dissolved Oxygen Impact Chapter 2 - Nutrient/Eutrophication Impacts Chapter 3 - Toxic Substances Impacts

Because predictions are needed in a variety of different situations, there is no one set of technically acceptable procedures that can be put forth as a standard method. The appropriate level of effort, and thus the appropriate approach, depends on the difficulty with which pollutant controls can be implemented, the complexity of the environmental problems, the resources available, and the technical expectations of all parties involved. Consequently, the intent of this document is to describe a variety of different approaches, covering a wide range of complexity, to help guide the analyst in choosing a calculational framework, or model, appropriate to the specific problem. Rather than recommending particular levels of effort as appropriate for analyzing particular WLA situations, this document is intended to help guide the WLA analyst toward the most effective use of whatever resources are available.

The remainder of this document is organized into the following sections:

Section 2.0 describes mathematical frameworks for predicting toxicant concentrations in rivers. The approaches span a range of complexity, from dilution calculations to complex, multi-dimensional, time-varying computer models. This section describes assumptions and limitations associated with each approach.

Section 3.0 presents the mathematical formulation of important fate and transport process and provides background information for specifying the parameter values.

Section 4.0 presents technical guidance for conducting waste load allocations for toxicants. It suggests that the analysis progress through three phases from simple to complex and discusses the associated needs for and management of supporting data. Quality assurance and cost estimates are covered for both field data and model parameters. This section also contains technical guidance in applying models and assessing the adequacy of site-specific model predictions.

Section 5.0 presents a case study of modeling metals transport in the Flint River, Michigan. Emphasis is on the calibration of the toxicant model with field data obtained under three very different flow regimes. A sensitivity analysis of the model parameters relative to the Flint River calibration is also presented.

Finally, there are appendices containing (A) derivations of model equations, (B) a discussion of sediment exchange and transport modeling, (C) a summary of Flint River (case study) survey methods, and (D) chlorine behavior. In addition, two other reports are attached. One contains metals partition coefficients derived from field data collected nationwide. The other is a catalogue of 14 models designed for toxicant studies. It briefly summarizes each model's theory, input and output, strengths and limitations, and resource requirements.

SECTION 2.0

BASIC MODEL FRAMEWORKS AND FORMULATIONS

2.1 GENERAL

This section provides a summary of modeling frameworks, with associated equations and assumptions, applicable to predicting concentrations of discharged toxicants, as affected by stream hydrology and morphology, reactions, and sediment interactions. Because the intent of this document is to present a range of approaches, it is useful to consider a means of categorizing water quality models according to their components and characteristics. In selecting an approach, a WLA analyst is likely to be interested in environmental simulation capabilities, which can be categorized as follows:

A. System components

- Water column
- Bed sediment
- Terrestrial watershed

B. Processes modeled

- Dilution
- Advection, dispersion
- Decay, transformation, speciation
- Transfer between water, sediment, and air

C. Spatial variability or resolution

- 0, 1, 2, 3-Dimensional variability
- Near or far field

D. Time variability

- Steady state
- Time variable

The analyst must also be concerned with the input data and hardware requirements associated with any approach. These tend to follow from the capability characteristics listed above.

A general schematic framework for illustrating many factors that determine the concentration of toxicants in a river is depicted in Figure 2.1. The conceptual elements include: (a) mixing of effluent and upstream waters, (b) partitioning of toxicant between dissolved and particulate phases in both the water column and the bed, (c) exchange between the water column and the bed, (d) decay by irreversible chemical transformations, (e) losses by burial and volatilization, and (f) downstream transport via stream flow and bed load. Simple analytical frameworks may employ only a few of the elements shown; sophisticated computer codes, on the other hand, may articulate more complex arrangements than shown in the figure.

The selection of any approach requires a trade-off between system realism and analytical efficiency. The simplest approaches tend to hinge on a few critical assumptions (as will be described shortly); the technical issues and uncertainties that surface thus tend to be few in number but could be intractable in nature. Furthermore, restrictions in the form of their results can constrain the formulation of the basic questions they are intended to answer. Complex analyses, on the other hand, with their numerous input parameters, call for the support of considerable laboratory and field data. The assumptions they rest on and the uncertainties they surface may be greater in number but more subtle in nature than those of the simpler approaches. The complex approaches are applicable to a wider range of questions than the simpler approaches.

It may not be necessary to choose a model at the outset of a project. Rather, as discussed in Section 4.0, it may be efficient to apply the analysis in stages, starting simply, and then moving to the appropriate level of complexity, as the issues, costs, benefits, and

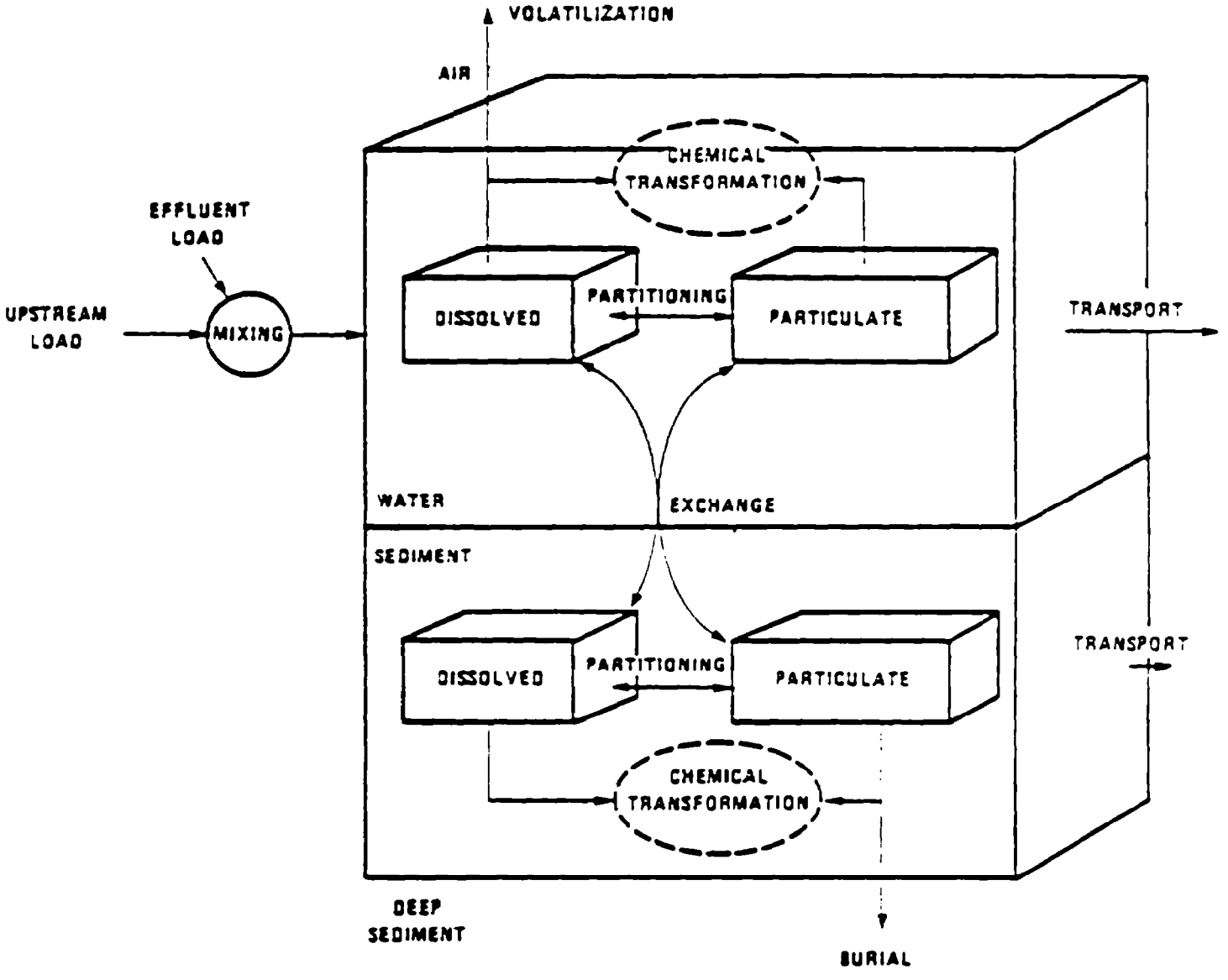


FIGURE 2.1 IMPORTANT FATE AND TRANSPORT PROCESSES FOR TOXICANTS IN RIVERS

decision needs evolve. Nevertheless, because the collection of field data can be the most expensive project component, no major field surveys should be done before the analytical framework has been selected and the input data requirements identified.

The approaches covered in this document can, for purposes of discussion, be placed in the following types of catagories:

- Point of discharge dilution calculations for total pollutant; steady-state or dynamic.
- One-dimensional, steady-state models for conservative total pollutant.
- One-dimensional, steady-state models for nonconservative total pollutant.
- One-dimensional, steady-state models for separate dissolved and particulate phases; having bed interactions and multiple process rates.
- Multi-dimensional, and/or dynamic models for separate dissolved and particulate phases or multiple species; having bed interactions and multiple process rates.

The approaches differ in discerning spatial and temporal variations, environmental media, and pollutant forms and behavior. The approaches are described in the sections that follow. Mathematical derivations of fundamental equations are provided in Appendix A.

2.2 DILUTION CALCULATIONS - POINT OF DISCHARGE

The mixing of the effluent flow with the river flow is the first process normally evaluated in predicting ambient concentrations of toxicants. At the point where mixing has been completed, the concentration of the total pollutant is given by:

$$C_T(0) = \frac{C_{Tw} Q_w + C_{Tu} Q_u}{Q_w + Q_u} = \frac{W_T}{Q_T} \qquad (2.1)$$

where, $C_T(0)$ = Concentration of total pollutant immediately after complete mixing (ug/ℓ)

C_{Tw} = Effluent concentration (ug/ℓ)

C_{Tu} = Upstream concentration (ug/ℓ)

Q_T = Combined effluent flow (Q_w) plus upstream flow (Q_u) (ℓ/sec)

W_T = Combined effluent plus upstream load (ug/sec)

This formulation assumes that:

1. Mixing is relatively rapid.
2. Decay or settling is slow compared to mixing.

The combination of these two assumptions implies that little decay has time to occur before mixing is complete. The formulation says nothing about the size of or concentration within the mixing zone. Nor does it say anything about the concentrations further downstream of the discharge.

Used by themselves without regard for downstream fate, dilution calculations have found considerable use in setting water quality based effluent limitations for both conservative and nonconservative pollutants. This is because Water Quality Standards are often implemented in such a way that the toxicant concentration is not permitted to exceed the numerical criterion at any point (outside the mixing zone), without regard for the length of the stream affected. Consequently, for single dischargers in a regulatory situation that gives no consideration to the number of stream miles affected, the analyst may simply apply the dilution formula (Equation 2.1) to determine the concentration occurring immediately below the discharge, before any processes (except for upstream dilution) can act to reduce the concentration.

This approach is not suitable for situations where two or more discharges, separated by a substantial distance, affect the toxicant concentration. In this case some consideration of the pollutant

behavior in the reach between the two discharges is needed in order to predict the concentration (C_{Tu}) above the second discharger. The approach is nevertheless applicable in the numerous situations where only one of the several dischargers is of importance for a particular toxicant.

Because toxicants may rapidly partition between the dissolved and suspended solids phases in the water column, or may rapidly interconvert between different species or complexes, the concentrations in Equation 2.1 are usually interpreted as being the total concentration of the toxicant. When only one form of the pollutant is biologically active (such as unionized ammonia), it is customary to determine the dilution concentration as total, and then to separately determine what fraction will be biologically active. For example, the fraction of unionized ammonia is determined by pH and temperature.

Perhaps the chief disadvantage of the dilution calculation at the point of discharge is that it says nothing about the spatial extent of the problem, which in turn partially determines the environmental benefits of pollution control. The restricted vision of this approach thus somewhat hampers the analyst's ability to respond to decision-makers' questions about environmental benefits.

The spatial restriction of this approach may be partially offset by the comparative ease with which the temporal confines can be expanded. It is not unduly difficult to determine the frequency distribution of the output concentration ($C_T(0)$) using the frequency distributions or real time sequences of the four input parameters (C_{Tu}, Q_u, C_{Tw}, Q_w). Facile methods for determining the overall frequency of standards violations at the point of discharge are being refined (DiToro and Fitzpatrick 1983) and appear to promise substantial improvements in the evaluation of toxicity problems.

2.3 ONE-DIMENSIONAL, STEADY-STATE MODEL OF CONSERVATIVE TOTAL POLLUTANT

This approach goes beyond that of the previous section in that it predicts the concentration profile throughout the downstream reach. This requires an assumption about downstream behavior. In this case the assumption is conservative pollutant behavior because the discharged load is not reduced as it travels downstream. Consequently, since dilution is the only process affecting the concentration, the model equation is the previously described dilution formula (Equation 2.1).

This formulation assumes:

1. The pollutant is essentially conservative (i.e., does not decay or settle from the water).

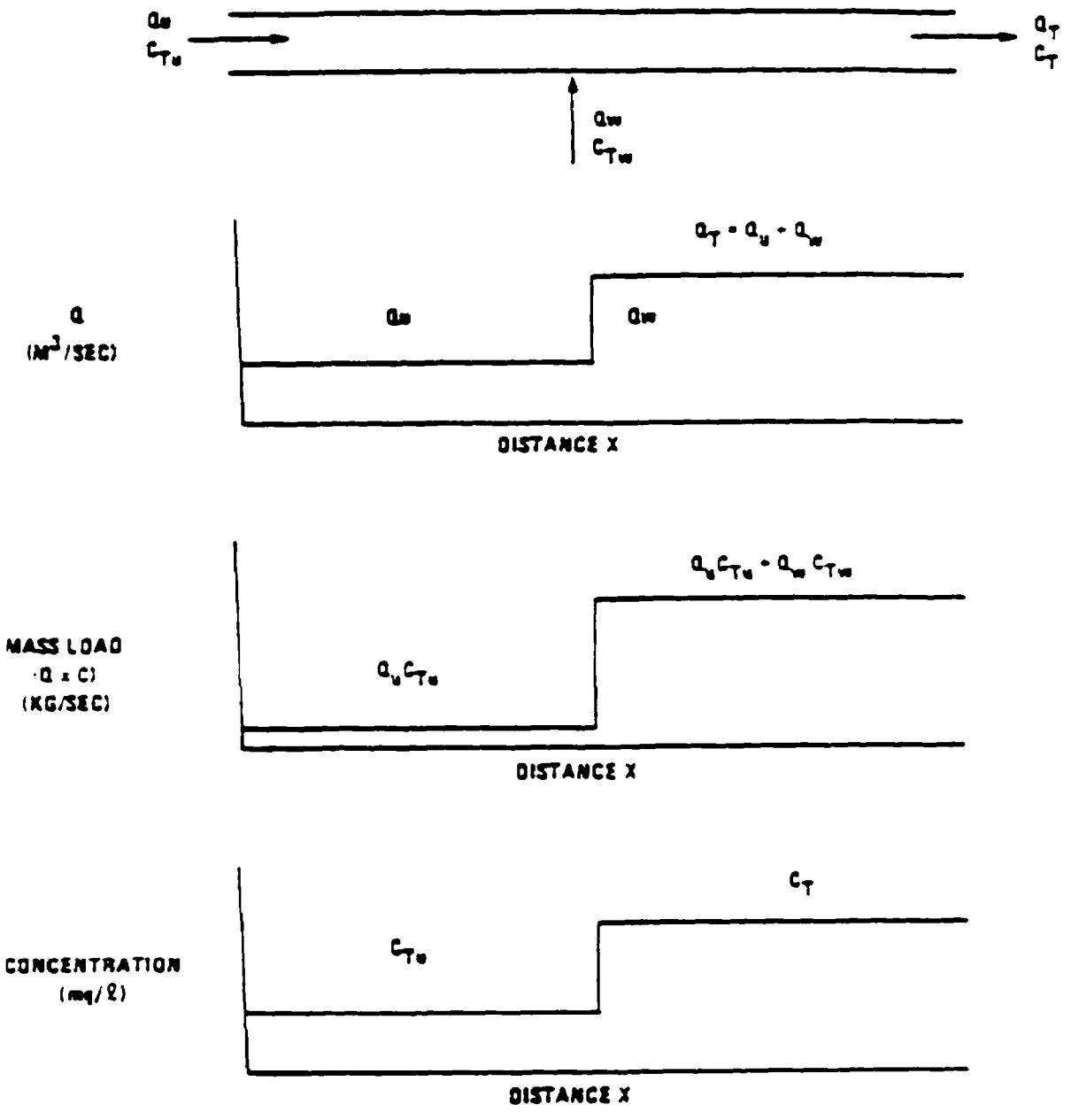
2. The system is represented by average conditions over some representative time period so that the model equations can be solved for $dc/dt = 0$ (i.e., no variations in time - steady-state).

3. The pollutant is mixed essentially instantaneously with the river (i.e., the model does not discern concentration variations within a mixing zone).

Figure 2.2 depicts this model. If multiple discharges were present, concentrations along the length of the river would increase in steps.

Chloride in dilute concentrations is an example of a non-degradable substance with little tendency to precipitate or absorb to sediment. It can be expected to remain in the water column with its steady state stream concentration determined only by dilution.

Priority pollutants, however, may undergo a wider range of processes than chloride. The organics undergo degradation and transfer to air and sediment. Metals (as total metal), although not degradable, also generally have an affinity for bed sediments. Individual metal ions and complexes can undergo transformation to other species. Thus, an a priori assumption of conservative behavior will often be unsound. Such an assumption is gener ll least appropriate when allied to the dissolved fraction of a pollutant, since adsorption can be a rapid process.



$$C_T = \frac{(Q_u \times C_{Tu}) + (Q_w \times C_{Tw})}{(Q_u \times Q_w)} = \frac{W_T}{Q_T}$$

FIGURE 2.2 STEADY-STATE, CONSERVATIVE BEHAVIOR.

Nevertheless, where the spatial distance under study is very small, conservative assumptions may hold up quite well for the total form of most pollutants. Thus, it has been customary to consider behavior within legal mixing zones to be conservative, since the time of passage is so small. Some other conditions under which conservative behavior may be predicted are described in Section 2.5.2.

2.4 ONE DIMENSIONAL, STEADY-STATE MODEL OF NONCONSERVATIVE TOTAL POLLUTANT

This approach predicts the concentration of the total form of a nonconservative pollutant in the water column throughout a one-dimensional stream reach under steady-state conditions. The model formulation is:

$$C_T(x) = C_T(0) \; e^{-K_T \frac{x}{U}} \qquad (2.3)$$

where, $C_T(x)$ = Concentration at points downstream of effluent (ug/ℓ)

$C_T(0)$ = Concentration immediately below effluent (from Equation 2.1) (ug/ℓ)

K_T = Overall loss coefficient (1/day)

U = Stream velocity (m/day)

x = Distance downstream of effluent (m)

Several assumptions accompany this model:

1. K_T, the overall first order decay coefficient, includes net settling and all other losses or transformations.

2. The average river and waste load conditions represent a steady-state condition ($dc/dt = 0$) over some time period.

3. The pollutant discharge is mixed instantaneously with the river (i.e., no mixing zone or lateral and vertical concentration gradients).

4. Dispersion is negligible in the longitudinal direction (i.e., only advective transport is considered significant: plug flow).

5. Average flow, average cross-section area, and average depth sufficiently represent conditions within a single reach.

Figure 2.3 depicts this model graphically. This model is directly analogous to BOD disappearance in a classical Streeter-Phelps DO model. The model equation is applied to each river reach with calculated concentration from the end of an upstream reach becoming the upstream boundary concentration for the next downstream reach. The selection of reaches is determined by significant changes in river geometry, flow, and location of point source tributaries.

The overall decay coefficient is both site- and time-specific, possibly varying with changes in controlling parameters such as flow, cross-sectional geometry, solids concentrations, aquatic vegetation, temperature, sunlight, and pH. Usually this approach is applied to a specific site where sufficient field data are available to calibrate K_T to the observed rate of disappearance. That is, K_T is adjusted until the calculated concentrations reasonably match the measured concentrations along the length of the river downstream of the effluent. As in BOD modeling, it is considered undesirable to spatially vary the decay coefficient without a good underlying justification. The observed data must be expected to exhibit scatter about the predicted curve, due to time variations and measurement errors.

While this empirical approach is somewhat data intensive, it is fairly straightforward, with few degrees of freedom to manage. A key limitation is that is sheds no light on the factors that control K_T. In contrast to the situation with BOD and ammonia, there is little experience to indicate reasonable values for loss rates of most priority pollutants. Consequently, the analyst has little basis for recognizing or evaluating the uncertainties of applying the model, particularly under conditions not yet observed (for example, under conditions of improved wastewater treatment). A more theoretical model, although still tied to some calibration parameters, provides a better basis for dealing with the uncertainties inherent in such applications.

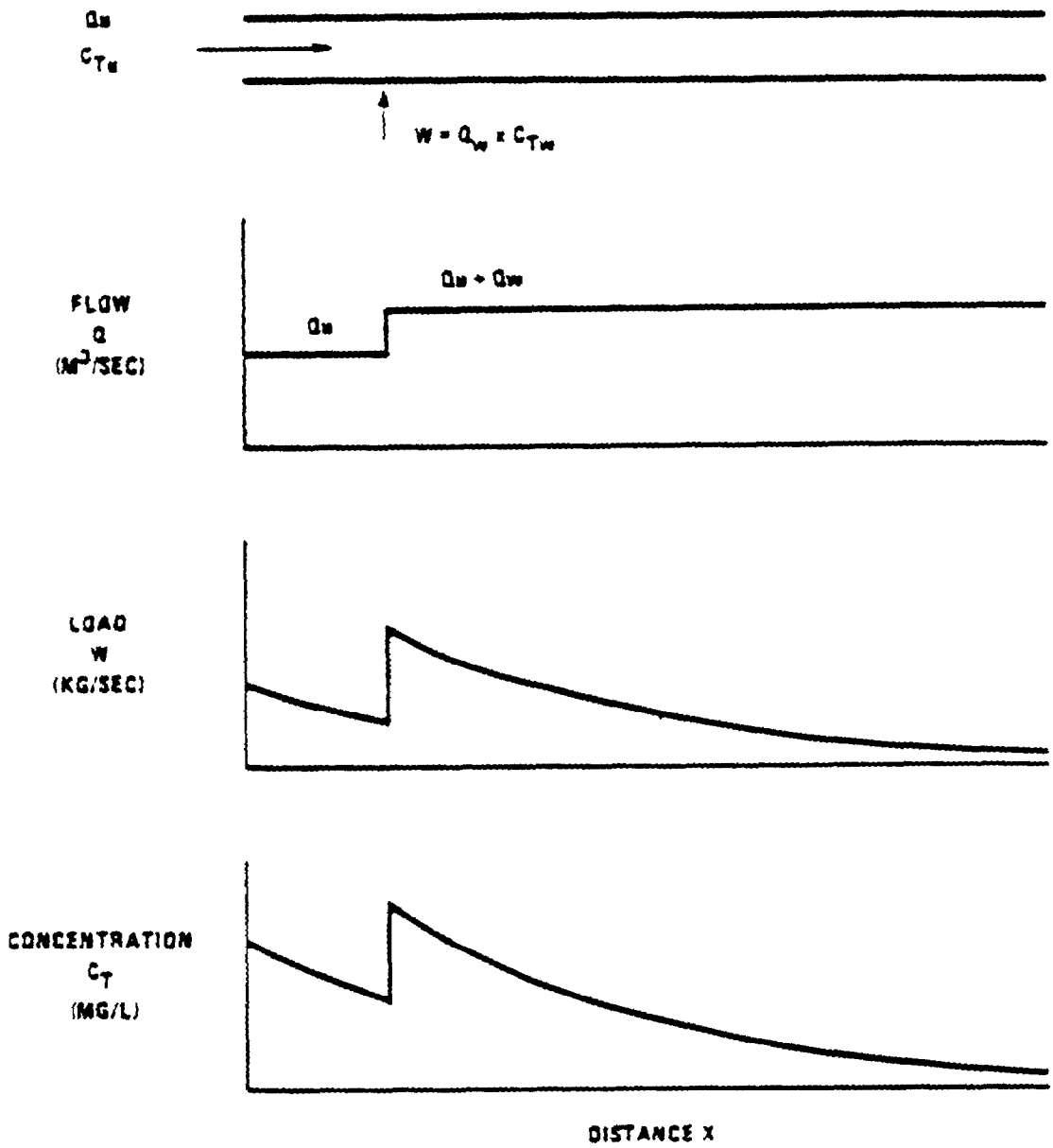


FIGURE 13 SIMPLE FIRST ORDER DECAY ANALYSIS FOR TOTAL POLLUTANT

Nevertheless, this general approach has been applied to phenols and cyanide in the Mahoning River (EPA 1977). Application of this approach to the settling of metals in the Flint River is described in Appendix A.

2.5 ONE-DIMENSIONAL, STEADY-STATE MODELS FOR SEPARATE DISSOLVED AND SUSPENDED PHASES, HAVING BED INTERACTIONS AND MULTIPLE PROCESS RATES

Unlike the approaches described previously, this approach was developed specifically for toxic pollutants which have important interactions with the bed sediments, and which may vary in biological activity and other behavior, depending on form. Because this type of model discerns multiple individual processes, it provides a more complete understanding of pollutant behavior. The trade-off is that there are more parameters to specify, and it is more difficult to rigorously validate using field data. On the other hand, because this type of model relates some aspects of pollutant behavior to readily observable physical properties of the site and to known chemical properties of many pollutants, some model predictions may be attempted without having surveyed the pollutant's downstream profile at the site.

This level of analysis is sufficiently complex that a computer program is helpful (but not essential) for executing the computations. The Simplified Lake and Stream Analysis (SLSA), which is available as both a calculator algorithm and a computer program, is perhaps the simplest version of this type of model. This program was developed by Hydro-Qual and is available from the Chemical Manufacturers Association. The computer program MICHRIV has a somewhat similar framework but is more rigorous and flexible in its handling of a particulate bound pollutant. This program was developed by the EPA Large Lakes Research Station, Grosse Ile, specifically for WLA purposes.

2.5.1 Model Framework

The framework for this type of model is illustrated in Figure 2.4. The model discerns two media, water and bed sediment, and two forms of pollutant within each media, dissolved and particulate bound. Process

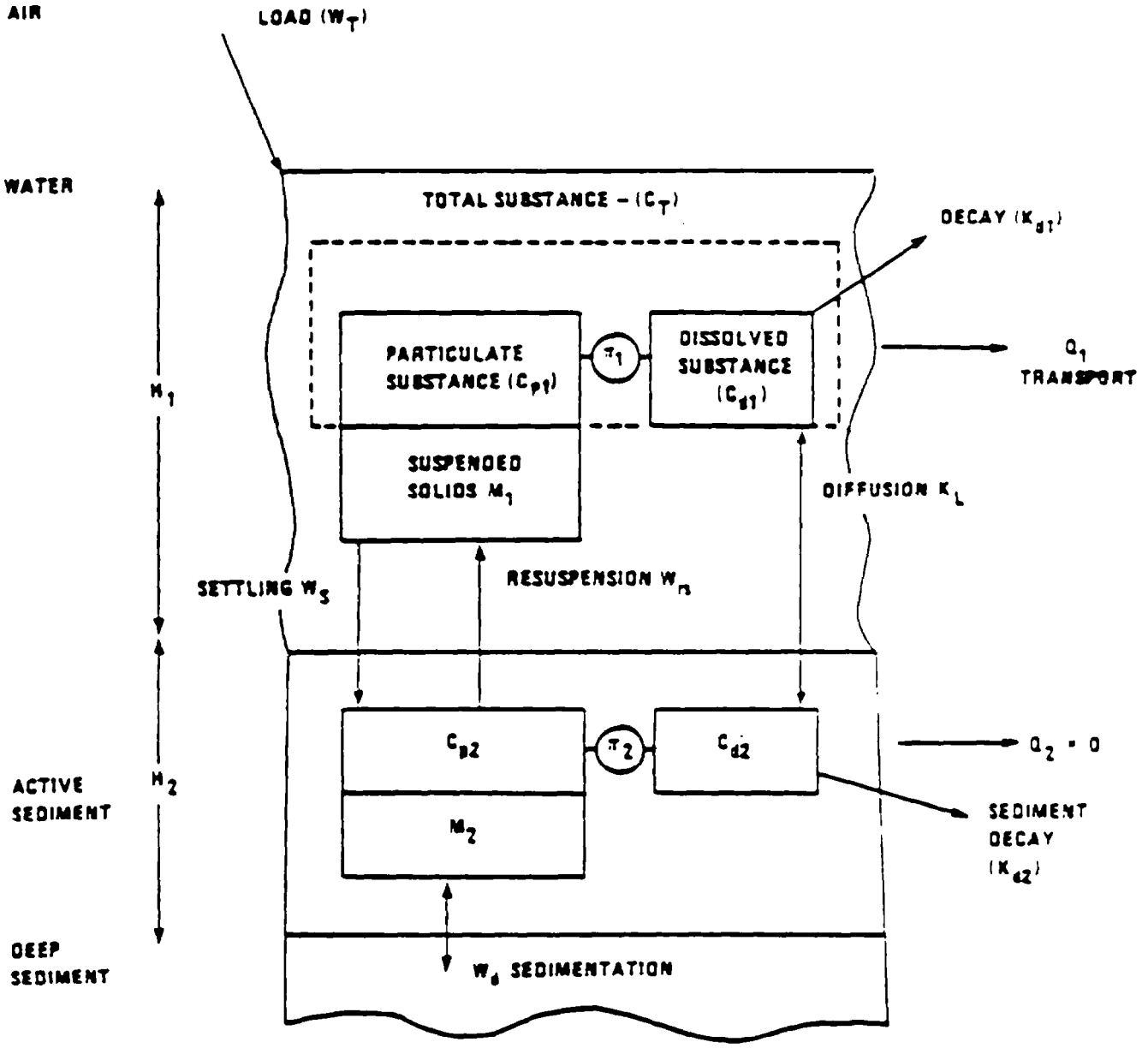


FIGURE 2.4 MICHRIV FRAMEWORK

rates are specific to the media and to the pollutant form: for example, only the particulate phase in water settles to the bed, and only the dissolved phase in water volatilizes. Derivation of the model equations and listing of assumptions are presented in Appendix A.

In summary, the MICHRIV program predicts the dissolved and particulate concentrations in water and bed sediment, using the following types of input data: flows and loads, hydraulic geometry, water-bed exchange parameters, partition coefficients, and decay coefficients. Nomenclature for the following discussion is presented in Table 2.1.

The first major step in MICHRIV's solution (after applying the dilution formula, Equation 2.1) is to predict the concentration profile of suspended solids downstream of a point source. The downstream solids concentration, $m_1(x)$, is related to the initial concentration, $m_1(0)$, and to the settling and resuspension velocities, w_s and w_{rs}, by the expression:

$$m_1(x) = m_1(0)e^{-\frac{w_s}{H_1}\frac{x}{U_1}} + \frac{w_{rs}\,m_2}{w_s}\left(1 - e^{-\frac{w_s}{H_1}\frac{x}{U_1}}\right) \quad (2.4)$$

for which all parameters are defined in Table 2.1. It is assumed that the bed solids concentration, m_2, is constant throughout the reach. (SLSA differs from MICHRIV in that it also treats m_1 as a constant, rather than a state variable, and thus omits Equation 2.4.)

The sediment exchange velocities are related by assuming that the mass (or thickness) of the active bed layer does not change over time. Balancing the solids fluxes results in:

$$w_s m_1 = (w_{rs} + w_d)\, m_2 \quad (2.5)$$

TABLE 2.1: NOMENCLATURE FOR WATER/SEDIMENT MODEL

Parameters	Water Column	Sediment
<u>Concentrations and Loads</u>		
Total toxicant (μg/ℓ)*	C_{T1}	C_{T2}
Dissolved toxicant (μg/ℓ)*	C_{d1}	C_{d2}
Particulate toxicant (μg/ℓ)*	C_{p1}	C_{p2}
Particulate toxicant (μg toxicant/ mg solids)	r_1	r_2
Total solids (mg/ℓ)*	m_1	m_2
Toxicant load (μg/sec)	W_T	---
<u>Partitioning</u>		
Dissolved fraction	f_{d1}	f_{d2}
Particulate fraction	f_{p1}	f_{p2}
Partition coefficient (ℓ/mg) ($\tau = r/C_d = C_p/mC_d$)	τ_1	τ_2
<u>Channel Geometry</u>		
Downstream distance (m)	x	x
Cross-sectional area (m^2)	A_1	---
Depth (m)	H_1	H_2
Flow (m^3/sec)	Q_1	---
Velocity (m/sec) ($U = Q/A$)	U_1	---

TABLE 2.1: NOMENCLATURE FOR WATER-SEDIMENT MODEL (Continued)

Parameters	Water Column	Sediment
<u>Rate Parameters</u>		
Aggregate decay rate coefficient		
- for dissolved (1/day)	K_{d1}	K_{d2}
- for particulate (1/day)	$K_{p1} = 0$	$K_{p2} = 0$
- for total (1/day)($K = K_d f_d + K_p f_p$)	K_1	K_2
Settling velocity (m/day)	w_s	--
Resuspension velocity (m/day)	--	w_{rs}
Sedimentation (burial) velocity (m/day)	---	w_d
Sedimentation loss coefficient (1/day)	---	K_s
Diffusive exchange coefficient (m/day)	K_L	K_L

*In terms of bulk volume.

The sedimentation or burial velocity, w_d, reflects the rate of change in elevation of the benthal surface at a particular point over time. A positive value for w_d indicates that the channel is gradually filling in during the modeled condition; material is being lost to deep (inactive) sediment, beneath the boundary of the modeled system. A negative value indicates downcutting of the channel, and brings material into the modeled system.

This type of attention to solids behavior is necessary because the movement of adsorbed toxicant follows the movement of solids. The fraction of total toxicant that is adsorbed on particulates (f_{p1} in water, f_{p2} in bed) and the fraction that is dissolved (f_{d1}, f_{d2}) depend on the partition coefficients applicable to the water and bed (τ_1 and τ_2, respectively), and the solids concentrations (m_1 and m_2 respectively):

$$f_p = \frac{C_p}{C_T} = \frac{m\tau}{1 + m\tau} \tag{2.6}$$

$$f_d = \frac{C_d}{C_T} = \frac{1}{1 + m\tau} \tag{2.7}$$

where all parameters apply together either to the water column or to the bed. Use of the partition coefficients assumes that the dissolved and particulate phases are in dynamic equilibrium <u>within</u> their respective media. It also assumes that the equilibrium adsorption isotherms are linear. But it does not assume that any type of equilibrium exists between the bed and the overlying water column. (Such an equilibrium can be set up under certain conditions: $w_d = 0$ and $K_2 = 0$ will cause the fluxes of total pollutant between the water column and bed to cancel each other at steady-state; however, unless the additional condition $\tau_1 = \tau_2$ were imposed, a net movement of particulate pollutant could occur, for example, out of the water column, balanced by a net movement of dissolved pollutant out of the bed.)

The steady state solution for the total toxicant concentration in the water column can be expressed in a familiar form:

$$C_{T1}(x) = C_{T1}(0) \quad e^{-K_T x/U_1} \tag{2.8}$$

The overall removal rate coefficient, K_T (1/day), can be expressed by the function:

$$K_T = K_1 + \frac{\beta r_2}{r_1}(K_2 + K_s f_{p2}) \tag{2.9}$$

where K_{d1} and K_{d2} are the toxicant decay coefficients in the water and bed, respectively, and K_s is the sedimentation loss coefficient, which is related to the burial velocity by the expression:

$$K_s = w_d/H_2 \tag{2.10}$$

The aggregate decay coefficients K_1 and K_2 are simply the sum of the coefficients specific to each competing process, such as hydrolysis, biolysis, photolysis, and volatilization.

The parameter group $\beta r_2/r_1$ controls the importance of sediment decay and loss processes in Equation 2.9. The parameter β, called the sediment capacity factor (DiToro et al. 1982), is defined in terms of solids masses in water and sediment (proportional to mH) and fractions particulate, f_p:

$$\beta = \frac{m_2 \; H_2 \; f_{p1}}{m_1 \; H_1 \; f_{p2}} \tag{2.11}$$

The ratio of toxicant concentrations on particulates, r_2/r_1, is determined from the expression:

$$\frac{r_2}{r_1} = \frac{(w_{rs} + w_d)f_{p2} + K_L(\tau_2/\tau_1)f_{d2}}{(w_{rs} + w_d)f_{p2} + K_L \; f_{d2} + K_2 \; H_2} \tag{2.12}$$

This ratio is controlled by sediment exchange velocities, $w_{rs} + w_d$ (or w_s through Equation 2.5); the diffusion coefficient, K_L, for exchange between the water column and the interstitual water of moderate to high porosity sediments; the decay velocity in sediment, K_2H_2; and the fractions dissolved and particulate.

Finally, the total concentration of toxicant in the bed, C_{T2}, is given by:

$$C_{T2}(x) = \frac{\beta r_2 \; H_1}{r_1 \; H_2} \; C_{T1}(x) \tag{2.13}$$

It should be noted that Equation 2.9 and 2.11 utilize f_{d1} and f_{p1} as if they were constant throughout the reach, when in fact they vary with $m_1(x)$. Consequently, in order to treat them as constants, the MICHRIV program divides each reach into small computational increments, within which m_1 is virtually constant, and solves the equations for each increment, moving downstream.

It can be seen that the model is not entirely simple. Most first-time users may find some aspects of its behavior not intuitively obvious; some sensitivity runs coupled with examination of the formulating equations may be helpful to obtain a good feeling for how the model responds to its input parameters. DiToro et al. (1982) discuss many aspects of the behavior of this type of formulation. Appendix A of this document provides a more complete derivation of model formulation. Section 3.0 provides information on selecting parameter values; Section 5.0 describes a case study using the model. Thomann (1984) suggests a simplification of this type of model.

2.5.2 Relationship with Other Approaches

In predicting the total pollutant in the water column, it can be seen that MICHRIV and SLSA use the same first order decay formula (Equation 2.8) a the simple empirical approach (Equation 2.3). In

MICHRIV, however, unlike SLSA and the empirical approach, the decay coefficient, K_{T1}, is not necessarily constant within a reach. Rather, it is a function of the fractions dissolved and particulate (per Equations 2.9), which in turn vary with any change in the suspended solids concentration moving downstream (per Equations 2.6 and 2.7), as previously mentioned.

Consequently, if the suspended solids levels do not vary within the reach (such as would happen if deposition and resuspension fluxes balanced each other), a steady-state loss of toxicant would occur only as a result of degradative processes or volatilization.

For metals and other nondegradable, nonvolatile substances the sole mechanism for reduction of the water column load is burial beneath depositing sediment (or possibly transport downstream as bed load). Consequently, the behavior of such substances would be predicted to be conservative under the conditions of (a) steady pollutant loading to (b) a graded stream with (c) insignificant bed load and (d) steady flow. A graded stream is one where neither downcutting nor sedimentation is significant; the bed elevation is not significantly changing over time. Solids settling and resuspension fluxes would thus balance under the above conditions. When a pollutant loading first began, exchange processes would cause a net transfer of pollutant out of the water column into the previously uncontaminated sediments. After a period of steady conditions, however, the bed concentrations would reach equilibrium with (become saturated with respect to) the water column concentrations. Then the pollutant flux out of bed would balance the flux into the bed and no reduction of the water column load would take place.

In real systems, however, time variable flows and loads would produce unsteady concentrations and disequilibrium between the water column and sediment bed. While the long term loading of the total form of a pollutant may be conserved within the water column, short term loadings (such as measured during field surveys) may not be conserved. During periods of high concentrations in the water column or of net deposition of sediment, the stream bed may act as a sink. During periods of low concentrations in water or of resuspension of the bed, it may act as a source.

In evaluating metals or other nonvolatile nondegradable substances, MICHRIV differs from simple first order decay models in that loss through burial only takes place until the suspended solids attain their equilibrium concentration or (if resuspension equals zero) until only the dissolved fraction remains. In any case, the asymptote which the total metal concentration approaches is not zero, as illustrated in Figure 2.5.

Overall, the main advantages of using MICHRIV (or SLSA) are that they discern between dissolved and particulate phases and they predict the degree of contamination of the bed. In addition, they better delineate the factors affecting the overall loss rate, thereby allowing better utilization of previous collective experience in determining parameter values and producing a much better understanding of the controlling factors. The number of degrees of freedom, however, complicates the calibration procedure; in some situations more than one set of parameter values may fit the field data.

Relative to some of the more complex models described in the next section, the most important limitations of this approach might be that it is one-dimensional, steady-state, and plug flow. In addition, MICHRIV and SLSA lack complex kinetic routines for internally deriving a chemical degradation rate from input data.

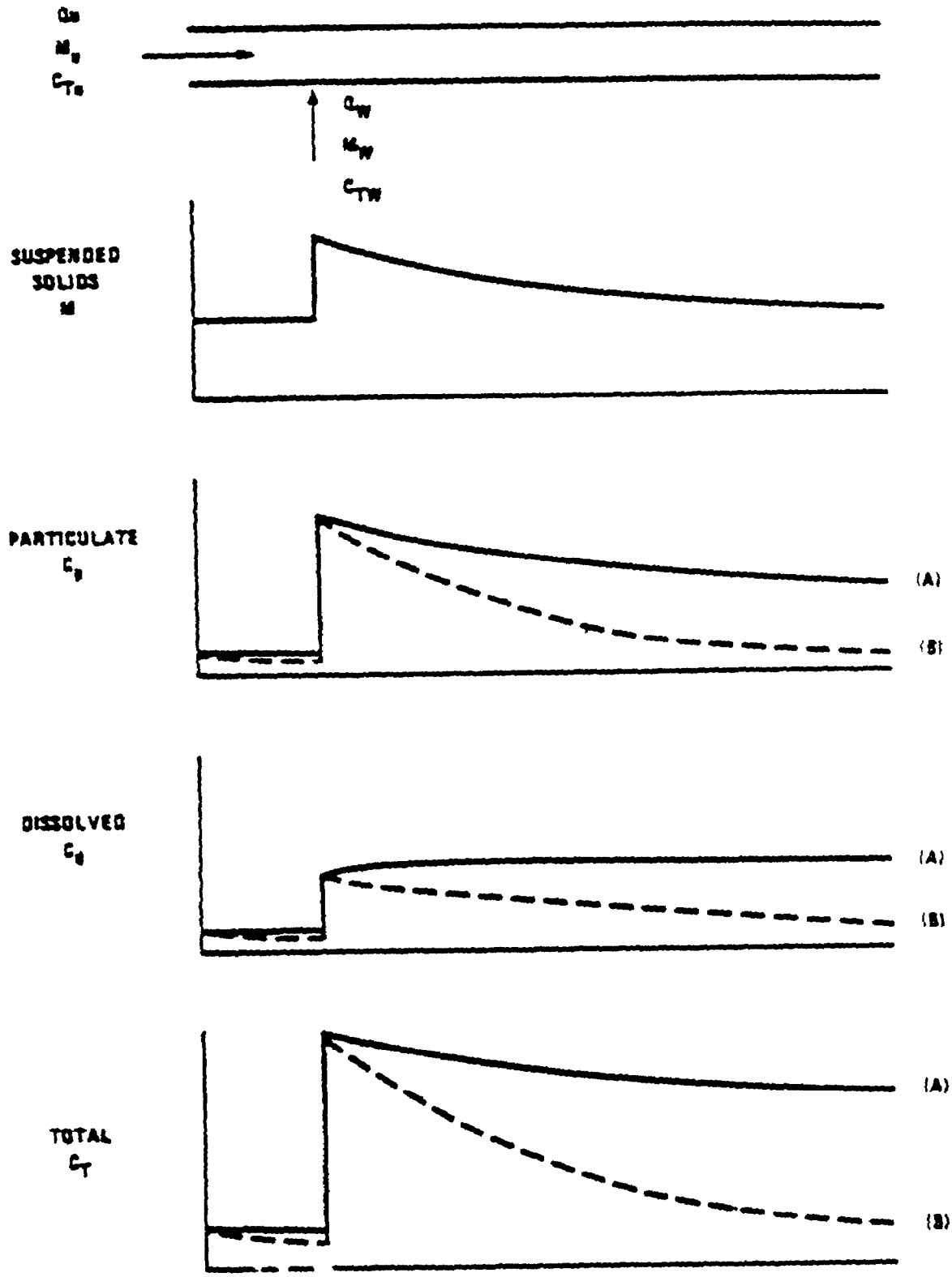


FIGURE 2.5 TYPICAL BEHAVIOR PREDICTED BY MICHRIV FOR (A) METAL, AND (B) DEGRADABLE ORGANIC.

For studies of far field impacts (as opposed to mixing zone impacts), lateral and vertical variations in concentration are seldom sufficient in rivers and streams to justify modeling in more than one dimension. Longitudinal dispersion is likewise seldom sufficient in rivers and streams to discourage use of a plug flow assumption (Driscoll et al. 1983). The plug flow assumption does deter applying such models to estuaries, however.

The steady-state assumption affects the rigor with which time variability can be analyzed. When successive runs of steady-state model are used to simulate a time sequence of events, the output of each successive run is independent of the previous run. Unlike a dynamic model, the steady-state model has no memory of the previous state of the system: it assumes that the modeled conditions have persisted since time immemorial. To the extent that the real system can "remember" its previous condition, for example through longitudinal dispersion and a long hydraulic retention time, a modeling error is generated. In this case the steady-state model would tend to overpredict during periods of high or steadily rising concentrations and underpredict during periods of low or steadily decreasing concentrations.

Mulkey et al. (1982) have compared the frequency distributions of concentrations predicted by state-state and dynamic models. They applied the steady-state model EXAMS and the dynamic model HSPF to a situation of a constant effluent load discharging to a river with variable flow. (Both models are described in Section 2.6 and in Attachment II.) With the steady-state model, a frequency distribution of dissolved chemical concentration in the water column was generated by making several runs, each with a different flow having a known frequency of occurrence. With the dynamic model, the frequency distribution was constructed from a continuous, day-by-day simulation operated from the daily flow record. They found the frequency distribution produced by the steady-state model to be nearly identical to that pr.tuced by the dynamic, continuous

simulation model, regardless of whether the chemical was assumed to be strongly or weakly adsorbed by the sediments. It is essential to note, however, that this equivalence between the frequency distributions generated by the two approaches applies only to rivers and only to the water column. It does not apply to waters having considerable longitudinal dispersion and long hydraulic retention times, such as impoundments and estuaries, and it does not apply to concentrations in the bed sediment (which similarly has a long retention time). Also, it may not necessarily apply to situations where the effluent load or other key factors are rapidly varying over a wide range.

2.6 COMPLEX MODELS HAVING MULTI-DIMENSIONAL, DYNAMIC, OR SPECIATION CAPABILITIES

The waste load allocation models described in the previous section were one-dimensional, steady-state, water column and sediment models with equilibrium partitioning and linear transformation kinetics. The models described in this section employ less restrictive assumptions and contain more degrees of freedom. They tend to involve more process-oriented descriptions of chemical transport, sorption, speciation, and transformation. Enhanced process descriptions can provide a more confident extrapolation of model results from the calibration conditions to different conditions at the same site or to similar conditions at a different site. These models can also be operated to provide more detailed resolution in time or space.

Choice of a model will depend on characteristics and variability of the waste load and the receiving environment, the level of certainty required in model extrapolation, and the type of data available. For a given level of predictability, the more complex models generally require a greater variety of data, but with fewer constraints than simpler models. For example, steady-state models require data averaged over steady conditions, whereas dynamic models can use data taken during steady or unsteady periods. The use of more complex models requires now

technical competence and resources to obtain predictions, but not necessarily more wisdom and experience to interpret the predictions and gain insight into the problems.

A variety of fairly complex models exist or will soon be available. Those general purpose toxic chemical model codes described in this section include: EXAMS, EXAMS 2, and TOXIWASP, developed by Athens Environmental Research Laboratory; HSPF, developed by Hydrocomp and Anderson-Nichols for Athens ERL; SERATRA, TODAM, and MEXAMS, developed by Battelle Pacific Northwest Laboratory for Athens ERL; WASTOX, developed by Manhattan College for Gulf Breeze ERL; UTM-TOX, developed by Oak Ridge National Laboratory for the Office of Toxic Substances; TOXIC, developed by University of Iowa for Athens ERL; and CTAP, developed by Hydro-Qual for the Chemical Manufacturers Association. To assist comparison, MICHRIV and SLSA, the slightly less complex models described in the previous section, are tabulated here as well.

Table 2.2 categorizes these computer codes. General characteristics of concern are the type of aquatic system that can be simulated (general aquatic system or river), the chemical capabilities (generalized pollutant that could be a metal or an organic compound, metal species, and daughter product), the sediment capabilities (descriptive input, one size fraction simulated, or several size fractions simulated), the dimensionality (one-dimensional, two-dimensional, or box, which can be arrayed as pseudo three-dimensional), the numerical solution technique (finite difference, finite element, steady-state algorithms), the time frame (steady-state, seasonal, dynamic), and their availability. Attachment II of this document contains additional information.

Clearly, a range of models is available with widely differing capabilities. Table 2.3 summarizes what components of these models can be corsidered more complex or more general than those of MICHRIV and SLSA: their transport, sorption, speciation, or t an:formation

Table 2.2 General Categorization of Computer Models
(listed in alphabetical order)

	AQUATIC SYSTEMS	CHEMICALS	SEDIMENT SIZES	DIMENSIONALITY	NUMERICAL SOLUTION	TIME FRAME	AVAILABILITY
CTAP	G	O	5	B	SS	SS	C
EXAMS	G	O	D	B	SS	SS	A
EXAMS2	G	O,D	D	B	FD	S	A
HSPF	R	O,D	3	1	FD	D	A
MEXAMS	G	M	D	B	SS	SS	A
MICHRIV	R	O	1	1	SS	SS	GI
SERATRA	R	O	3	2V	FE	D	A
TODAM	R	O	3	1	FE	D	
TOXIC	G	O	1	B	FD	D	
TOXIWASP	G	O	1	B	FD	D	A
UTM-TOX	R	O,M	4	1	FD	D	
WASTOX	G	O	3	B	FD	D	A

G - General Aquatic System; R - River
O - Generalized Pollutant; M - Metal, Specifically; D - Daughter Product
D - Descriptive Input, Not Simulated
B - Box Approach, Pseudo 3-Dimensional; 2V - Two Dimensions (x-z)
FD - Finite Difference; FE-Finite Element; SS - Steady State
S - Seasonal; D - Daily
A - Available from EPA Center for Water Quality Modeling, Athens, GA
C - Available from Chem. Manuf. Assoc.; GI - Available from EPA Grosse Ile Lab

See Attachment II for additional information.

Table 2.3 Model Components which could be considered somewhat more complex or general than MICHRIV

	TRANSPORT	SORPTION	SPECIATION	TRANSFORMATION	HYDROLOGICAL, FLOW MODELS	EFFECTS
CTAP	*					
EXAMS			*	*		
EXAMS2	*		*	*		
HSPF	*	*		*	*	S
MEXAMS		*	*			
MICHRIV,SLSA						
SERATRA	*	*		*	*	S
TODAM	*	*		*		S
TOXIC	*			*		
TOXIWASP	*			*	*	(F)
UTM-TOX	*			*	*	
WASTOX	*			*		F

S - Frequency-Duration Summary
F - Food Chain Model
(F) - Food Chain Model from WASTOX Expected to be Compatible

algorithms, or their linkage to hydrologic, flow, and/or effects models. Those components not labeled as more complex may be roughly equivalent to, or even simpler and more restrictive than MICHRIV and SLSA.

Generally it is sound practice to use the simplest approach that will properly handle the problem. Nevertheless, to satisfactorily resolve some WLA problems, it may be necessary to apply a very complex analysis to some facets of the modeled system. To help discern the range of analytical complexity available, the major model components are discussed below.

2.6.1 Transport and Bed/Water Exchange

Movement of both dissolved and particulate phase contaminants may occur within the water column, within the bed, and between the bed and the water column. (Transfer between the water column and the air is presented elsewhere in the guidance manual as "volatilization".) In the less intricate MICHRIV and SLSA, transport in the water column follows the one-dimensional steady-state solution to the advective transport equation for chemical and suspended sediment. Settling and resuspension velocities are specified for particulates (and thus sorbed chemical). Less restrictive transport and bed/water exchange assumptions can allow multiple sediment size fractions with different sorption and settling properties, vertical or lateral resolution in the spatial grid, and in many cases, unsteady flow. These properties are tabulated in Figure 2.4.

In place of a single mixed layer of bed, some models discern multiple layers in the bed. Dissolved chemical may be transported through the bed by pore water percolation, or exfiltration, or diffusion. Sorbed chemical may be transported by sedimentation, erosion, or physical mixing of the sediment. Some models allow horizontal movement of the upper bed layer (representing "fluid mud" or bed load). Other models can represent this process with benthic water column segments carrying a high suspended solids load. These properties are tabulated in columns 4 and 5 of Table 2.4 for each model.

Table 2.4 Transport and Bed/Water Exchange Properties

	UNSTEADY FLOW	SEDIMENT SIZES	DIMENSIONALITY	BED LAYERS	BED LOAD	BED-WATER DISPERSION	SCOUR-DEPOSITION
CTAP		5	B	M		P	C
EXAMS		D	B	M		P,T	
EXAMS2	*	D	B	M		P,T	
HSPF	*	3	1	1		S	F
MEXAMS		D	B	M		P,T	
MICHRIV, SLSA		1	1	1		P	C
SERATRA	*	3	2V	M	W	S	F
TODAM	*	3	1	M		S	F
TOXIC	*	1	B	1	W	P	C
TOXIWASP	*	1	B	M	W	P,T	C
UTM-TOX	*	4	1	3	*	P	F
WASTOX	*	3	B	M	*	P	C

* - Capable
D - Descriptive Input, Not Simulated
B - Box Approach, Pseudo 3-Dimensional; 2V - Two Dimensions (x-z)
M - Multiple Bed Layers
W - Bed Load Approximated with Lower Water Layer
P - Pore Water Dispersion; T - Enhanced Diffusion From Bioturbation or Physical Mixing; S - Direct Sorption between Bed and Water Column
C - Calibrated (Emphirical) Scour-Deposition Parameters
F - Functional Scour-Deposition Paramete s

In MICHRIV and SLSA, chemical transport between the bed and the water column occurs through pore water diffusion and through steady scour and deposition of sediment. Some of the models considered here omit pore water diffusion and describe this exchange as direct, first order sorption between bed and water column. Mathematically, the results are the same, given equivalent parameter values. Other models add a parameter to describe enhanced dispersive exchange due to bioturbation or physical mixing. The value of this parameter can be specified in a qualitative sense only. Finally, in place of the above calibration input parameters, some models can internally compute sediment exchange parameters from functional relationships between flow, shear stress, and scour. These properties are tabulated in columns 6 and 7 of Table 2.4.

2.6.2 Sorption

Sorption of a chemical onto sediment is generally considered to proceed rapidly compared to other transport or transformation processes. MICHRIV and SLSA assume adsorption and desorption are completely reversible, and proceed rapidly. Mathematically, these two assumptions lead to the use of a partition or distribution coefficient for sorption/desorption. This coefficient can be measured in the laboratory and adjusted for conditions in the environment.

Many of the other models also use partition coefficients adjusted for organic carbon content of the sediment. One model also automatically adjusts the coefficient for sediment concentration based on higher partitioning at lower sediment concentrations. Some models make use of the Langmuir or Freundlich isotherms widely used in soil science. These empirical relationships predict progressively less additional sorption as chemical concentrations become higher, reflecting the saturation of binding sites on the sediment particles. At low chemical concentrations, these isotherms approximate a linear isotherm, or partition coefficient. Use of these isotherms, then, should be important only when relatively high chemical concentrations are expected.

Other models assume a linear isotherm at equilibrium, but specify a first-order rate at which equilibrium is achieved. This may be important when transport or transformation processes proceed as rapidly as sorption (say, on the order of minutes to an hour). It can also be important close to the point of discharge of an effluent high in solids entering a river low in solids (as illustrated in the Flint River case study), or visa versa.

Three types of theoretically-based sorption algorithms have been used in these models: ion exchange, constant capacitance double layer, and triple layer site binding. The ion exchange technique can be useful for ionic compounds where selectivity coefficients for exchange reactions are available. The constant capacitance and triple layer models consider charge-potential relationships at the surface and the changing properties of the surface as a result of changes in pH or ionic strength (Felmy et al. 1983). They require specific experimental work to obtain the parameters, and are thus limited to applications where sorption-pH dynamics are important, and where experimental work is possible.

Table 2.5 tabulates the sorption properties of the general purpose models considered here. It is important to note that research is active in this field, that other formulations have been described in research models, and that these formulations will be tested and available in general purpose models within a few years.

2.6.3 Speciation

Many chemicals or metals discharged into an aquatic environment will be found in several species or complexes. A common speciation process is ionization, which is controlled by pH. Both chemical reactivity and toxicity can be significantly affected by the extent of ionization.

Table 2.5 Sorption properties.

	PARTITION COEFF., KP	KP = F(SEDIMENT CONCENTRATION)	LANGMUIR OR FREUNDLICH	LINEAR "KINETIC" ISOTHERM	ION EXCHANGE	THEORETICAL DOUBLE TRIPLE LAYER
CTAP	*					
EXAMS, EXAMS2	*					
HSPF				*		
MEXAMS	*		*		*	*
MICHRIV, SLSA	*					
SERTRA				*		
TODAM				*		
TOXIC	*					
TOXIWASP	*					
UTM-TOX						
WASTOX		*				

For metals, an important process is inorganic complexation. Table 2.6 gives, for example, the possible dissolved species of lead in water containing nitrate, chloride, sulfate, fluoride, and carbonate (Felmy et al. 1983). To calculate these species, one needs experimental data on the equilibrium constants and environmental data for pH, chloride, sulfate, flouride, nitrate, and carbonate. A reliable thermodynamic data base is available for inorganic complexation of some metals, and incorporated into some geochemical models, including MEXAMS, the only geochemical speciation model listed in this section.

Another important process for metals in many natural waters is organic complexation. The experimental data base is more limited than for inorganic complexation. Some data for fulvic and humic acids are incorporated into certain geochemical models (including MEXAMS). Experimental data from a particular site, however, would be better for waste load allocations at that site.

EXAMS and EXAMS 2 have the capability of discerning up to 5 ionic species of any organic pollutant under study. Unlike MEXAMS, it does not predict metal speciation. The other models have no accounting of ionic species.

2.6.4 Transformation

Transformation of a compound within an aquatic environment can result from physical, chemical, or biological reactions. The standard set of reactions includes photolysis, hydrolysis, oxidation, and biolysis. Because volatilization (transfer into the atmosphere) is handled in a mathematically equivalent way, it too can be treated as a transformation reaction. These processes are discussed in Section 3.3 of this guidance document.

The simplest approach, such as that used in MICHRIV and CTAP, is to utilize a single first-order rate coefficient specified in the program

Table 2.6. Dissolved Species of Pb

Pb^{2+}	$PbCl^{+}$
$Pb(OH)_2$ (AQ)	$PbCl_2$ (AQ)
$Pb(OH)_3^-$	$PbCl_3^-$
$Pb_2(OH)^{3+}$	$PbCl_4^{2-}$
$Pb_3(OH)_4^{2+}$	PbF_3^-
$PbNO_3^+$	PbF_4
$PbSO_4$ (AQ)	PbF_2 (AQ)
$Pb(C)_3)_2^{2-}$	PbF_4^{2-}

From Felmy et al. 1983.

input data. The analyst may obtain this rate coefficient by theoretical calculation or by calibration. First order rate coefficients for competing processes are combined by simple addition to obtain an overall first order rate coefficient (with no loss of rigor). SLSA performs this addition internally.

The other ten models allow decay to be formulated as a second-order process: proportional to the toxicant concentration, and proportional to some other concentration or environmental parameter, such as hydrogen ion concentration (in acidic hydrolysis), or bacterial concentration (in biolysis).

$$\text{Rate} = KC_A C_B$$

where, K = Second-order coefficient

C_A = An environmental parameter

C_B = Concentration of toxicant

With respect to the toxicant, the product KC_A is sometimes called a "pseudo" first-order decay coefficient: a first-order coefficient which varies as a function of another parameter. To combine multiple processes, the models internally add together the "pseudo" first-order coefficients in order to obtain an overall first-order decay coefficient.

In four of the eight time-variable models considered here, the overall reaction rates can vary in response to the time variation of the relevant environmental properties, such as temperature, pH, light, wind or current velocity. These four models are EXAMS2, HSPF, TOXIWASP, and UTM-TOX.

Lastly, EXAMS 2 and HSPF are able to handle daughter products along with parent compounds in a single simulation. Other models require two separate simulations, with internal loadings from the parent compound specified as external input to the second simulation.

SECTION 3.0

ESTIMATION AND USE OF MODEL PARAMETERS

The purpose of this section is to provide information for estimating parameters for a model of intermediate complexity, such as MICHRIV, described in Section 2. Some discussion of the basis for estimating process rates will be presented; however, this document will not duplicate chemical-specific data and coefficients presented elsewhere: Mabey et al. (1982) tabulate values for the kinetic coefficients required by EXAMS (and similar models) for the organic priority pollutants; Callahan et al. (1979) review the fate characteristics of the 129 priority pollutants; Mills et al. (1982) summarize fate data for selected pollutants; Lyman et al. (1982) present methods for estimating chemical properties; and Mill et al. (1982) present laboratory protocols for evaluating the fate of organic chemicals.

The section will cover partitioning between aqueous and particulate phases, exchange between the water column and the bed, exchange between the water column and the atmosphere, and transformation or degradation of the chemical. In order to maintain focus on toxicant modeling, the discussion will not cover transport of the bulk fluid (advection and dispersion); such transport is adequately covered in conventional pollutant texts. Furthermore, downstream movement of the bed will not be dealt with here, as this process is ordinarily not expected to be important for toxicant transport and is not included in most models.

3.1 EXCHANGE BETWEEN BED AND WATER

In modeling the transport and fate of chemicals in aquatic systems, it has been increasingly evident that knowledge of how a given chemical is distributed among various phases - solution, suspension, air and bottom sediment interfaces, biota - is essential. One of the most significant mechanisms for the movement of toxic chemicals through the

aquatic environment is the adsorption or uptake of the chemical by both nonviable and viable particulate matter, followed by the transport of the interacting particulates. Association with suspended matter not only alters the transport regime of a chemical - by introducing additional mechanisms such as deposition and entrainment - but the process can also indirectly affect the rate and extent of transformations and biotic accumulation. For example, partitioning of a portion of a chemical in suspended solids will reduce the flux of that chemical into the atmosphere via volatilization of the soluble phase. On the other hand, such solid phase partitioning would be likely to increase the chemical flux into the bottom sediments by deposition processes. Accordingly, accurate determination of the transport and fate of a chemical requires concurrent knowledge of the transport and fate of interacting particulate matter.

Literature on sediment transport in riverine systems is extensive; however, accurate prediction of sediment dynamics from basic theory appears tenuous. Rather than attempt an extensive development of the theory involved in river sediment transport, the focus of this subsection will be to provide some methods for estimating sediment transport parameters. A further development of concepts is appended (Appendix B) .

3.1.1 Particle Transport and Exchange

The capacity for particles to interact with aqueous toxicants is related to the particulate surface area. As small particles have greater surface-to-volume ratios than large particles, it is the smaller (silt and clay sized) particles that tend to be more important in determining pollutant behavior. Smaller particles are also more readily carried by the streamflow than large particles.

Within the MICHRIV modeling framework, the variables or parameters which control the exchange of particles between the bed and the water column are: m_1 and m_2, the solids concentrations in the water and

bed; and w_s, w_{rs}, and w_d, the velocities (m/day) of settling, resuspension, and burial (sedimentation). The thickness of the active bed is assumed constant. Specifying any four of these five variables allows the last one to be calculated from:

$$w_d(x) = \frac{m_1(x)}{m_2} w_s - w_{rs} \tag{3.1}$$

As MICHRIV and SLSA (as well as some more complex models) recognize only one particle size or type, the parameters may represent average or median values.

In several model frameworks, including MICHRIV and SLSA, the bed solids concentration, m_2, is a user specified constant. For a typical river bottom with water content 60-90% by weight, and a typical solids density of 2.5 g/cm^3, m_2 will vary in the range 50,000-500,000 mg/ℓ (in terms of bulk volume). Flint River bottom sediments were measured at 200,000 mg/ℓ (Section 5).

In most models (including MICHRIV but excluding SLSA and EXAMS) the solids concentration in the water column, m_1, is a state variable predicted from the solids loadings and the settling and resuspension velocities. In MICHRIV (as described in Section 2), m_1 is given by:

$$m_1(x) = m_1(0)e^{-\frac{w_s x}{H_1 U_1}} + \frac{w_{rs} m_2}{w_s}\left(1 - e^{-\frac{w_s x}{H_1 U_1}}\right) \tag{3.2}$$

where all parameters are constant.

It is useful to identify three basic conditions of particle exchange. First, a condition may exist where m_1 remains constant (moving downstream) and the sediment bed is neither accumulating nor scouring way. Although solids settling and scour may be occurring, they

are in a state of equilibrium (i.e., they balance each other); consequently, $w_d = 0$.

In the second condition, m_1 decreases moving downstream because the settling flux exceeds the resuspension flux. As the bed cannot move horizontally in MICHRIV, the resulting excess in settled solids is buried at velocity $w_d > 0$. In the third conditon, m_1 increases because the resuspension flux exceeds the settling flux; for the resulting net scour, $w_d < 0$. These three possibilities are depicted in Figure 3.1.

It must be noted that in models which allow downstream movement of the bed (bed load), w_d could be given a different interpretation. For example, when settling exceeds resuspension ($w_d > 0$), an increase in bed load (at the expense of the suspended load) could be permitted to remove the excess sediment. In this case w_d could reflect the rate of increase of the bed load. As noted in Appendix B, however, bed load is seldom expected to be an important transport mechanism for adsorbed toxicants.

If the downstream profile of m_1 follows Equation 3.2, then it may be possible to evaluate w_s and w_{rs} (or w_d) indirectly. The procedure is analogous to determining a first order decay coefficient from the disappearance profile, but has the complication of an additional degree of freedom. In the following discussion it is assumed that m_2, U_1 (velocity), H_1 (depth), and Q_1 (flow) are known constants throughout the reach, $m_1(x)$ has been measured at several points through the reach, as illustrated in Figure 3.1, w_s and w_{rs} are unknown but constant, and $w_d(x)$ is unknown and variable (per Equation 3.1). It is also assumed that steady state conditions prevail and that the bed is the only source of solids below the head of the reach (for example, no nonpoint loads and no phytoplankton growth).

By evaluating Equation 3.2 for large values of x, w_s can be related to the m_1 asymptote:

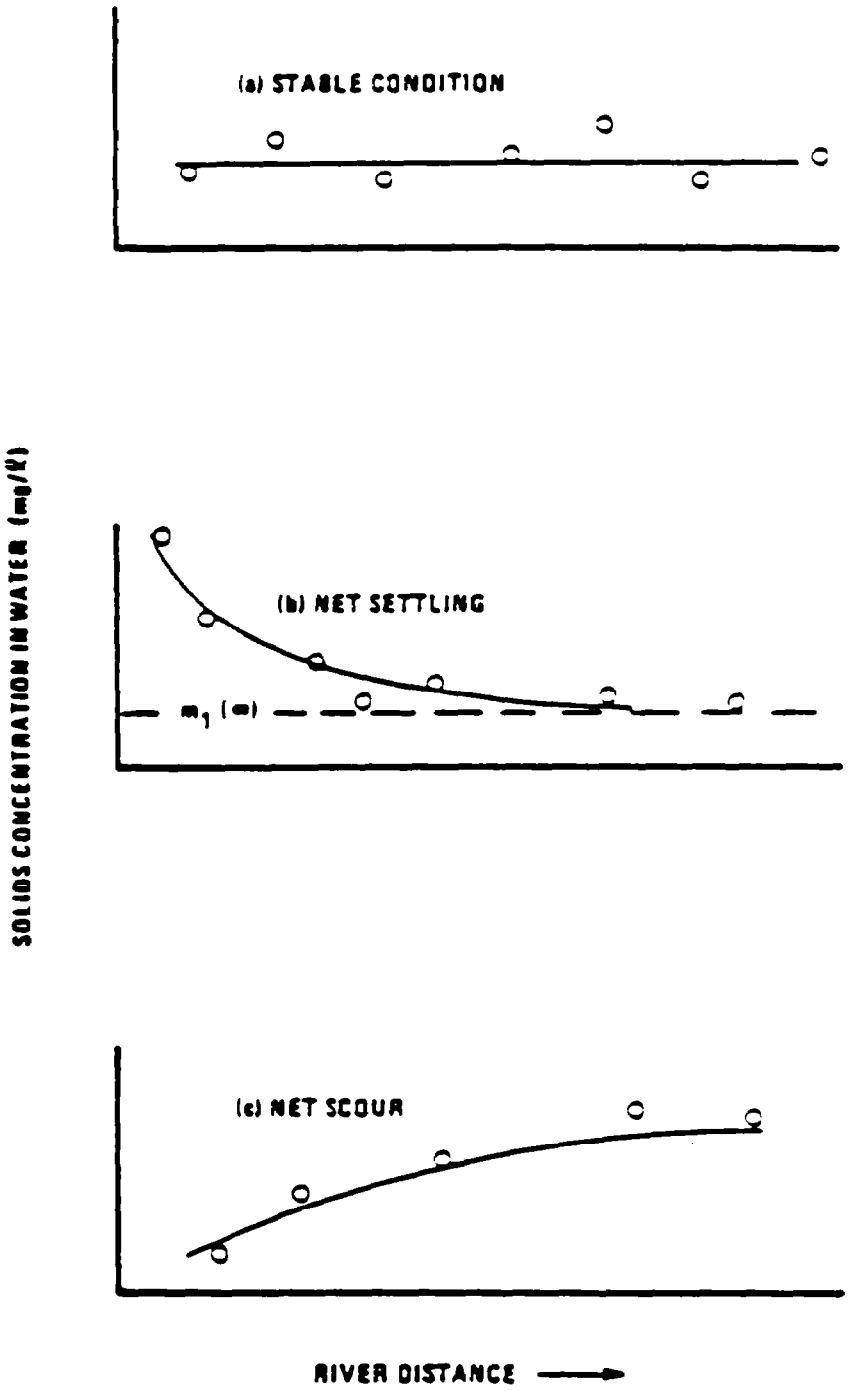

(a) STABLE CONDITION
(b) NET SETTLING
m_1 (∞)
(c) NET SCOUR
SOLIDS CONCENTRATION IN WATER (mg/ℓ)
RIVER DISTANCE

FIGURE 3.1

$$w_{rs} = \frac{m_1(\infty)}{m_2} w_s \tag{3.3}$$

where $m_1(\infty)$ is the asymptote ($m_1(x)$ at $x = \infty$), estimated visually from a profile such as shown in Figure 3.1(b). If Equation 3.2 is normalized for the asymptote and put in logarithmic form, the derivative (slope) of the resulting expression is directly related to w_s:

$$w_s = -U_1 H_1 \frac{\Delta \log_e [m_1(x) - m_1(\infty)]}{\Delta x} \tag{3.4}$$

This in analogous to determining a decay coefficient from the slope of a semi-logarithmic plot of concentration versus time. Having thus determined w_s and w_{rs}, the value of $w_d(x)$ is given by Equation 3.1.

Alternatively, the value of $w_d(x)$ at any particular point can be expressed in terms of the linear (rather than semi-logarithmic) slope of the profile:

$$w_d(x) = -\frac{U_1 H_1}{m_2} \frac{\Delta m_1(x)}{\Delta x} \tag{3.5}$$

The value of w_s would then be given by combining Equation 3.1 and 3.3, and the value of w_{rs} by Equation 3.3.

The indirect estimation of solids exchange velocities, as described above, may be difficult in many practical situations. If hydraulic conditions (such as U_1 and H_1) vary along the length of the river, then w_s and w_{rs} may also vary. Normal scatter in the suspended solids data (such as caused by time variability) may make identification of slope and asymptote ambiguous. The analyst may thus need other means

for estimating w_s and w_{rs}. Both may be independently estimated, or having independently estimated one, the other can be more easily calibrated using the solids profile (as illustrated in the Flint River case study). In any case, calibration is assisted by recognizing that the magnitude of w_s (or w_d) controls the distance needed to approach the asymptote, while the ratio w_{rs}/w_s controls the value of the asymptote.

A direct estimate of the settling velocity, w_s, can be made using Stokes' equation. Figure 3.2 illustrates the solution of this formula.

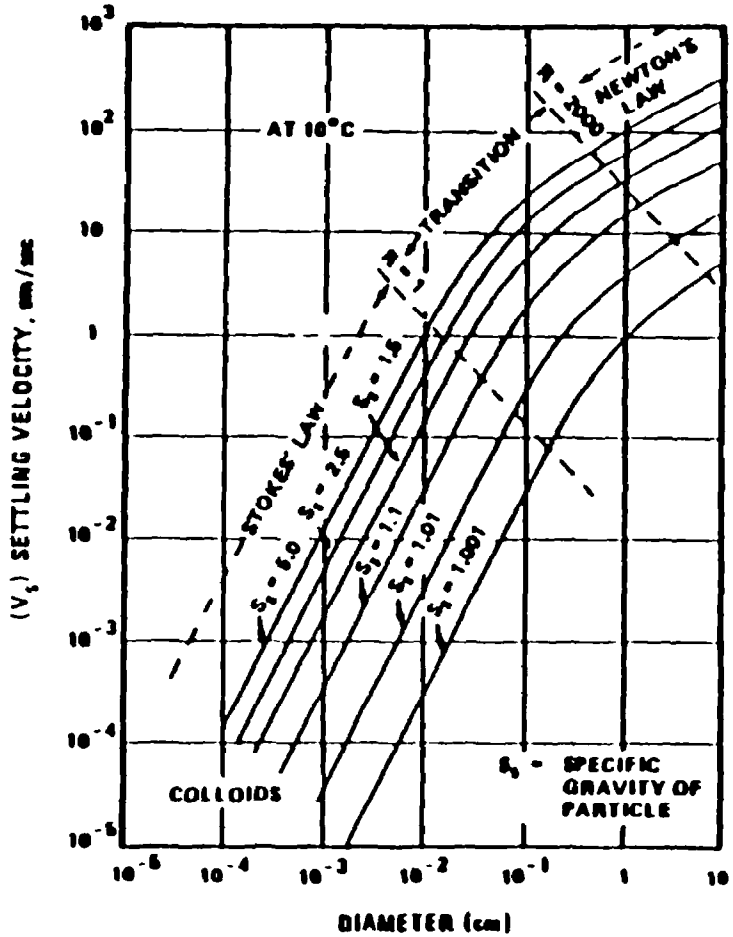
$$v_s = \frac{gd^2}{18\nu} (S_s - S_w) \qquad (3\text{-}6)$$

where, v_s = Stokes' settling velocity (cm/sec)
g = Gravitational acceleration (approx. 980 cm/sec^2)
d = Particle diameter (cm)
ν = Kinematic viscosity (cm^2/sec) (Figure 3.2B)
S_s = Specific gravity of particle (dimensionless ratio)
S_w = Specific gravity of water (1.0).

This calculation is intended to apply to noncohesive spherical particles in a quiescent medium. Substantial differences may exist between the calculated Stokes' velocity, v_s, and the effective settling velocity, w_s, of natural particles under both laboratory and field conditions. Such differences may result from particle interactions and fluid turbulence and shear.

Coagulation or clumping together of suspended particles creates larger diameter particles having higher Stokes' settling velocity. The inter-particle collisions necessary to bring this about may result from (a) Brownian motion (diffusion), (b) shear (velocity gradients) internal to the fluid, and (c) differential settling velocities, causing more rapidly settling particles to intercept slower settling particles beneath them (O'Melia 1980, Hayter and Mehta 1982). The inter-particle cohesiveness needed to produce aggregates from colliding particles may result from (a) van der Waals forces, (b) electric charges on particle

(A)



PROCEDURE:

STEP 1 – ESTABLISH:
(a) MEDIAN PARTICLE DIAMETER
(b) PARTICLE SPECIFIC GRAVITY

STEP 2 – FROM FIGURE A SELECT (V_s)

STEP 3 – FROM C CALCULATE REYNOLDS NUMBER (R)

STEP 4 – (a) IF R < 1 CONTINUE
(b) IF R > 1 CANNOT USE STOKES VELOCITY

STEP 5 – USING D MODIFY V_s FROM 10°C TO AMBIENT TEMPERATURE

(B)

TEMP. (°C)	KINEMATIC VISCOSITY (ν)
0	1.79×10^{-2} cm²/sec
5	1.52×10^{-2}
10	1.31×10^{-2}
15	1.15×10^{-2}
20	1.01×10^{-2}
25	0.89×10^{-2}
30	0.80×10^{-2}

(C) REYNOLDS NUMBER (R)

$$R = \frac{V_s \cdot d}{\nu}$$

WHERE: R = REYNOLDS NUMBER
V_s = SETTLING VELOCITY (cm/sec)
d = PARTICLE DIAMETER (cm)
ν = KINEMATIC VISCOSITY (cm²/sec)

(D) V_s AT TEMP. =

$$V_s \text{ AT } 10 \times \left(\frac{\nu \text{ AT TEMP.}}{1.31 \times 10^{-2}}\right)$$

ADAPTED FROM HYDROQUAL 1982

FIGURE 3.2 OBTAINING THE STOKES SETTLING VELOCITY (V_s)

surfaces, (c) interactions of aqueous ions attracted to the charged surfaces (double layer), (d) chemical bonds, and (e) other mechanisms (Partheniades 1971). As a result of coagulation into larger particles the observed settling velocity may be orders of magnitude larger than the Stokes' velocity of the disaggregated particles (Uchrin and Weber 1980).

Hayter and Mehta (1983), in modeling fine sediments in estuaries, indicate that the effective deposition velocity, w_s, decreases with increasing shear stress, τ, produced by the fluid passing over the bed. Shear stress in an open channel is determined as follows (Graf 1971):

$$\tau = \gamma R S \tag{3.7}$$

where, τ = Shear stress (Newton/m^2)
γ = Specific weight of water (approximately 9807 N/m^2)
R = Hydraulic radius, approximately equal to stream depth (m)
S = Slope of the energy grade line, approximately equal to the bed slope (m/m)

If the stream velocity, U, is assumed to follow Manning's equation, then the bed shear can be expressed as follows:

$$\tau = \gamma (n\ U/1.486)^2/R^{1/3} \tag{3.8}$$

where n is Manning's roughness coefficient. Under this condition, bed shear is related to the square of velocity.

Parthenaides (1971) notes that there is some critical velocity or shear above which no deposition of fine particles will occur. As velocities drop below this critical value a rapidly increasing proportion of the fine particles are capable of depositing.

In this vein, HydroQual (1982) recommends settling w_s equal to 25-50% of the Stokes' velocity in most rivers, and to as little as 10% of the Stokes' velocity in shallow streams. They also point out that the Stokes calculation should be treated as a preliminary estimate, to be modified by calibration to the suspended solids data.

For quiescent waters, Thomann (1982b) and Richardson et al. (1983) have calculated w_s in the range 0.1-5 m/day. In the Flint River case study, w_s was calibrated at 0.25 m/day during low flow and 0.6 m/day during a higher flow period. (An increase in settling velocity with an increase in flow is the result of suspension of larger or denser particles by the higher flows). The manual Sedimentation Engineering (ASCE 1975) presents a thorough discussion of the effects of sediment and fluid properties on the settling velocity.

Direct instream measurements with sediment traps can be used to estimate w_s. HydroQual (1982) briefly discusses such measurements, summarizing the findings of Blomquist and Hakansom (1981) on the accuracy of various types of sediment traps.

The resuspension velocity, w_{rs}, also depends on the shear stress, τ, as well as on the strength of bed to resist shear. The strength of the bed is related to the nature the particles and the deposition history (including age and degree of consolidation). Below some critical velocity or shear, little or no resuspension may take place, while above this critical value, resuspension may increase rapidly (Parthenaides 1971, Hayter and Mehta 1983). The parameters determining resuspension rates must generally be empirically measured.

Bonazountas and Mathias (1984) discuss data and methods, and propose algorithms for determining both deposition and resuspension. Their computer model, SEDIM, is intended to be used for estimating the input parameters of commonly used toxicant models. It employs the formulations of Einstein, Meyer-Peter and Mueller, and Toffaleti, adapted to account for the field data available to the analyst.

3.1.2 Diffusion Between the Water Column and Pore Water

Diffusion of dissolved pollutant between the water column and the sediment interstitial water operates to move materia. from the region of

higher concentration to the region of lower concentration, in accordance with Fick's Law. If no dissolved concentration gradient exists then diffusion is unimportant. Water column and pore water would be expected to attain the same concentration under the following condition: (a) steady state with (b) partition coefficients equal in the bed and the water column, and (c) no decay within the bed.

Unsteady conditions produce concentration gradients that can make diffusion important. In addition, if partition coefficients are lower in the bed than in the water column due to the higher solids concentration in the bed (O'Connor and Connolly 1980), then deposited particulate pollutant may have the opportunity to desorb and diffuse back into the water column in the dissolved phase. Decay in the bed, on the other hand, would tend to depress pore water concentrations relative to water column concentrations. Thomann (1984) indicates that for metals copper, cadmium, and zinc, sediment diffusion is an important process in waters having suspended solids concentrations less than about 10 mg/ℓ.

The exchange coefficient describing dissolved exchange between the bed and water column has been termed K_L in Section 2. HydroQual (1982) notes that this parameter is difficult to measure directly. They believe that K_L in the range 10 - 100 cm/day may appear reasonable based on field and microcosm calibration results.

Both molecular diffusion and physical stirring of the bed may contribute to the magnitude of the exchange coefficient K_L. Where only molecular diffusion is important K_L can be estimated from the expression (HydroQual 1982):

$$K_L = D_L \phi^n / \phi \delta \qquad (3.8.1)$$

where:

D_L = molecular diffusivity of chemical in water (cm^2/day)
ϕ = sediment porosity (dimensionless)
δ = length of vertical concentration gradient in sediment (cm)
n = a power

The sediment porosity ϕ appears the numerator to account for the reduction in diffusion caused by the tortuosity in sediments. It appears in the denominator to account for the conversion of concentration units from interstitual volume to bulk volume. The vertical concentration gradient length δ may be taken to be equivalent to the active sediment thickness H_2 used in Section 2.5. The value of n is a sediment dependent property indicating the relationship between porosity and tortuosity. HydroQual (1982) assigns the value n = 2; however Chapra and Reckhow (1983) indicate that other values may also apply.

Chapra and Reckhow (1983) present the molecular diffusion coefficient data of Li and Gregory (1974). For priority pollutant metals D_L is frequently between 6×10^{-6} and 12×10^{-6} cm^2/sec at 25°C. Diffusivity is roughly linearly related to temperature; values at 0°C are about half of those at 25°C.

Equation 3.8.1 does not include the effect of physical stirring of the bed sediment caused by currents and benthic animals (bioturbation). Heathershaw (1976) and Fisher et al. (1980), among others have noted the importance of bioturbation in increasing the effective rates of diffusion.

Additional explanation of sediment diffusion processes and formulations are provided by Berner (1980), Chapra and Reckhow (1983), and DiToro and Connolly (1980).

3.2 PARTITIONING PROCESSES

3.2.1 Metals Partitioning

The interaction between dissolved metal species and riverine particulate matter, under normal physicochemical conditions, generally leads to a large fraction of the metal being associated with solids. When a significant fraction of the total metal in a system is in the solid phase, the fate, transport, and bioavailability of the metal are

altered considerably. There is ample evidence in the literature that metal associates with particulate matter; however, theoretical (as opposed to empirical) approaches have not been widely applied to quantifying this process in natural systems. The purpose of this section is to present the theoretical considerations that have led to the simple parameterization of metals partitioning commonly used, and to indicate the factors which influence partitioning.

The accumulation of heavy metals in aquatic solid substances can be characterized by the following five major mechanisms (Gibbs 1973): 1) adsorptive bonding on fine-grained substances, 2) precipitation of discrete metal compounds, 3) coprecipitation of metals by hydrous Fe and Mn oxides and by metal carbonates, 4) association with organic molecules, and 5) incorporation into crystalline minerals. Inconsistent interpretations of metal solids interactions in natural waters can easily arise in situations where different mechanisms are operating under different environmental conditions. For example, even though adsorption is a necessary first step for heterogeneous surface precipitation, Corey (1981) distinguishes between the two as follows: 1) adsorption is a two-dimensional, surface layer process while precipitation involves three-dimensional crystal buildup, and 2) in adsorption, solution adsorbate concentration is controlled by surface site concentration whereas the degree of precipitation is controlled by solution concentration. For heterogeneous precipitation to occur conditions leading to a critical supersaturation of the adsorbate ion must exist. In a system where the ultimate result is the formation of a precipitate, however, the strict assumption of an adsorption-desorption equilibrium may be invalid.

In most cases encountered in river systems it would seem that adsorption of metals to inorganic surfaces is the dominant binding mechanism. However, in situations where there is a large fraction of biological solids, sorption into biomass or binding by c ganic surface

functional groups can play an important role. In fact, most of the models describing the interaction of adsorbate ions and surfaces have an implicit definition of adsorption as a two-dimensional, surface phenomenon.

Adsorption models developed from a theoretical basis are generally a composite of surface complex formation theory (Schindler et al. 1976; Huang and Stumm 1973) and various electrostatic models (Gouy-Chapman-Stern model in Shaw 1978; Grahame 1955; James and Healy 1972). More recent models, such as the one proposed by Davis, James and Leckie (Davis et al. 1978; Davis and Leckie 1978; James et al. 1978), combine surface complexion with electric double-layer theory and interpret adsorption phenomena in terms of a knowledge of the speciation of the adsorbate and the adsorption site.

Current adsorption models have been reviewed by a number of authors (Westall and Hohl 1980; James and Parks 1981; Schindler 1981; Morel 1981) and have been shown to have a sound theoretical basis. The application of these models to well-characterized laboratory metal-ligand-surface systems have shown excellent agreement with experimental observations (e.g., Davis and Leckie 1978a; James et al. 1981; Theiss and Richter 1980; Benjamin and Leckie 1980). However, without further basic research and experimentation with natural aquatic sediments, it will be difficult to apply the theoretical models to adsorption in natural systems. The application to natural systems is mainly hampered by the need for data on numerous intrinsic parameters for each adsorbent phase in the system of interest.

Despite the lag that currently exists between the development of theoretical metal adsorption models and their practical application to natural systems, there has arisen (through model development and experimental observation) general agreement on many of the characteristic features o' ıdsorption reactions. Metal adsorption is considered to be

analogous to the formation of soluble complexes, with the only difference being that the ligand in the reaction is a surface site (Stumm and Morgan 1981; Benjamin and Leckie 1981). Therefore, the same factors affecting soluble complex formation also affect the interactions at surfaces.

Of course, pH is one of the most influential parameters in governing metal adsorption, affecting both the type of surface sites and the speciation of the metal ion in solution through hydrolysis reactions. For example, surface hydroxyl groups can exist in three possible charge states, with the relative distribution depending on the pH and acidity constants.

$$S\text{-}OH_2^+ \overset{K_{a1}^S}{\rightleftharpoons} S\text{-}OH \overset{K_{a2}^S}{\rightleftharpoons} S\text{-}O^-$$

At the same time the metal ion will undergo hydrolysis as pH increases. The resultant surface association of metal ions with hydrous oxide surfaces tends to demonstrate a rapidly increasing metal ion adsorption as pH increases over a very narrow range of 1-2 units (James and Healy 1972a; and many others).

This "pH adsorption edge," as it is commonly called, often is demonstrated by a plot of percent metal adsorbed versus pH. An example of a typical metal adsorption edge is shown in Figure 3.3. In most cases, fractional adsorption decreases (the pH edge shifts to the right) as total metal concentration (Me_T) in the system increases, other conditions being constant (Benjamin and Leckie 1980). This effect is most often evident at low adsorption densities, when excess surface sites are available.

In situations where complexing ligands (either organic or inorganic) are present in an adsorbing system, the above generalization for the relationship between metal adsorption and pH is not always true. In fact, depending upon the particular metal, ligand, adsorbent and pH

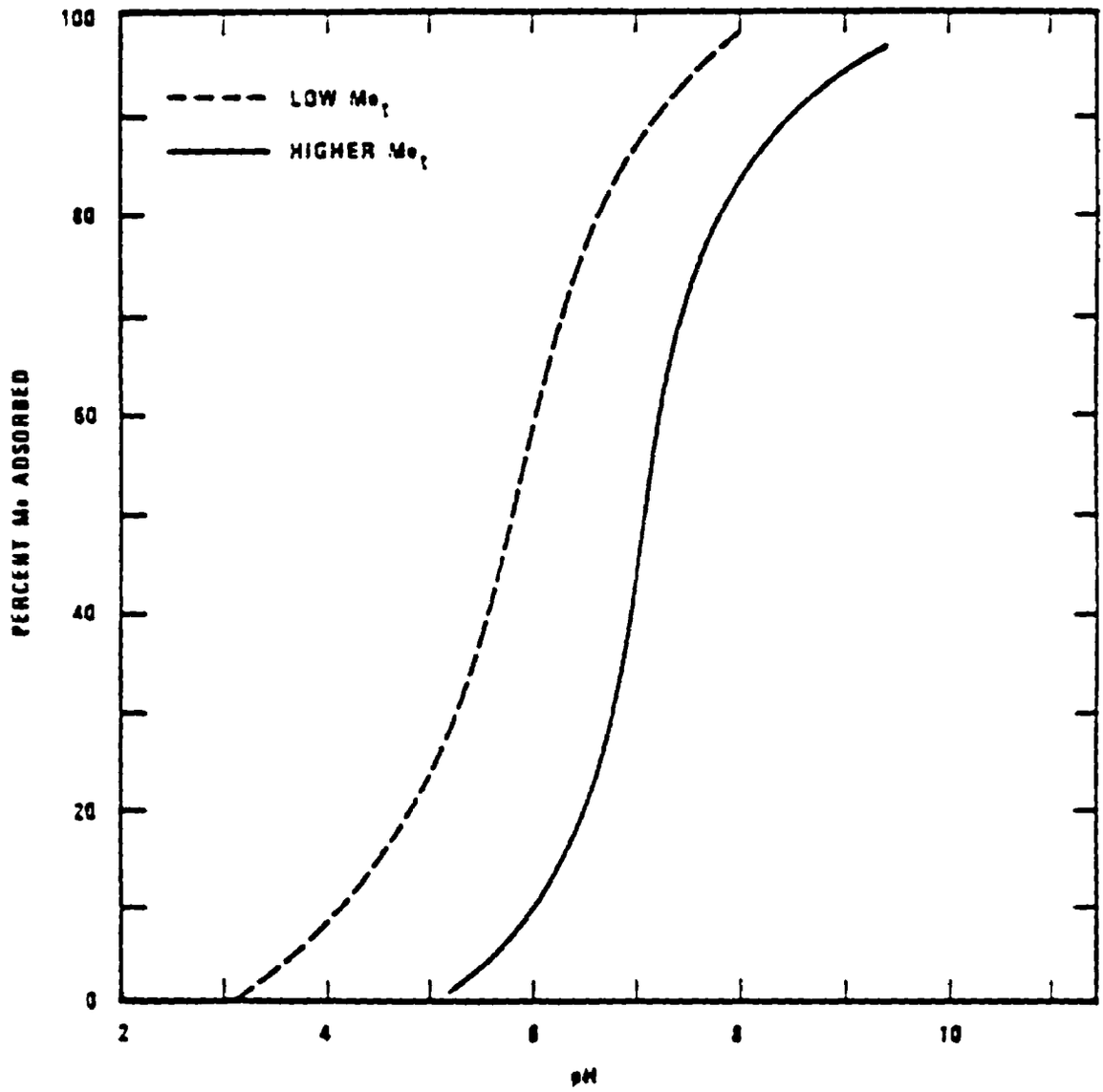


FIGURE 3.3 TYPICAL pH-ADSORPTION EDGE FOR METAL ADSORPTION
ON HYDROUS OXIDE SURFACE

range, fractional metal adsorption has been observed to decrease as pH increases (MacNaughton and James 1974). Benjamin and Leckie (1981; 1982) have proposed a conceptual model to explain this behavior, where the possibility exists for free metal, a metal-ligand complex, or free ligand to be associated with a surface. Then the percent adsorption of a metal-ligand complex will increase with pH if it behaves as a free metal in its surface interaction ("metal-like") and will decrease with pH if its adsorption reaction is similar to that of a free ligand ("ligand like").

Another characteristic feature of metal adsorption is competition between adsorbate metals. Major cations, such as calcium and magnesium, have been shown to influence the adsorption of a given metal ion. Predictability of the influence of major cation is difficult, and observations range from inhibition to no effect. At any rate the effect certainly seems to be smaller than those due to variations in pH and ligand levels.

Competitive adsorption inhibition among adsorbing trace metals is observed even at very low total adsorption densities (at most a few percent of all surface sites occupied). Benjamin and Leckie (1981) have suggested that the explanation for this phenomenon is the presence of several distinct groups of surface sites. Then the possibility exists for two metals to be competing for the same group of preferred binding sites, which may represent only a small fraction of all surface sites. The existence of multisite surfaces may also partially explain the variation of pH-adsorption edge among different metals adsorbed individually to the same adsorbent. In this case different binding sites are preferred by each metal.

Although numerous experimental adsorption studies with "model" adsorbents have been conducted, the number of laboratory studies investigating the uptake of trace metals by natural aquatic sediments is

relatively small. The results of these adsorption experiments of trace metals partitioning measurements made in natural aquatic systems are generally quantified in terms of relatively simple empirical expressions, including general exchange equilibrium expressions (Langmuir 1981) and adsorption isotherms (Oakley et al. 1981) of the Freundlich or Langmuir type.

The data from a typical metal adsorption isotherm run at specified environmental conditions, when plotted as the adsorption density versus equilibrium dissolved metal concentration, generally can be fit to a Freundlich or Langmuir isotherm (Figure 3.4). The Freundlich isotherm is an empirical equation having the general form

$$\Gamma = K_F [M]^{1/n} \tag{3.9}$$

where K_F and n are fitting constants. The Langmuir equation has a more theoretical base and may be deduced from either kinetic or thermodynamic considerations (Weber 1972). The Langmuir equation assumes that maximum adsorption density corresponds to a saturated monolayer surface covering of adsorbate, that the energy of adsorption is constant regardless of adsorption density, and that there is no migration of adsorbate in the surface plane. As shown in Figure 3.4 the Langmuir equation can be expressed

$$\Gamma = \frac{\Gamma_m [M]}{(\Gamma_m / K_a) + [M]} \tag{3.10}$$

where Γ = Specific adsorption density of the metal [Moles Me/mg Adsorbent] ("gamma"),

Γ_m = Maximum adsorption density in forming a complete monolayer [Moles/mg] (i.e., number of usable surface sites per unit mass of solid), and

[M] = Equilibrium dissolved metal concentration [Moles/ℓ].

The constant Γ_m/K_a, which normally is written 1/b in the Langmuir equation, is shown in this manner because K_a can be thought of as a

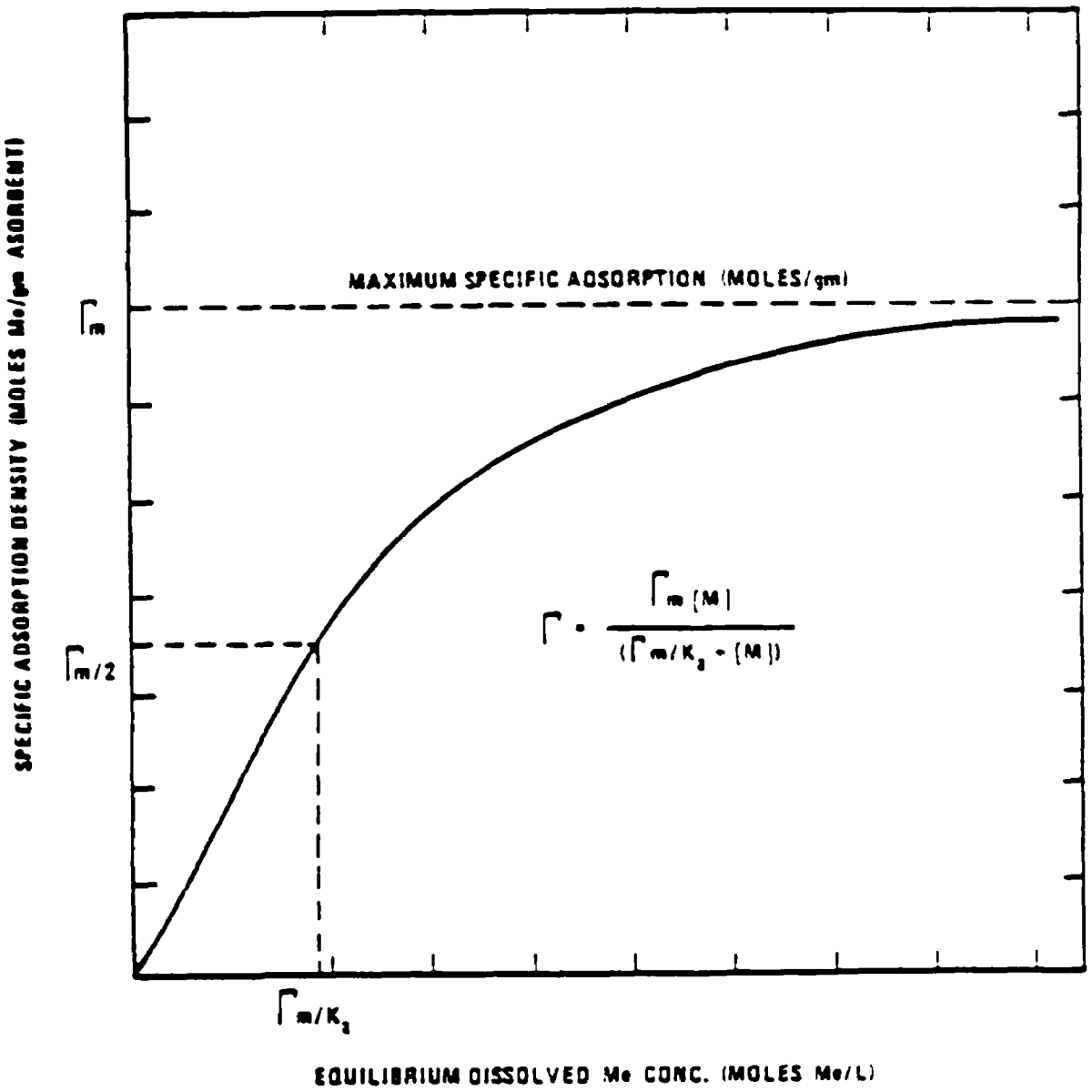


FIGURE 3.4 EXAMPLE OF PARAMETERIZATION OF LANGMUIR ADSORPTION ISOTHERM FOR METAL ADSORPTION ON A SURFACE

conditional adsorption equilibrium constant (ℓ/mg) for a surface-metal complexation reaction of the form:

$$M + S \xrightleftharpoons{K_a} M\text{-}S$$

K_a is termed a conditional equilibrium constant because its value in only a constant for specified surface and bulk solution chemical conditions.

It is convenient to express the Langmuir adsorption isotherm equation in the above form because, due to low metal adsorption densities in natural systems, adsorption is often linear with respect to dissolved metal concentration. Then, since $\Gamma_m/K_a >> [M]$, Equation 3.10 reduces to

$$\Gamma = K_a[M] \quad \text{or} \quad K_a = \frac{\Gamma}{[M]} = \frac{[M\text{-}S]}{[M]S_T} \tag{3.11}$$

where [M-S] = Concentration of metal in metal-surface complex (mole/ℓ) and

S_T = Total concentration of interacting (adsorbing) solids (mg/ℓ).

Converting the Langmuir nomenclature to the toxicant modeling nomenclature of Section 2.5 (Table 2.1), it can be recognized that K_a is the same as π (ℓ/mg), [M] (mole/ℓ) corresponds to C_d (ug/ℓ), [M-S] (mole/ℓ) corresponds to C_p (ug/ℓ), S_T is m (mg/ℓ), and Γ (mole/mg) corresponds to r (ug/mg). Thus, Equation 3.11 can be written:

$$\pi = \frac{r}{C_d} = \frac{C_p}{C_d m} \tag{3.12}$$

The distribution of metal between dissolved and solid phase can therefore be determined by specifying the partition coefficient and the concentration of interacting solids.

It should be emphasized that the value of the partition coefficient for a given metal is dependent on a number of environmental conditions such as pH, pe, ionic strength, concentration of complexing organic and inorganic ligands, concentration of competing surfaces, and concentration of competing adsorbate species. The use of π is, therefore, limited to conditions very similar to those for which it was determined. If a wide range of environmental conditions are encountered, then π must be quantified (either experimentally or theoretically) for the conditions of interest in order to accurately compute the soluble/solid phase metal distribution. This point became apparent during the model application to the Flint River system.

The partition coefficient might be adjusted as a function of environmental factors, as described below:

1) Metal adsorption is highly dependent on the type and relative amount of each solid phase making up the solids in an aquatic system. Oakley et al. (1981) demonstrated this postulate using bentonite clay, amorphous iron oxide, hydrous manganese oxide, and humic acid. Sediment organic content can be highly correlated with metal partitioning for those metals, such as copper, that have a high affinity for humic acids (Oakley et al. 1981; Ramamoorth and Rust 1978; Suzuki et al. 1979).

2) Metal partition coefficients depend on the size distribution and concentration of adsorbing aquatic sediments. It is obvious that smaller particles would have a larger surface area-to-mass ratio, thus having a higher capacity for the metal (Tada and Suzuki 1982). It is not obvious why a higher solids concentration gives a lower calculated partition coefficient, although it has been observed in a number of studies on both metals and organics (O'Connor and Connolly 1980; DiToro et al. 1982).

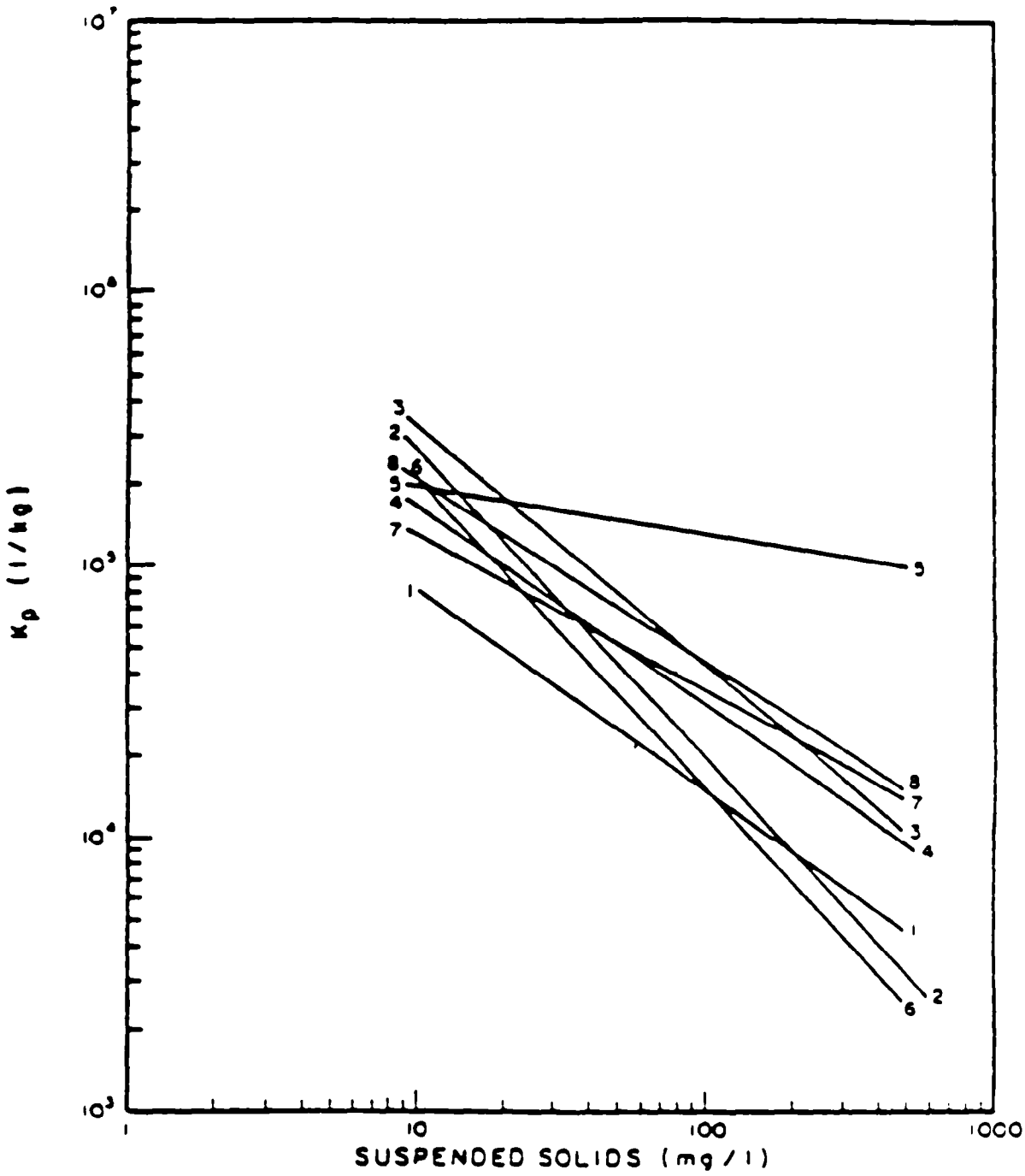
3) Of course, pH and other water chemistry parameters (particularly the presences and concentration of metal-complexing and adsorbing ligands) will affect partition coefficients. Many of the same observations made on "model" systems in controlled laboratory studies have been observed in studies of natural aquatic sediments (Gardiner 1974; Huang et al. 1977; Vuceta and Morgan 1978; Tada and Suzuki 1982; Brown 1979).

An alternative to adjusting metals partitioning as a function of environmental conditions based on theory and laboratory experimentation would be to empirically derive correlations from extensive field data. By measuring partition coefficients for a range of water quality in a given system or by reviewing partition coefficient data from many different river systems, a multiple regression might be found for a given metal partition coefficient versus such important water quality parameters as temperature, pH, hardness, alkalinity, suspended solids, dissolved organic carbon, and chlorophyll a. Attachment 1 contains a summary of data retrieval of field measurements of metals partition coefficients with pertinent water quality parameters. Figure 3.5 summarizes the regression results for the major metals for data obtained from streams. These data are useful for estimating metal partition coefficients for specific river systems where actual field data are not available.

3.2.2 Organics Partitioning

Most organic contaminants of concern tend to be relatively hydrophobic, non-polar compounds. Such organic compounds tend to have strong affinity for natural aquatic particulate material, making solution/sediment distribution of these chemicals as important in predicting their fate and transport as it is for heavy metals.

The sorption of hydrophobic organics is considered by most researchers to be a true equilibrium partitioning between the water and sediments. The linearity of sorption isotherms in dilute sediment/water systems and the lack of competitive effects between two sorbates have led to the proposition that partitioning to sediment organic matter is the primary mechanism of sorption of nonionic organic compounds (Chiou et al. 1982). This being the case, much emphasis on the characterization of this sorption process has been focused on the properties of the chemicals



METALS:

1 - ARSENIC
2 - CADMIUM
3 - CHROMIUM
4 - COPPER
5 - LEAD
6 - MERCURY
7 - NICKEL
8 - ZINC

FIGURE 3-5.

PARTITION COEFFICIENT AS FUNCTION OF SUSPENDED SOLIDS
ALL METALS IN STREAMS

related to their solubility and hydrophobicity and on the size and organic content of the sorbents.

Data relating the chemical concentration in the aqueous phase to that in the solid phase are frequently expressed in terms of the Freundlich or Langmuir isotherms previously described (Equations 3.9 and 3.10). For typical environmental pollutant concentrations, sorption isotherms in the sediment/water suspension are very close to linear and both Freundlich and Langmuir equations can be reduced to:

$$r = \psi C_d \tag{3.13}$$

where r = chemical concentration in solid phase (ug/mg)

C_d = chemical concentration in aqueous phase (ug/ℓ)

ψ = partition coefficient (ℓ/mg)

The prediction of ψ for a given chemical/suspension system has relied on correlations with chemical solubility, octanol/water partition coefficients (K_{ow}), and the organic carbon/water partition coefficient (K_{oc}), coupled with the organic carbon content (weight fraction) of the sediments. In general, the more insoluble and hydrophobic a chemical is the more likely it is to have a larger ψ. Likewise, in comparing sorption of a given chemical among various sediments, the sediment with the highest organic content is likely to sorb the most chemical and produce the largest ψ.

In quantifying the above relationships the first useful correlation is between the octanol/water partition coefficient and the chemical's aqueous solubility. This work was pioneered by pharmacological interests in the partitioning of drugs into the aqueous and fatty phases of living tissues (Hansch et al. 1968). More recently correlations have been developed for organic chemicals of environmental interest in aquatic systems (Freed et al. 1977; Chiou et al. 1977; Banerjee et al. 1980; Mackay et al. 1980).

Given either the aqueous solubility (S) or the octanol/water partition coefficient (K_{ow}) of a compound, a correlation can be developed between π and S or K_{ow} for a range of chemicals. More often than not, however, recent experimental interpretations have included several sediments with a range of organic carbon content. Then, by dividing the measured partition coefficient (K_p) by the organic carbon weight fraction of the particular sediment (O.C.), a sediment-independent partition coefficient (K_{oc}) between the aqueous phase and the organic portion of the sediments may be obtained.

$$K_{oc} = K_p/O.C. \tag{3.14}$$

Table 3.2 contains a summary of empirical correlations for predicting sediment partitioning and biological partitioning (bioconcentration factors) of nonpolar organic compounds.

Care must be taken in applying the above (or other) empirical correlations to unstudied systems. While these correlations will probably give reasonable estimates for application to a WLA problem, there are a number of potential pitfalls that should be considered. Some of these considerations are discussed below:

1. These relationships are all log-log correlations; therefore, what may seem like a small deviation from the regression line could produce a rather large error in final fate and transport determinations.

2. These relationships are useful only for nonpolar compounds; they sould not be applied to semipolar or polar organic compounds, where electrostatic interactions may become significant (Pavlow, 1980; Leenheer, 1980).

TABLE 3.2. CORRELATIONS BETWEEN K_{OC} OR B_f AND AQUEOUS SOLUBILITY (S) OR OCTANOL/WATER PARTITION COEFFICIENT (K_{OW}) REPORTED IN RECENT LITERATURE

Empirical Equation	Reference
(a) $\log B_f = 0.542 \log K_{OW} + 0.124$ ($n=8$; $r^2=0.899$)	Neely, et al., 1974
(a) $\log B_f = 3.41 - 0.508 \log S$ ($n=7$; $r^2=0.930$)	Chiou, et al., 1977
(b) $\log B_f = 0.85 \log K_{OW} - 0.70$ ($n=59$; $r^2=0.897$)	Veith, et al., 1979
$\log K_{OC} = \log K_{OW} - 0.317$ ($r^2=0.980$)	Means, et al., 1982
$\log K_{OC} = 4.273 - 0.686 \log S$ (g/ml) ($r^2=0.933$)	Means, et al., 1982
$\log K_{OC} = 1.00 \log K_{OW} - 0.21$ ($n=10$; $r^2=1.00$)	Karickhoff, et al., 1979
$\log K_{OC} = 0.44 - 0.54 \log S$ (mole fraction) ($n=10$; $r^2=0.94$)	Karickhoff, et al., 1979
$\log K_{OC} = 0.72 \log K_{OW} = 0.49$ ($r^2=0.95$)	Schwarzenbach and Westall, 1981
(c) $\log K_p^z = 0.72 \log K_{OW}^z + \log f_{o.c.} + 0.49$	Schwarzenbach and Westall, 1981

(a) B_f = bioconcentration factor in trout

(b) B_f = bioconcentration factor in fathead minnows, rainbow trout, bluegills

(c) K_p^z = partition coefficient for a particular nonpolar molecule; f_{OC} = organic carbon sorbent

Note that fish bioconcentration (given by B_f) is very slow compared to particulate adsorption (given by K_{OC}).

3. The water chemistry of the aquatic system (in addition to the water concentration of the compound of interest) can alter the empirically predicted partition coefficient. For example, if the compound interacts by surface adsorption or ion exchange, then solution properties such as pH, ionic strength, and temperature will affect uptake on solids (Hollander et al. 1980). Even with hydrophobic compounds the presence of other dissolved organic matter has been shown to reduce sorption by river and sewage particulate matter (Hassett and Anderson 1982).

4. Properties of the sediments other than their organic carbon content may influence sorption. Hiraizumi et al. (1979) found a good correlation between partition coefficients of PCB and the specific surface area of adsorbing marine particulates. Of course, the concentration of adsorbing solids has been observed to affect partition coefficients for organics as well as metals (O'Connor and Connolly 1980).

5. Finally, the question of kinetics and hysteresis arises in all adsorption-desorption problems. Karickhoff (1980) has found that the kinetics of approach to equilibrium in sediment suspensions (either during adsorption or desorption) could be characterized by a rapid component and a much slower component that may require days or weeks to reach equilibrium. A possibly related problem has been observed by DiToro and Horzempa (1982) and DiToro et al. (1982), in that the lack of reversibility in PCB adsorption-desorption reactions could be described by invoking a two-component formulation. Adsorption and desorption are assumed completely reversible for the first component, following Equation 3.13. Adsorption is assumed irreversible for the second component. DiToro et al. (1983) presents the mathematical formulation for this model and shows the results of further laboratory testing. The practical difference between modeling with the classical reversible expression and modeling with the reversible-irreversible expression is that the former may predict higher dissolved concentrations, particularly in dynamic models.

3.3 TRANSFORMATION PROCESSES

Transformation processes are those in which the toxicant is essentially irreversibly destroyed, modified, or eliminated from the system. In most cases these processes apply only to organic compounds.

First-order decay coefficients for individual processes are additive; together they form an aggregate degradation co fficient:

$$K_d = K_B + K_H + K_P + K_V \tag{3.15}$$

where K_d = Aggregate degradation coefficient (1/day)
K_B = Biolysis coefficient (1/day)
K_H = Hydrolysis coefficient (1/day)
K_P = Photolysis coefficient (1/day)
K_V = Volatilization coefficient (1/day)

Some models also distinguish non-biological oxidation, K_O, separately, although this process is not important for most organics.

In models with simple first-order kinetic structures (such as MICHRIV), the analyst either enters the aggregate K_d or enters the individual process coefficients K_B, K_H, K_P, and K_V. In models with more elaborate kinetic routines (such as EXAMS), each individual first-order coefficient (K_B, etc.) is internally calculated as a function of several other parameters which the analyst must enter.

3.3.1 Biodegradation

Biological transformations (biolysis) are enzyme mediated reactions usually performed during metabolic activity, primarily by bacteria and fungi. The catalyzed transformations include oxidation, reduction, and hydrolysis. The rates of biologically mediated transformations can be very rapid in comparison to chemical transformations that lack enzymatic catalysts. It is precisely because of these accelerated rates that the biodegradation of organic contaminants is often the most important transformation loss process in aquatic ecosystems.

Conceptually, biodegradation should not be thought of as a single step process. Rather, it is a multi-step process where intermediate products may accumulate. The total conversion of organic substances to inorganic products, including carbon dioxide, is termed mineralization. The process termed biodegradation, however, often involves only the partial metabolism of an organic. For instance, detoxification of a contaminant may involve only the transformation to an innocuous intermediate compound.

Process Description

When heterotrophic microbes degrade organic compounds, energy and carbon are frequently obtained for growth, thereby accomplishing metabolism. Occasionally a compound may be biologically transformed without the responsible microbes acquiring growth requirements. Typically, this process of cometabolism will proceed at relatively slower rates and will not impact the activity of the decomposer community.

Frequently, when an organic contaminant is first introduced to an aquatic community an acclimation period is observed when the microbial community must adapt itself to the chemical. This acclimation period is most often termed a lag phase. The lag phase is marked by enzyme induction, selected population increases, and a progressive increase in the rate of observed biodegradation. Once the microbes have become acclimated to an organic pollutant, the rate of specific decay becomes of interest.

There are three primary factors that determine the extent and rate of biological decay of an organic in a natural system. These are: 1) the properties of the organic contaminant, including its structure, concentration, and history within its environment; 2) the characteristics of the acting microbial community, such as community diversity, size and general health; and 3) the status of the environment in terms of temperature, the presence of additional organics or supporting growth

requirements and, especially, the dissolved oxygen status.

Within the framework of a model designed to describe the fate of an organic contaminant, it is necessary to formulate and define a kinetic expression of biodegradation. This task is made difficult because of the great complexity of factors inherent in a natural system. Contemporary fate models have simplified this task by representing the loss or decay of an organic by first-order kinetics or in some cases second-order kinetics.

First-order kinetic representation in the WLA model is described as:

$$\frac{dC}{dt} = -k_1 C \tag{3.16}$$

where k_1 = First-order biodegradation rate constant ($time^{-1}$)
C = Concentration of an organic contaminant (mass/volume)

The concentration, C, susceptible to decay may be the dissolved fraction. Therefore, if a contaminant partitions onto solids, the respective particulate and dissolved fractions must be quantified. This expression describes the loss of an organic due to biological activity and is analogous to expressions commonly used for the decay of BOD. Larson (1981), among others, has shown that first-order kinetics represent the decay of organics reasonably well at bacteria concentrations evident in many environmental situations.

In many respects representation of second-order kinetics is a simplification of a modified Monod expression (Paris et al. 1981), represented as:

$$\frac{dC}{dt} = -k_2 CB \tag{3.17}$$

where B = Magnitude of bacteria (count or biomass/volume) and
k_2 = Second-order biodegradation rate constant (volume/organism time).

The decay of a contaminant is seen as not only a function of its concentration, as is the case in first-order kinetics, but also a function of the bacteria population. However, bacteria count has not always proven a reliable indicator of bacteria activity, especially in regard to a specific contaminant organic. This development in biodegradation process representation has been offered by many models (e.g., EXAMS) as a way of increasing the application of a single, contaminant-specific decay rate to a wide variety of environments. Since biodegradation is recognized as being influenced by ambient temperature, process representation can include a function relating the biodegradation rate to the temperature regime. The analyst may derive a temperature specific rate by making use of an Arrhenius function such as:

$$K_T = K_{20}\,\theta^{(T-20)} \qquad (3.18)$$

where K_T = Temperature specific biolysis rate,
K_{20} = Expected rate at 20° centigrade,
T = Characteristic temperature, and
θ = Temperature correction factor.

Theta (θ) is frequently between 1.04 and 1.095.

Rate Selection

In nearly every circumstance the selection of an appropriate decay rate is constrained by incomplete information regarding the contaminant or the system of interest. However, there are a number of approaches and relevant considerations to guide prudent selection of a representative decay rate. Inherent in this selection process is the realization that no rate is applicable to all conditions for a specific contaminant. Instead a range of estimates will more likely emerge that will impart to the analysis a range of output. The importance of this range may be established by a sensitivity analysis, whereby variability in model output is compared to incremental changes in the decay rate over the range of expected values.

A list of relevant considerations or approaches to estimating a decay rate is offered below. Although a ranking of these considerations by order of importance could only be made on a problem specific basis, awareness of an overall ranking is evident in the presentation.

A. Properties of Contaminant

A thorough literature survey of the properties of the organic contaminant of interest should logically be an initial step. Previously reported data relating decay rates for the organic in the laboratory or the field would be an important step in defining a probable range of decay rates. For each of the organic priority pollutants Mabey et al. (1982) have estimated the general susceptibility to biodegradation. Definition of likely metabolic pathways may also be helpful in several regards. Aerobic pathways will generally be more rapid and complete than anaerobic pathways. Also, the loss rate of one chemical may not be indicative of changes in toxicity, if intermediates form that are toxic and possess different decay characteristics. Therefore, the analyst would want information regarding the toxicity and biodegradability of probable intermediates. In cases where the knowledge of an organic is very sparse, it may be necessary to compare the structure and physical characteristics of the organic of interest to a host of better known contaminants. When approached in great detail, this procedure is called structure activity analysis.

B. System Examination

Information regarding the trophic level and pollution level of the target system may assist in defining the expected decay rate. More highly impacted waters have demonstrated shorter lag phases and greater decay rates of organics (Spain et al. 1981, Rodgers and Salisbury 1981). Previously reported field data may, to varying degrees, yield insight into the spatial and time distribution of the

organic, as well as important environmental factors (temperature regime, volume and flow). If available in sufficient quantity and quality, this information may allow the user to "calibrate" a biodegradation decay rate by accounting for other components of a mass balance and then solving for the magnitude of the biolysis term.

C. Experimental Program

Laboratory measurement of decay rates may be necessary in evaluating decay rates for organics for which no information is available. Methods for measuring decay rates have been demonstrated for both batch (Paris et al. 1981) and continuous cultures or by use of microcosms (Giddings et al. 1979). In site specific applications it is the practice to use the natural waters as the test media. Sterilization of the water before introduction of the test organic serves as a control. The batch cultures yield a decay rate by plotting the log concentration of organic vs. time, while continuous cultures can yield a decay rate via a mass balance approach since other sources and sinks can be controlled and thereby quantified. Should a second-order formulation be invoked, relating the rate to both the pollutant concentration and the microbial population, then the magnitude of the microbial population must be assessed.

D. Field Program

The Waste Load Allocation process may involve a field program. To assist in the accurate evaluation of a biodegradation rate, the measured parameters should include both total and soluble concentrations of the pollutant of interest, solids concentration, dissolved oxygen, CBOD, flow, temperature, and basic physical dimensions. Basic information regarding the biology of the system is desirable, especially bacteria counts and identification of toxic conditions which might influence bacterial activity. The spatial and temporal scale of sampling will impact the calibration and accuracy

of the biodegradation term, as well as all other kinetic processes. Data upstream and downstream of all major loads are important. The frequency of sampling should reflect the relative dynamic nature of the system in terms of hydraulic residence (flow regime) and the major forcing functions (temperature, loading, light, etc.). Some attempt to reflect the seasonal variation in forcing functions may be especially helpful.

3.3.2 Photolysis

Some substances that absorb sunlight in the ultraviolet and visible portion of the spectrum may gain sufficient energy to initiate a chemical reaction. Some of these photochemical reactions result in the decomposition or transformation of the substance. This process, photolysis, can determine the fate of certain pollutants in the aquatic environment. Zepp (1980) provides a more complete discussion of this process.

Process Theory

A summary of the theory involving the transformation of organics via photolysis is outlined from Mills et al. (1982). The basic characteristics of photolysis are as follows:

- Photolysis is an irreversible decay process activated by the energy of the sun.
- Molecules which absorb sunlight in the ultraviolet and visible portions of the spectrum gain sufficient energy to initiate chemical reactions.
- Products of photochemical decomposition may remain toxic; therefore, decomposition does not necessarily imply detoxification of the environment.
- The photolysis rate depends on several chemical and environmental factors.

The chemical and environmental factors controlling the rate are as follows:

A. Absorption Spectrum of the Pollutant:

The probability of a photon being absorbed varies with wavelength of light in a manner unique to every chemical species. To change a molecule's structure, the absorbed photon must be sufficiently energetic; generally, radiation with wavelengths in the visible or ultaviolet range, or shorter, has sufficient energy. Consequently, the pollutant's visible/ultraviolet absorption spectrum is most important.

B. Solar Radiation:

Radiant energy from the sun depends on the composition of the atmosphere (cloud cover) and geographic location.

C. Light Attenuation:

Light intensity reduces with depth in water column, due to reflection (< 10% reduction plus slight change in the spectrum) and absorption and scattering. Absorption is determined by Lambert's Law:

$$-\frac{dI}{dz} = KI \tag{3.19}$$

where I = Irradiance

K = Diffuse light attenuation coefficient, given by:

$$K = aD + S_b \tag{3.20}$$

where a = Absorption term

D = Radiance distribution function

S_b = Backward scattering of light

The value of K (diffuse light attenuation function) depends on variations in amounts and types of particulates and dissolved substances, i.e., suspended solids, chlorophyll a, dissolved carbon. The value of D, which represents variable light path lengths, is 1.2 where scattering is ignored. Average value for natural waters is 1.6 as reported by Miller and Zepp (1979).

An empirical relationship developed by Burns et al. (1981) enables the attenuation coefficient to be estimated based on system status:

$$K = D\,(A_w + A_a Chla + A_{doc} DOC + A_{ss} SS) \qquad (3.21)$$

where K = Diffuse light attenuation coefficient

A_w = Absorptivity of water, (m^{-1})

A_a = Absorptivity of chlorophyll a pigment, $(mg/\ell)^{-1}(m^{-1})$

A_{doc} = Absorptivity of dissolved organic carbon, $(mg/\ell)^{-1}(m^{-1})$

A_{ss} = Absorptivity of suspended sediments, $(mg/\ell)^{-1}(m^{-1})$

Chla = Concentration of Chlorophyll-a pigment, (mg/ℓ)

DOC = Concentration of dissolved organic carbon, (mg/ℓ) and

SS = Concentration of suspended solids, (mg/ℓ)

Mills et al. (1982) tabulate the values of A_w, A_a, A_{doc}, and A_{ss} for different wavelengths.

D. Quantum yield:

Not every absorbed photon induces a chemical reaction. The fraction of adsorbed photons resulting in the desired reaction is termed quantum yield, ϕ.

$$\phi = \frac{\text{moles of given species formed or destroyed}}{\text{moles of photon absorbed}}$$

Environmental factors affecting quantum yield include:

a) molecular oxygen -- as a quenching agent.
b) suspended solids -- change reactivity of compounds adsorbed (usually negligible).
c) chemical speciation -- photolysis rates may vary with pH, especially important when pKa is 7 $\pm$ 2.
d) temperature effect -- until further research is completed this is assumed to be negligible.

Type of photochemical reaction affects quantum yield. Quantum yields vary over several orders of magnitude depending on the nature of the molecule which absorbs light and the nature of the reactions it undergoes. Two major classes of photochemical reactions of interest in the aquatic environment are "direct" and "sensitized" photolysis.

Direct photolysis occurs when the reacting molecule directly absorbs light. Various reactions can occur: fragmentation, reduction, oxidation, hydrolysis, acid-base reaction, addition, substitution, isomerization, polymerization. Quantum yield data obtained from experimentation can assist the WLA analyst in determining whether or not to include direct photolysis in the analysis.

Sensitized (indirect) photodegradation occurs when a light-absorbing molecule transfers its excess energy to an acceptor molecule causing the acceptor to react as if it had absorbed the radiant energy directly. Natural humic acids (and synthetic organic compounds) can mediate such reactions, for example.

<u>Rate Estimation</u>

Photolysis follows a psuedo-first-order reaction:

$$\frac{dC}{dt} = -K_p \cdot C \qquad (3.22)$$

where K_p = Rate constant = $K_d + K_s$ ($Time^{-1}$),
K_d = Direct photolysis rate, and
K_s = Sensitized photolysis rate.

One practical means of obtaining the appropriate photolysis rate is to use experimental data from literature and extrapolate to the specific site in question. There are two methods reviewed below for using environmental data to calculate the expected photolysis rate.

One method involves extrapolating near surface rate data to a specific site (Mills et al. 1982):

$$K_d = K_{do} \frac{I}{I_o} \frac{D}{D_o} \frac{1 - e^{-K(\lambda^*) \cdot Z}}{K(\lambda^*) \cdot Z} \tag{3.23}$$

where K_d = Direct photolysis rate constant (day^{-1}),
K_{do} = Near surface rate constant (measured) (day^{-1}),
I = Total solar radiation ($langleys \cdot day^{-1}$),
I_o = Total solar radiation under conditions at which K_{do} was measured ($langleys \cdot day^{-1}$),
D = Radiance distribution function,
D_o = Radiance distribution near surface (approximate value = 1.2),
$K(\lambda^*)$ = Light attenuation coefficient calculated from Equation 3.20 for λ^*, the wavelength (nm) of maximum light adsorption, and
Z = Depth of water in meters.

The second method involves evaluating the rate constant integrals. If certain data are available for a substance (i.e., absorption spectrum $\epsilon(\lambda)$ or $\alpha_s(\lambda)$, and the quantum yields, Φ_d or Q_s), it is possible to estimate the photolysis rate for a specific site from the following (Mills et al. 1982):

$$K_d = 2.3 \cdot j \cdot \Phi_d \cdot D \cdot \sum \epsilon \cdot W' \frac{1 - e^{-K Z}}{K \cdot Z} \tag{3.23}$$

where i = wavelength interval index,

W = Photon irradiance near surface (photons cm^{-2} sec nm^{-1}),

W' = $W \cdot \Delta\lambda$

j = Conversion factor = 1.43×10^{-16} (mole cm^3 sec ℓ^{-1} day^{-1})

ϵ = Base 10 molar extinction coefficient (ℓmol^{-1} cm^{-1} of toxicant),

ϕ = Disappearance quantum yield,

K = Diffuse light attenuation near surface (m^{-1}),

Z = Mixed water depth (m) and,

α = Base e absorption coefficient of the sensitizer (mg^{-1} cm).

For toxicants for which photolysis may be significant, Mabey et al. (1982) provides data on absorption spectrum and quantum yield.

3.3.3 Hydrolysis

Certain organic compounds may be chemically transformed by direct reaction with water. This occurrence in an aquatic system is termed hydrolysis. A hydrolysis reaction may either be acid, neutral or base dependent. Essentially, this means that the concentration of hydrogen and hydroxide ions, and therefore pH, is often an important factor in assessing the rate of a hydrolysis reaction.

Products of hydrolysis may be either more or less toxic than the original compound. For this reason one should be aware of the probable products of transformation processes. In addition, transformation via hydrolysis will likely alter other characteristics of the chemical including its susceptability to other transformation processes.

Process Representation

In a natural system hydrolysis may be either microbially mediated or be abiotic and dependent only upon the status of the water. Microbial influence is covered in Section 3.3.1; consequently only direct, abiotic hydrolysis wi ; be examined here.

Abiotic hydrolysis is normally represented by a first order reaction which in its most simplified form is:

$$\frac{dC}{dt} = - K_H C \qquad (3.25)$$

where C = Concentration of an organic (Mass/volume) and,
K_H = Specific first-order hydrolysis rate constant ($Time^{-1}$).

In the scientific literature K_H is typically represented as:

$$K_H = k_n + k_a [H^+] + k_b [OH^-] \qquad (3.26)$$

where k_n = Neutral hydrolysis rate constant ($Time^{-1}$),
k_a = The acid catalyzed hydrolysis rate constant ($Molar^{-1}$ $Time^{-1}$),
k_b = The base catalyzed hydrolysis rate constant ($Molar^{-1}$ $Time^{-1}$),
$[H^+]$ = Molar concentration of hydrogen ions and,
$[OH^-]$ = Molar concentration of hydroxide ions.

This representation conveys the strong pH dependence often observed in hydrolysis reactions and is a convenient method of representing detailed laboratory results.

The adsorption of an organic onto solids often removes the particulate fraction from hydrolysis reactions. Therefore, the hydrolysis rates in Equation 3.25 and 3.26 are only applied to the soluble fraction of the toxicant. If the model being employed does not discern between dissolved and particulate phases, then the observed partitioning should be used in adjusting the magnitude of the rate constant.

Rate Selection

A great deal of data has been reported in the chemical literature regarding the observed hydrolysis of chemicals in distilled water. Natural waters, however, contain organics and metals which may catalyze and accelerate hydrolysis. Consequently, the query which consistently

emerges is, how applicable are distilled water rates to field conditions? Research designed to answer this question has been reported within the last several years (e.g., Zepp et al. 1975). The approach has been to use field samples and to remove as many competing processes as possible. For example, dark conditions were used to eliminate photolysis and ultra-filtration to remove the biological community, thereby eliminating biolysis.

Specific hydrolysis coefficients for many organics or classes of compounds are reported in the professional, governmental, and industrial publications. Recent sources include Wolfe (1980), Mabey and Mill (1978), and Mabey et al. (1982). These coefficients should give the user a range of values from which to calibrate the model or to guide a sensitivity analysis. Wolfe (1980) also reviewed a technique based on linear free energy relationships (LFER) for estimating hydrolysis rate coefficients when experimental values are not available. When there is a paucity of reported values for a chemical of interest, other measures may be taken to estimate a rate. The general format would be similar to that presented for the biolysis rate constant in Section 3.3.1.

Lastly, in translating literature values into computer model input, it should be noted that some values are reported as second-order coefficients because they are a function of either the hydrogen or hydroxide ion concentration (as represented in Equation 3.26). In using first-order kinetic models the analyst must translate these second-order values into pseudo-first-order rate coefficients by multiplying by the appropriate ion concentration.

3.3.4 Volatilization

Volatilization, loss of toxicants from the water column to the atmosphere, is customarily treated as an irreversible decay process, because of its mathematical similarities to these processes. Actually,

however, it is a reversible transfer or environmental partitioning process, in which the concentrations in air and water shift toward equilibrium. The volatilization rate depends on the properties of the chemical as well as the characteristics of the water body and possibly the atmosphere. The chemical properties favoring volatilization are high vapor pressure, high diffusivity, and low solubility. The environmental conditions favoring volatilization are high surface-to-volume ratio and turbulence.

The partitioning of pollutant between water and air is described in terms of an air/water partition coefficient, H_c:

$$H_c = C_g(eq)/C_d(eq) \tag{3.27}$$

where H_c = Henry's law constant (dimensionless, mass/vol. basis),
$C_g(eq)$ = Gas phase concentration at equilibrium (mg/ℓ), and
$C_d(eq)$ = Dissolved aqueous concentration at equilibrium (mg/ℓ).

The value of H_c can be determined by measuring C_g and C_d in an equilibrated system. More commonly, however, it is calculated from the toxicant vapor pressure (equivalent to the gaseous concentration in equilibrium with the pure toxicant phase) and solubility (aqueous concentration in equilibrium with the pure toxicant phase):

$$H_c = 16.04 \quad PM/TS \tag{3.28}$$

where P = Vapor pressure (torr),
M = Molecular weight (g/mole),
T = Temperature (K°), and
S = Solubility (mg/ℓ).

It should be noted that H_c may be reported in an assortment of units or nonequivalent dimensionless bases. One useful conversion is:

$$H_c \text{ (dimensionless)} = H_c \text{ (atm - m}^3\text{/mole)/RT} \tag{3.29}$$

where $R = 8.206 \times 10^{-5}$ atm - m^3/°K - mole. For the organic priority pollutants the values for P, M, and S in Equation 3.28 are provided by Callahan et al. (1979), and the values of H_c provided directly by Mabey et al. (1982). For other substances data may be available in Mills et al. (1982), Perry and Chilton (1973), and Mackay et al. (1982). If vapor pressure data are not available, Mackay et al. (1982) suggests the following equation for estimating P (torr) for hydrocarbons or halogenated hydrocarbons with boiling point greater than 100°C:

$$\ln (P/760) = -(4.4 + \ln T_B) \times (1.803 (T_B/T - 1) - 0.803 \ln (T_B/T) - 6.8 (T_M/T - 1)$$

where:

T = Ambient temperature (K)
T_B = Boiling point (K)
T_M = Melting point (K)

If the melting point T_M is less than the ambient temperature T, than the third term is eliminated.

The net rate of transfer (mg/ℓ - day) from water to air is governed by the difference between (a) the gross transfer from water to air, proportional to the actual dissolved concentration C_d, and (b) the gross transfer from air to water, proportional to the air concentration C_g:

$$\text{Rate} = K_V (C_d - C_g/H_c) , \tag{3.30}$$

where K_V = Volatilization rate coefficient (1/day).

The term C_g/H_c is the water concentration which would be in equilibrium with (saturated with respect to) the local air concentration. Unlike common gases like oxygen, the environmental concentrations of toxicants, C_d and C_g/H_c, typically vary over many orders of magnitude. Consequently, it is usually the case that either (a) $C_d << C_g/H_c$, and the net input from the atmosphere is a constant load, essentially independent of the modeled C_d, or (b) $C_d >> C_g/H_c$, and the volatilization rate is essentially independent of the air concentration:

$$\text{Rate} = K_V C_d \tag{3.31}$$

Most computer models incorporate Equation 3.31 rather than Equation 3.30.

The <u>rate</u> coefficient K_V (1/day) is related to the <u>mass transfer</u> coefficient (or velocity), k_V (m/day) by:

$$K_V = k_V/H \tag{3.32}$$

where H is the water depth (the inverse of the surface to volume ratio).

The "two film" theory is generally applied to the calculation of the mass transfer coefficient. This theory envisions diffusion resistances in a liquid surface film and a gas surface film as controlling the mass transfer (Canale and Weber 1972; Liss and Slater 1974; Mills et al. 1982). Reciprocals of mass transfer coefficients are used to represent these resistances:

$$\underbrace{\frac{1}{k_V}}_{\text{Overall resistance}} = \underbrace{\frac{1}{k_\ell}}_{\text{Liquid film resistance}} + \underbrace{\frac{1}{H_c k_g}}_{\text{Gas film resistance}} \tag{3.33}$$

where k_ℓ = liquid film transfer coefficient (m/day), and
k_g = gas film transfer coefficient (m/day).

It is useful to discern three basic cases. (a) When $k_l << H_c k_g$, then k_v in Equation 3.33 is essentially equal to k_l (liquid phase controlled); (b) when $k_l >> H_c k_g$, then k_v is essentially equal to $H_c k_g$ (gas phase controlled); and (c) when k_l and $H_c k_g$ are of the same magnitude, then both contribute significantly to k_v.

As the chemical-to-chemical variability of H_c tends to be greater than the site-to-site variability of k_l and k_g, the value of the H_c tends to be more important than the environmental conditions in determining whether the liquid or gas phase resistance controls the volatilization rate.

Gas Phase Resistance

The movement of air causes a mixing of the air surface film which results in an increase in k_g. Because the evaporation of water is controlled by k_g, and because this process has considerable engineering importance, data are available relating k_g (for water vapor) to the ambient windspeed. Such data are presented by O'Connor (1980) and HydroQual (1982). By including theoretical effects of diffusivity and viscosity, they arrive at an expression applicable to any substance:

$$k_g = 0.001\ (D_g/\nu_g)^{0.67}\ W \qquad (3.34)$$

where D_g = Diffusivity of substance in air (cm^2/sec),
ν_g = Kinematic viscosity of air (= 0.15 cm^2/sec), and
W = Wind speed (L/T).

As the expression is dimensionally correct, consistent units will result in k_g having the same units as W. Average windspeeds tend to be in the neighborhood of 5 m/sec. Although transient periods of no wind are common in many localities, such periods are not long. Consequently, use of a steady state condition of little or no wind in Equation 3.34 (or 3.35) may not produce a realistic result.

Mills et al. (1982), using a similar type of data and analysis as O'Connor (1980) and HydroQual (1982), suggest the general relationship:

$$k_g = 170\ (18/M)^{1/4} W \tag{3.35}$$

where W is in m/sec.

Molecular weight, M, enters the expression because of its relationship to diffusivity. For water vapor, Equation 3.34 and 3.35 are nearly identical. Since $D_g/\nu_p = 1.6$ for water vapor equation 3.34 reduces to $k_g = 140W$ while Equation 3.35 becomes $k_g = 170W$. Thus, at a typical wind speed of 5 m/sec, k_g (water vapor) would be around 700-800 m/day.

Liquid Phase Resistance

In the environment the transfer of oxygen, a well studied WQ parameter, is always controlled by k_ℓ, the liquid transfer coefficient, rather than K_g, the gas transfer coefficient. Because $H_c k_g(O_2) >> k_\ell(O_2)$, equations 3.32 and 3.33 become:

$$k_\ell(O_2) = k_v(O_2) = HK_v(O_2) \tag{3.36}$$

where $K_v(O_2)$, in 1/day, is the commonly used reaeration coefficient. Consequently, it is useful to relate k_ℓ (toxicant) to $k_\ell(O_2)$, through an expression involving liquid diffusivities:

$$\frac{k_\ell(\text{toxicant})}{k_\ell(O_2)} = \left(\frac{D_\ell(\text{toxicant})}{D_\ell(O_2)}\right)^n \tag{3.37}$$

where n may vary from 0.5, in flowing waters, possibly up to 1.0 in standing waters (Mills et al. 1982).

Mills further suggests that D_ℓ is inversely proportional to the square root of molecular weight, and thus, for flowing waters:

$$\frac{k_\ell(\text{toxicant})}{K_\ell(O_2)} = \left(\frac{M\ (O_2)}{M(\text{toxicant})}\right)^{0.25} \tag{3.38}$$

Mills notes, however, that in field studies using radioactive tracers (Rathbun and Tai 1981), such relationships were difficult to discern. Rather, the volatilization rate could be adequately predicted by:

$$k_\ell(\text{toxicant}) = 0.655\ k_\ell(O_2) \tag{3.39}$$

Mabey et al. (1982), using a more complicated procedure relating D_ℓ to molar volume, has calculated the toxicant/oxygen transfer rate ratios for all volatile priority pollutants.

In any case, the difficult step in this approach is not to obtain the above ratio, but rather to predict the oxygen transfer coefficient, $k_\ell(O_2)$, correctly. This coefficient is a function of water turbulence, which may be generated either by water flow or by wind.

In free flowing rivers, water turbulence is generated by the flow, and numerous formulas are available for calculating $k_\ell(O_2)$ (i.e., $HK_v(O_2)$) from hydraulic parameters such as velocity, depth, and slope. Wilson and Macleod (1974) and Rathbun (1977) review many of the reaeration formulas which have been proposed over the last three decades. One example of such a formula is that of O'Connor:

$$k_\ell = (D_\ell\ u/H)^{0.5} \tag{3.40}$$

where u is stream velocity and units for parameters on both sides of the equation are chosen to be consistent. D_ℓ for O_2 is 1.81×10^{-4} m^2/day. The equation can be used to directly calculate k_ℓ(toxicant) if D_ℓ(toxicant) can be estimated.

In impounded waters and other slow moving water bodies, water turbulence may be generated by wind. O'Connor (1980) and HydroQual (1982) summarize data relating k_ℓ to windspeed, W. These dat suggest a relationship:

$$k_\ell = 0.17\ C_D\ (D_\ell/\nu_\ell)^{0.67}\ W \tag{3.41}$$

where C_D = Drag coefficient (unitless), and

ν_ℓ = Kinematic viscosity of water (=0.0100 cm^2/sec).

The units of all other parameters must be chosen to be compatable. C_D also appears to vary with windspeed, W, but may maintain a value around 0.001 for W less than 10 m/day. As with using Equations 3.34 and 3.35, sustained periods of little or no wind are not common; $k_\ell(O_2)$ values substantially less than about 0.5 m/day are not usually expected. Table 3.3 illustrates parameters needed to determine a wind controlled volatilization rate for two toxicants.

Hydroscience (1971) and EPA (1976) present data and a nomograph for estimating $k_\ell(O_2)$ for a variety of hydraulic conditions. Their data suggest that $k_\ell(O_2)$ would not be expected to be much less than about 0.6 m/day nor much more than about 12 m/day, except under unusually stagnant or turbulent conditions.

Identifying the Important Parameters

Equation 3.33 can be examined in light of the observed relationships of k_ℓ and k_g versus windspeed, and the reasonable range of k_ℓ suggested by Hydroscience (1971) and EPA (1976). Some simplifications of the two film analysis are thereby indicated.

If H_c is less than about 3×10^{-4}, then the gas phase coefficient will control the overall transfer coefficient k_v in all aquatic environments, even standing waters. This is because $H_c k_g$ will increase much more slowly than k_ℓ as a function of windspeed. In this case, the analyst need not consider the turbulence of the water body at all. Furthermore, surface transfer will be slow for substances of this type, and the rate will decrease as H_c decreases. Benzo(a)pyrene, dieldrin, and pentachlorophenol are examples of compounds in this class.

TABLE 3.3 VOLATILIZATION PARAMETER VALUES

Parameter			Aroclor 1242	Aroclor 1260
D_g	Diffusivity of PCB in Air	cm^2/sec	0.04652	0.03673
D_ℓ	Diffusivity of PCB in Water	cm^2/sec	5.387×10^{-6}	4.253×10^{-6}
ν_g	Kinematic Viscosity of Air	cm^2/sec	0.15	0.15
ν_ℓ	Kinematic Viscosity of Water	cm^2/sec	0.01	0.01
C_D	Drag Coefficient	-	0.001	0.001
W	Wind Speed	M/sec	5.0	5.0
p	Vapor Pressure	mm Hg	4.06×10^{-4}	4.06×10^{-5}
C_s	Saturation Concentration	mg/ℓ	0.35	0.027
M	Molecular Weight	g/mol	261	372
T	Temperature	K	289	289
H	Henry's Law Constant	-	0.01676	0.0309

If H_c is greater than about 3×10^{-1}, then the liquid phase coefficient k_l will control the overall transfer coefficient k_v under nearly all conditons, even when the water is very turbulent ($k_l(O_2) = 12$ m/day) and the air calm ($W = 2$ m/sec). For H_c in this range the analyst need not consider the air phase parameters. It is also important to note that among substances with a high H_c, the volatilization rate is independent of H_c; rather, it is dependent on the substance's water diffusivity. As diffusivities vary relatively little among most toxicants, the volatilization rates of all highly volatile toxicants are nearly identical. Examples of such compounds are vinyl chloride and tri- and tetrachloroethylene.

If H_c falls between about 3×10^{-4} and 3×10^{-1}, there can be some environmental conditions under which resistance in both the liquid and the gas phase controls the rate of volatilization. Nevertheless, under other environmental conditions only one phase may still control the overall rate. For example, under conditions of moderate turbulence ($k_l(O_2) = 2$ m/day) and wind ($W = 5$ m/sec), the liquid phase solely controls for any H_c greater than about 2×10^{-2}.

SECTION 4.0

GUIDANCE FOR MODEL APPLICATION

4.1 APPROACH TO WASTE LOAD ALLOCATION PROBLEM

Within the pollutant-by-pollutant modeling context considered by this document, the basic question confronting the waste load allocation analyst is, "How much of a specific substance can be allowed to be discharged in a receiving water, yet not violate the numerical water quality standard?" This section of the guidance document provides some principles and direction to answering this question. The intent here is not to provide a standard method to be followed verbatim. The various models and example application are provided as guides to be used to gain insight into the process. Modeling results, as depicted in Figure 4.1 should be used by decision makers in conjunction with water quality standards to develop waste discharge permit limitations. This process assumes that the decision makers (e.g., state water quality boards or administrators) have the the desire and legal means to allow use of the assimilative capacity of water systems. The models may assist in choosing some optimal mix of treatment, production modification, standard modification, and time schedule for implementation. It is important that the analyst be involved in this process and communicate modeling results including estimates of accuracy and uncertainty to others involved.

Furthermore, it is desirable to get the affected parties involved in the process early in order to identify the most important issues. By obtaining agreement on the approach for defining and evaluating the water quality problem, the regulatory agency, the dischargers, and any interested citizen groups may be able to work within a cooperative rather than adversarial context. Considering the level of uncertainty inherent in estimating allowable ambient concentrations, allowable recurrence intervals, and allowable effluent loadings, such agreement may be helpful for successfully completing the endeavor.

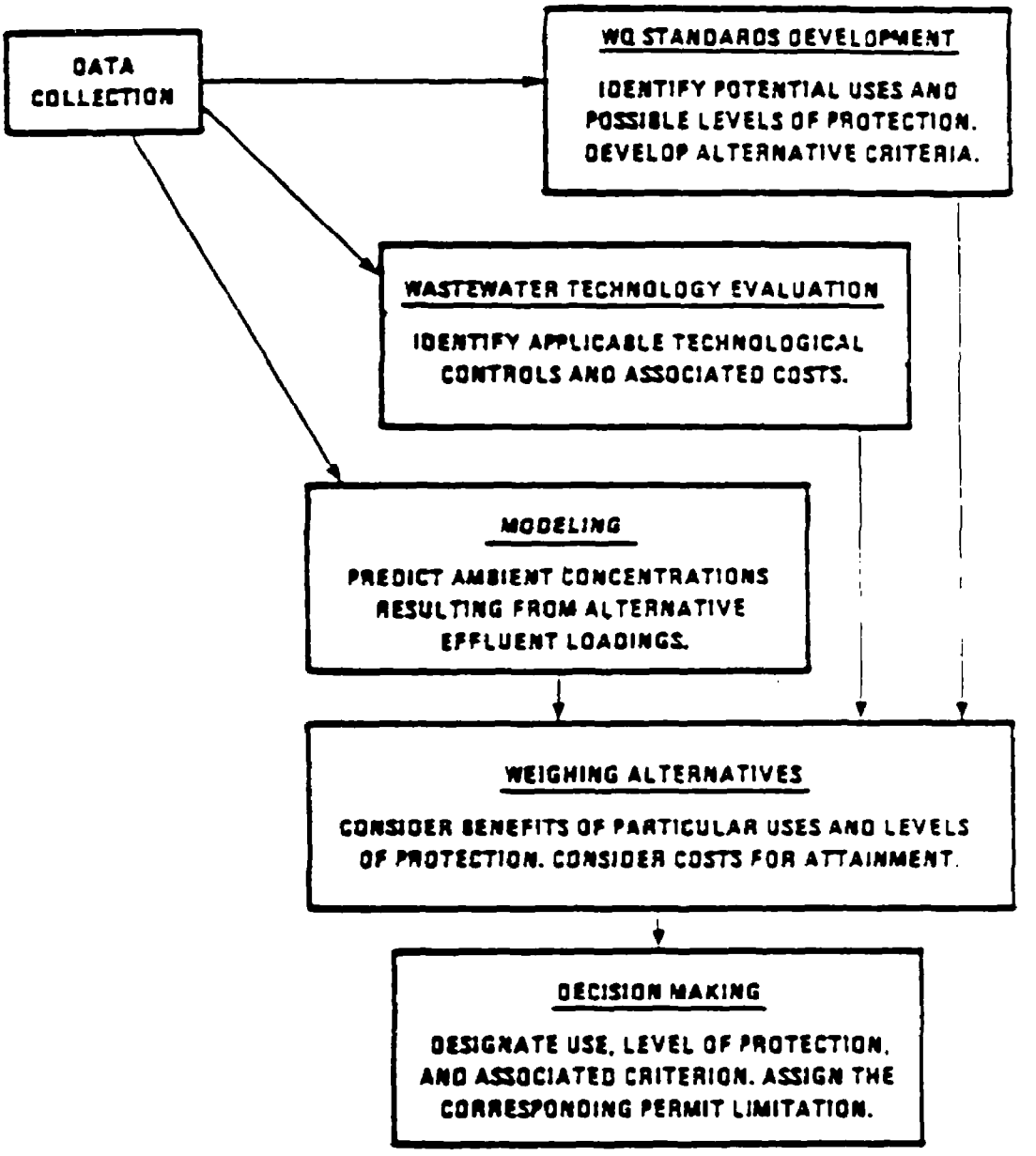


FIGURE 4.1 WASTE LOAD ALLOCATION PROCESS

An important issue confronting WLA analysts and managers concerns the amount of effort needed to make a sound, scientifically credible analysis. The appropriate level of effort depends partially on the complexity of the environmental problem. Single discharger, single toxicant, and relatively uncomplicated river problems can be expected to require less analysis effort than multiple discharge, multiple toxicant, and hydrologically complex problems. Nevertheless, the appropriate level of effort depends on other factors as well: such as the expectations of the decision makers, affected dischargers, and other parties. These expectations may be related to their previous WLA experiences, to the anticipated costs and the potential benefits, and to the resources available. The appropriate level of effort depends heavily on the consequences of a wrong decision.

Thus, it is not desirable for this document to attempt to specify from afar a particular level of effort as appropriate to a particular environmental problem. Rather, Section 2 has suggested a range of analytical approaches. Furthermore, the discussion that follows suggests a phased procedure for efficiently approaching whatever type of analysis is finally selected.

Phase 1: Dilution Calculation

A dilution formula calculation (Section 2.2) determines the concentration at the point of discharge, before any fate processes can act to remove or destroy the pollutant. The inputs required are the effluent flow and concentration and the upstream flow and concentration. The effluent data should be available from the permit application. Upstream flow may be available from USGS or previous pollutant reports for the area, or they may be estimated from the drainage area. Upstream concentration may be available from STORET or other water quality records; in many cases, the upstream toxicant load may be nearly zero compared to the effluent load.

Stream concentrations can be provided for flows and loads associated with a particular design event or for any number of events having various return frequencies (as described by DiToro 1982). This analysis for the point of discharge, however, provides no information on the downstream concentration, the area of impact, or the fate of the pollutant. These factors may need consideration primarily if (a) the load must be allocated among two or more dischargers spread out along the reach (in order to assess the degree of depuration occurring between dischargers), or if (b) the environmental benefits must be assessed (since they depend on the size of the impact area). Less probable reasons for pursuing fate modeling are if (c) sensitive downstream reaches require special protections, or (d) the pollutant produces hazardous degradation products.

For many permits, there may be little reason to proceed beyond the dilution calculation.

Phase 2: Downstream Estimates

The purpose of Phase 2 would usually be to estimate the spatial extent of the problem or, for multiple discharges, to estimate the additivity of loads. Beyond Phase I, this entails predicting the downstream behavior of pollutants using a fate and transport model (such as described in Sections 2.5 and 2.6). The model's input parameters would be estimated from whatever data are already available on the hydraulic and water quality characteristics of the reach, together with published information on the chemical characteristics of the pollutants. The model could then be used to estimate concentrations throughout the reach, for various control alternatives under various environmental conditions.

Computer data bases, such as STORET, IFD, Reach File, CHEM FATE, ISHOW, and individual state information systems, allow rapid retrieval of some types of information needed to apply the model. Table 4.1 summarizes the contents of these data bases and how to obtain access.

TABLE 4.1. AVAILABLE COMPL DATA BASES OF POSSIBLE ASSISTANCE FOR MODELING TOXIC SUBSTANCES*

Data Base	Achronym	Person/Organization and User Assistance Telephone No.	Description	Access
Storet-Water Quality File	STORET-WQF	US EPA STORET System User Assistance 800/424-9067 202/382-7220	Ambient water quality data as stored by States, EPA, USGS, and other agencies. USGS gaged flow records, some effluent records, some biologically related data.	Direct Batch and Real Time
Stream Reach Files	REACH	Phillip Taylor US EPA OWSR 202/382-7046	Contains 72,050 river reaches for the U.S. used to link other file information hydrologically. Provides linkage between WQF, IFD, GAGE, and WSBD6 files.	Direct Batch and Real Time
Industrial Facilities Discharge	IFD	Phillip Taylor 202/382-7046	A comprehensive national data base of about 44,000 discharge locations in 21 industrial categories, likely to contain any of 129 priority pollutants, files contain information on NPDES Permit Nos., flows, SIC codes, location, keyed to other files by stream reach.	Direct Batch and Real Time
Drinking Water File	WSBD6	Phillip Taylor 202/382-7046	Information on surface public water supplies in the U.S.	Direct Batch and Real Time
Stream Gaging Inventory File	GAGE	Phillip Taylor 202/382-7046	Summary of river flow data for 36514 gages in the U.S., basin characteristics, location, mean annual flow and 7 day-10 year flow.	Direct Batch and Real Time
Pollution Caused Fish Kills File	FISH	Phillip Taylor 202/382-7046	Reports of 12,000 fish kills in the U.S.	Direct Batch and Real Time

TABLE 4.1 (Cont'd.)

Data Base	Achronym	User Assistance Telephone No.	Description	Access
REACH Retrieval Method	RRM	Phillip Taylor 202/382-7046	Information from the WQF can be retrieved interactively by hydrological order.	Direct Batch and Real Tim
-	DATALOG	Syracuse Research Corp. 315/425-5100	A bibliographic environmental fate data base containing over 20,500 records on 2,600 chemicals - CAS Reg. No., Abbreviated reference, data types.	Direct Batch and Real Tim
-	CHEMFATE	Syracuse Research Corp. 315/425-5100	Data-value file containing literature derived data that is pertinent to the environmental fate of 220 chemicals.	Direct Batch and Real Tim
-	X-REF	Syracuse Research Corp. 315/425-5100	Contains references cited in DATALOG and CHEMFATE	Direct Batch and Real Tim
Information System for Hazardous Organics in a Water Environment	ISHOW	US EPA Env. Res. Lab-Duluth 218/726-7831	Contains data on chemical, biological, and physical properties of organic chemicals	Direct Batch and Real Tim
Oil and Hazardous Technical Assistance Data System	OHMTADS	NIH/EPA 800/424-9600	Contains a wide variety of physical, chemical biological, toxicological, and commercial data on many substances.	Direct Batch and Real Time

*Other d/ bases exist and should be added to list as r information becomes available.

This phase, relying on existing information, does not undertake the collection of new field data. While published information on the chemical characteristics of many toxicants is often reasonably sound, the site-specific environmental data are often sparse. In particular, bed/water exchange parameters, partition coefficients, some pollutant degradation parameters, and even the channel depth and velocity may be uncertain. Depending on potential environmental benefits and treatment costs estimated (using the model) to hinge on the WLA, it may be desirable to implement a monitoring program designed specifically to calibrate and verify the model, thus proceeding to Phase 3. A sensitivity analysis of model parameters can be used to identify the key uncertainties.

Phase 3: Monitoring and Model Validation

When modeling results indicate that the WLA decision is sensitive to poorly defined or understood parameters, then more intensive data collection may be warranted. Unlike the Phase 2 gathering of existing information, the Phase 3 monitoring program would be designed and implemented for the specific purpose of relating the receiving water response to the pollutant input, through calibrating and verifying the model.

Such monitoring of rivers is most effective if performed as intensive surveys. Their success requires careful design and substantial resources. Survey programs can vary greatly in magnitude, from single "plug flow" surveys, such as illustrated by the December 1981 Flint River survey (described in Section 5) ranging to large regional programs, such as the Delaware Estuary study (Thomann 1972).

The resources needed for a single intensive survey are determined largely by the size and complexity of the system. As the normal variability of the environment and effluent can be considerable, a fragmentary survey may often produce data that are impossible to

reconcile satisfactorily with modeling results. Consequently, if undertaken at all, an intensive survey should be tailored to the needs of the model, and designed to be insensitive to temporary aberrations in the system, as will be discussed further.

Having demonstrated accord between the model predictions and field observations for one or two or more conditions, the Phase 3 model can be used to forecast entirely new conditions with somewhat greater confidence than the Phase 2 model.

4.2 DATA NEEDS

Site-specific calibration of a toxic substance model for a Phase 3 analysis requires (a) waste load and boundary condition data, (b) environmental and chemical data for process rate estimation, and (c) calibration and verification data. The amount of data needed to be collected in time and space depends on the particular site, the variability of the system, the accuracy desired, and the resources available. The desire here is to suggest a realistic, achievable data collection plan.

The reader is referred to Book II, Streams and Rivers, Chapter 1: Biochemical Oxygen Demand/Dissolved Oxygen and Ammonia Toxicity, Section 4, for a thorough discussion of general problem definition and data requirements for stream models. The toxic substance problem should be considered as a special case of stream modeling, building upon a historical base of conventional monitoring and research.

In the following discussion, it is assumed that the WLA analyst has defined the problem, reviewed historical data, made preliminary modeling calculations, presented the initial findings to management, and developed a consensus to proceed with the collection of additional field data. It is also assumed that the WLA analyst can direct or at least recommend a monitoring plan and that he or she has visited the site and obtained a "feel" for the situation.

4.2.1 Obtaining Model Input Data

Table 4.2 summarizes typical data needs for setting up and calibrating a toxicant model. Not all items are applicable to all pollutants. Generally, channel data are needed for all types of pollutants; in addition, velocity and depth ordinarily have significant flow dependencies which must be ascertained. Effluent and boundary concentrations and flows are likewise needed for all pollutants. Sediment related data (partition coefficients, settling and resuspension velocities, and bed characteristics) are needed for pollutants which readily adsorb to particulates. Degradation rate data are needed for organic pollutants, depending on which processes (hydrolysis, photolysis, etc.) are applicable to the particular compound. References like Callahan et al. (1978), Mabey et al. (1982), and the CHEM FATE data base can be consulted to determine what processes are important for particular chemicals and to provide selected non-site-specific coefficients or data. Once the initial estimates are made, adjustments may be necessary during model calibration.

Site-specific environmental parameters can be obtained or inferred from direct measurements over the appropriate time period. The time frame selected would be determined by considering:

1. Residence time of the pollutant in the system.

2. Time variability of the system.

3. Time and frequency qualification to the water quality standard or criteria.

4. The expected critical time period -
   a. low flow with little dilution.
   b. high flow, with nonpoint loadings and sediment resuspension.
   c. periods critical to fish survival.

5. Production and treatment schedules and cycles.

TABLE 4.2 MODEL DATA NEEDS

Variable	Symbol	Unit	Remarks/Qualificatons
Channel Data			
River Flow	Q_1	m^3/sec	Measure or obtain from USGS Gage.
Velocity	U_1	m/sec	Measure directly with time-of-passage dye study, or compute from area and flow: $U = Q/A$.
Cross Section Area	A_1	m^2	Compute from measured width and depth, or compute from velocity and flow.
Reach Length	L	m	Reaches determined by significant morphometric changes, tributaries, or point sources; measure from charts, confirm in field.
Depth of Water	H_1	m	Measure directly or compute from cross section area and measured width.
Loading Data			
Upstream "Boundary" Concentration			
Toxicant	C_u	μ/ℓ	Direct measurement.
Suspended Solids	m_1	mg/ℓ	Direct measurement.
Point Sources			
Flow	Q_w	m^3/sec	
Concentra'.on Toxicant	C_w	μg/ℓ	
Load Toxi'ant	W	kg/day	Product of flow and concentration.
Concentration-Sus. Solids	-	mg/ℓ	
Load-Sus Solids	-	kg/day	
Bed and Particulate Data			
Thickness of Active Sediment	H_2	m	Estimate from core samples, measuring vertical distribution of organic contaminants; or use typical published values. This parameter has no effect on steady state results unless significant decay ·urs in e l ·

TABLE 4.2 MODEL DATA NEEDS (continued)

Variable	Symbol	Unit	Remarks/Qualificatons
Solids Concentration in Bed	m_2	mg/ℓ	Measure or estimate: m_2 = (particle density) (1-ϕ)
Porosity	ϕ	-	
Solids type	-	-	
Size Distribution	-	μm	
Settling Velocity	w_s	m/day	Estimate from particle-size distribution and stream turbulence coupled with published data or Stokes formula. Measure with sediment traps or in lab. Adjust by calibration.
Resuspension Velocity	w_{rs}	m/day	Calibrate to m_1 data; estimate from theory.
Partition Coefficient	π	ℓ/mg	Calibrate for dissolved and particulate data: $\pi = C_p/mC_d$. Otherwise, use literature values; for metals, use Attachment 1 data.
Sediment Diffusion	K_L	m/day	Literature values.
Degradation Rates			
Volatilization Coefficient	K_V	1/day	Calculate from theory. For volatile hydrophobic pollutants, compare with reaeration rate.
Reaeration Coefficient	$K_V(O_2)$	1/day	Calculate using stream depth, velocity, and possibly slope.
Solubility	S	mg/ℓ	Published data.
Vapor Pressure	P	torr	Published data.
Photolysis Rate	K_p	1/day	Use estimation method in Section 3; direct measurements made using Actinometer.
Chlorophyll a	CHL A	mg/ℓ	Standard methods.
Diss. Organic Carbon	DOC	mg/ℓ	Standard methods.
Suspended Solids	SS	mg/ℓ	Standard methods.
Solar/UV Radiation			UV radiometer.
Near Surface Rate	K_{pD}	1/day	Measured by Actinometer at water surface.
Biolysis Rate	K_B	1/day	Sterile vs. non-sterile dark bottle experiments.
Cell Count		#/mℓ	

TABLE 4.2 MODEL DATA NEEDS (continued)

Variable	Symbol	Unit	Remarks/Qualificatons
Hydrolysis Rate	K_H	1/day	Laboratory experiment at different pH or published data.
pH		SU	
Ancillary Data: Temperature		°C	
Calibration/Verification Data			
Suspended Solids	m_1	mg/ℓ	Standard methods - usually using 0.45 μm filter.
Toxicant Concentration -			In water column and bed sediment.
- Total	C_T	μg/ℓ	Direct measurement at appropriate times and places.
- Dissolved	C_d	μg/ℓ	Defined according to filter used; i.e., 45 μm.
- Particulate	C_p	μg/ℓ	Calculated: $C_p = C_T - C_d$.

Whenever possible, point source surveys should be scheduled for seasons when the system is likely to be most stable, unless specifically designed to evaluate time variability.

4.2.2 Calibration and Verification: Comparing Prediction with Observation

Calibration refers to the procedure of adjusting the input parameters until the output predictions (e.g., dissolved and total toxicant profile and suspended solids profile) reasonably match the observed concentrations. In multi-parameter models such as described in Sections 2.5 and 2.6, numerous different combinations of input values may allow a fit between predictions and observations. Consequently, before attempting to fit the data, it is customary to fix the values of as many parameters as possible, based on direct measurements. It may then be feasible to adjust the values of a small number of parameters, within the range of uncertainty for those parameters, in order to match the observations.

Verification generally refers to comparing predictions with observations for a second independent survey or time period. In practical WLA contexts (in contrast to some academic or research contexts), the distinction between calibration and verification may become hazy; the initial calibration may be modified or compromised such that the model can reasonably match both surveys. It is considered best if a single set of decay, partition, and sediment exchange coefficients fit both (or all) surveys adequately; however, it may be the case that some coefficients may need to vary between surveys, as illustrated in the Flint River study. If this is the case, then it is essential that the values vary in consistent, reasonable, readily justifiable ways.

Ideally, then, the WLA monitoring program would include at least two independent surveys. One survey might be more intensive because of the requirements for calibration. This survey may cover a longer time period, perhaps several days. It may include some master stations to

discern diurnal variations, particularly for those organic compounds which photolyze readily, and for sites where waste flows comprise a large fraction of the river flow. Station locations depend on the sources, tributaries, and stream characteristics. At a minimum, there should be one station to define boundary concentrations upstream from the first point source, one station just downstream of the mixing zone, and at least one some distance (travel time) downstream, reflecting the effect of the loss processes. The final plan would reflect the complexity of the system and the resources available.

A second survey might be less intensive, covering a shorter time period or perhaps employing a "plug flow" or "slug sampling" survey strategy. This strategy, illustrated in the December 1981 Flint River survey, involves sampling the point sources and river according to the passage of a plug of flow marked by a dye tracer. Although this method entails considerable coordination in the field, fewer samples are required to be analyzed and, as a result, it is less costly. This method also has the advantage of filtering out many variations, which is ideal for steady state models. Resource estimates for survey options are discussed further in Section 4.4.

Many WLA studies have not used two or more surveys for support. Obtaining complete and unambiguous data is more important than performing a particular number of surveys. Faced with a situation where resources are sufficient for only a single good comprehensive survey, the analyst may be better off with implementing the one survey than with splitting the resources between two abbreviated or fragmented surveys.

While the supporting site-specific data are a key element of any WLA analysis, the ability of the model to curve fit a verification data set is hardly the only measure of adequacy. Its consonance with aggregate modeling experience, the overall reasonableness of its input values, and the general understanding demonstrated by the analyst are at least as important.

Model Accuracy

The question will undoubtedly arise concerning the accuracy of the model. Without any calibration or verification data, the question for any site-specific situation may never be answered satisfactorily. With or without water quality data, however, the appropriateness of the model input values (and possibly the model formulation) may always be questioned.

Some indication of predictive reliability can be obtained by sensitivity analysis: varying, one at a time, the key model parameters, such as partition and decay coefficients, over a reasonable range. Such an analysis shows the sensitivity of the results to errors in estimating model parameters. For a more thorough evaluation, all key model parameters can be varied at the same time using either of two approaches: (a) Monte Carlo simulation and (b) first-order variance propagation. Both techniques require specifying a probability distributin of values for each input parameter of the model. In the Monte Carlo simulation, parameter values are selected randomly from the specified distributions, and the model run over and over again, each time with a different set of parameter values. The model output at each station can then be described by a frequency distribution. In first-order variance propagation, the variance in the output distribution is calculated directly from variances of the input distributions. Burges and Lettenmaier (1975) illustrate application of both techniques to BOD-DO models; Scavia et al. (1981) illustrate their application to eutrophication models. Chapra and Reckhow (1983) provide a more detailed description of these techniques.

For comparing model predictions with field observations, several measures of model accuracy have been suggested by Thomann (1982). These include regression analysis of observed and predicted values, relative error, t-test comparison of means, and root mean square error. An analysis of observed and predicted values for the calibration/

verification runs of 15 dissolved oxygen models indicated an overall median relative error of 10%. Median relative error of individual models ranged from a few percent to about 60 percent. For a eutrophication model of Lake Ontario with complex kinetics and fine spatial scales, median relative error over a 10-year simulation period for 5 variables was 22 to 32%. Relative error is defined as

$$\epsilon = \frac{\bar{x} - \bar{c}}{\bar{x}}$$

where ϵ is the relative error, x is the average observed concentration at each station, and c is the computed average concentration. This statistic, it should be noted, behaves poorly for small x, and tends to weight overprediction more heavily than underprediction.

Typical accuracies of toxicant model applications have not been evaluated. Because the aggregate experience with toxicant modeling is less extensive than with dissolved oxygen modeling, and because typical levels of almost any toxicant vary over a far wider range than do levels of dissolved oxygen, toxicant models may not always attain the accuracy of dissolved oxygen applications. However, as the effect levels for toxicants are so much more uncertain than effect levels for oxygen depression, the need for very high accuracy seems less pressing. Nevertheless, in the Flint River case study, the calibration/verification accuracy seemed quite satisfactory by conventional WLA yardsticks.

Predictive accuracy of either conventional or toxic pollutant models can be expected to be less for a new survey for which the model has not been calibrated. This is particularly true for an event with conditions outside the range of those for which the model was calibrated. Thus, predictive accuracy for conventional design events (extreme drought flows coupled with hypothetical improvements in effluent quality) may be somewhat less than the calibration/verification accuracy. In particular, it may be difficult to estimate to what degree lower stream flow and improved effluent quality will affect parameters such as the settling and

resuspension velocities (flow and particle-size dependent) or partition coefficient (also particle-size dependent). Such model adjustments must be based on analyst judgment.

In concluding this section it must be noted that an adequate discussion of approaches for evaluating model accuracy and uncertainty is beyond the scope of this volume (apparently along with the other volumes of this Manual, thus far). Chapra and Reckhow (1983), however, provide a more thorough treatment of the subject.

In actual WLA practice, the analysis of model uncertainty is seldom quantitative. It is most common to compare observation and prediction graphically, declare the model "validated," and proceed to apply the model for determining the allowable waste load. Although a sensitivity analysis may be performed on some of the input parameters, the results are unlikely to influence the decision-making process. Where the WLA is being done within an adversarial context, it is perhaps understandable that the analyst may not consider it helpful to spotlight the uncertainties. However, if the model verification is not treated as a pass/fail proposition, then quantitative estimates of model uncertainties can be more readily incorporated into the decision-making process. Once a Monte Carlo or first-order variance analysis has been set up for the model, pollution control alternatives can be evaluated in terms of their probability of bringing about particular water quality outcomes. Section 4.3 further discusses the use of Monte Carlo simulation for this purpose.

4.2.3 Additional Data

The data presented in Table 4.2 are directly applicable to setting up the model. Some additional parameter measurements may be useful for interpreting results and substantiating the actual existence and cause of the reach's use impairment. Incremental costs of this work would be small, since the major expense for the survey would be for the field crew and the chemical analyses of toxicants. The additional measurements could include:

a) Hardness and alkalinity: to interpret toxicity and determine metals criteria.

b) Conductivity: to confirm transport.

c) Total organic carbon.

d) Dissolved oxygen, ammonia, and chlorine residual: to interpret toxicity and biotic status.

e) Qualitative description of sediment bed: to support estimates of bed/water exchange.

f) Concentration of pollutant in biota: to indicate long term exposure.

Furthermore, it is preferable to coordinate the chemical sampling with a biological survey. As the numerical criteria of water quality standards are mostly derived from single-species laboratory tests, an observation that a criterion is violated for a certain time period may provide no indication of how the integrity of the ecosystem is being affected. In addition to demonstrating the impairment of use, a biological survey, coordinated with a chemical survey, can help in identifying the culprit pollutants and in substantiating the criteria values. The resulting data base may also provide information transferable to other sites. For multi-faceted surveys, it may be advantageous to try to coordinate efforts with universities, research institutions, or industries, especially if they can contribute their own resources.

4.2.4 Quality Assurance

The WLA analyst should refer to Book II, Chapter 1, Section 4.3, for a general discussion of quality assurance requirements for waste load allocation studies. This discussion will focus on the unique requirements for toxic substances.

During the development of the monitoring plan, the WLA analyst should meet with the laboratory director and quality assurance officer to

request a quality assurance proposal. The proposal should consider sample collection, handling, preservation, preparation, and analysis. Of particular concern to the WLA analyst would be the detection (quantitation) limit for each toxicant.

Some production laboratories, although very reputable, may not report concentrations at levels at or below criteria limits because doing so requires additional care and quality control, reduces the productivity in terms of numbers of analyses performed and may require alternate analytical methods. Water quality managers need to recognize this possibility and make special concessions for lower productivity during WLA comprehensive surveys.

Samples to be used for toxic substance analyses require special collection and handling procedures unlike those for conventional parameters. Depending on the specific chemical, precautions should be taken to prevent sample contamination from collection devices and containers. This is not a trivial concern.

Samples that will be filtered for particulate and dissolved fractions should be delivered to the field laboratory for filtration within the shortest period possible (one or two hours maximum for metals samples) or filtered and preserved on site. For unstable chemicals, samples should be preserved using prescribed methods.

Key to the entire effort is proper sample logging, recording of results, input of information into a computerized data based such as STORET, and verification and correction of data in the data base.

4.3 FORECASTING

The purpose for developing a site-specific model is to forecast the environmental consequences of pollution abatement alternatives. Environmental goals for a stream reach are, of course, embodied in the beneficial uses designated in its water quality standards. The water

quality needed to protect the designated uses may be specified as numerical criteria, which indicate acceptable chemical concentrations (if known). Criteria are generally derived from laboratory tests in which particular species are exposed continuously to a toxicant. As the tested concentrations do not vary over time, it is not obvious precisely how they should be related to ambient concentrations, which often vary considerably over time. It is not clear how often the criteria can be violated without impairing the use.

In actual practice, lacking a firm technical basis for specifying a target frequency of attainment, WLA analyses have often incorporated the convention of designing for the criteria to be met during the 7-day, once in 10-year (7Q10) low flow. This assumes that upstream dilution has a dominant influence on water quality, a premise which is correct for many water courses and pollutants, but not true for all. Indeed, several other time-variable parameters may also affect the modeling results; for example, temperature affects most degradative processes, pH affects acid and basic hydrolysis, wind velocity affects volatilization in sluggish waters, solar radiation and turbidity affect photolysis, and suspended solids affect partitioning. In BOD and ammonia WLAs, the other key parameters, usually temperature, upstream concentrations, and pH, have been specified by various procedures; depending on the procedure used, the values may either frequently or seldomly be expected to accompany the 7Q10 low flow.

In judging pollution control alternatives within such a framework, the measure of effectiveness generally applied is the change in concentration during the single rare event. Other measures are not easily applied because the conventional procedure generally obscures both the expected frequency of violation and the overall toxicant exposure level, due to:

a. The use of a single rare event.

b. The nature of the extreme value statistics used to generate the flow recurrence intervals.

c. The lack of consideration for the probability distributions of other environmental input parameters.

As a consequence, neither the analyst nor the decision-maker may realize what level of protection the design condition is providing. Indeed, they may not even realize that 7Q10 design conditions provide different levels of protection in different streams. For example, in a large river the upstream dilution flow may be less than or equal to the 7Q10 only 1% of the time, but in many small streams it may be at a zero flow 7Q10 for a substantial percentage of the time.

An alternative framework for model forecasting has been proposed by Freedman and Canale (1983). They suggest a conceptually simple Monte Carlo technique which can account for both the time-variability and the uncertainty in all model parameters: (a) environmental conditions, (b) effluent quality, (c) rate coefficients, and (d) water quality criteria values. By generating a probability distribution of water quality outcomes for each pollution control alternative, the framework can provide a more realistic comparison of their likely effectiveness.

The analyst begins by describing the probability distribution for each of the key model input parameters. Statistical evaluation of the historical data can define the variability of parameters such as flow, upstream concentrations, effluent loads, pH, and temperature (using daily, weekly, monthly, or any other averaging periods). Published data and analyst judgment can suggest the uncertainty of parameters such as decay and partition coefficients. The distributions can be defined in terms of standard statistical functions such as normal, log normal, gamma, or uniform distributions, or they can be numerically defined in terms of the probability of exhibiting discrete values. Correlations between parameters may need to be taken into account.

A Monte Carlo simulation can then be performed by randomly selecting model input values from the assigned distributions. By tallying the water quality predictions resulting from each set of randomly selected inputs, the overall distribution of resulting water quality is generated. A simple illustration of applying this procedure to a few of the input parameters for a model of a stream with two dischargers is shown in Figure 4.2.

Some other methods can also provide probability distributions of water quality, accounting for time variability but not necessarily parameter uncertainty. A computationally simple technique has been suggested by DiToro (1982). Using log normal distributions for flow, loading, and other environmental parameters, it generates a log normal distribution of concentration immediately below the outfall. The method was intended for dilution calculations, not downstream fate predictions.

Perhaps the most straight-forward means of addressing time variability is to apply a continuous simulation model such as HSPF or SERATRA. A several year sequence of flow, temperature, loading, and other input is used to generate a time sequence of water quality, which may be summarized into a frequency plot or possibly evaluated in other more toxicologically relevant ways. While daily records for flow are usually readily available, time sequences for other model inputs may be more difficult to construct.

Compared with the deterministic analysis of a single rare event, probabilistic and continuous simulation techniques provide a broader perspective over the entire water quality response. In comparing different control options, the measure of effectiveness can be the probability of exceeding the criteria, or it can even be the frequency coupled with the severity of violation (as illustrated by the shaded area exceeding the criteria in Figure 4.2).

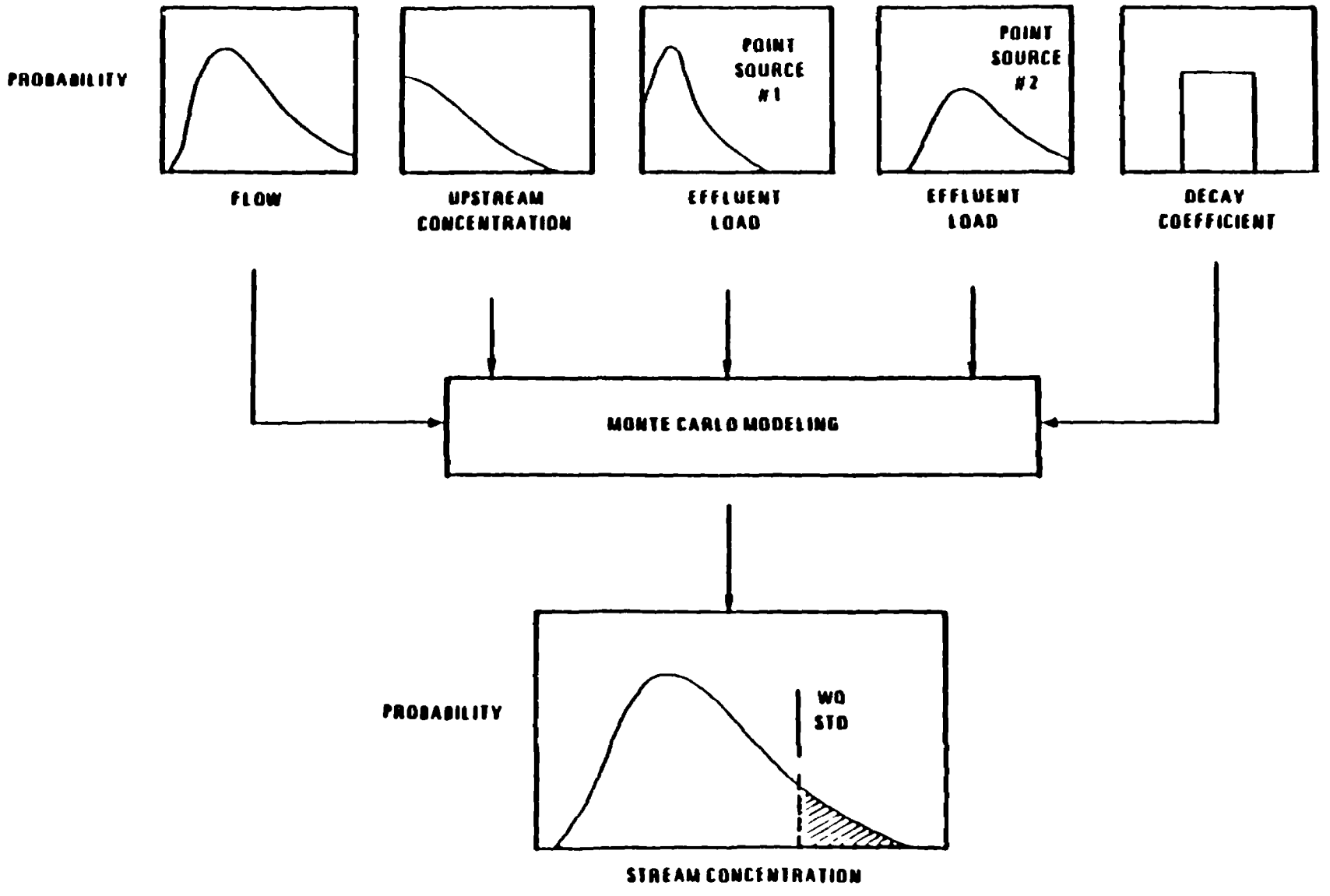


FIGURE 4.2 MONTE CARLO FORECASTING: INPUT VARIABILITY AND UNCERTAINTY GENERATES THE OUTPUT VARIABILITY AND UNCERTAINTY.

In situations where rules require that the WLA be designed for a particular flow, such as the 7Q10, the Monte Carlo technique can be applied to all input parameters except flow. Control alternatives can then be evaluated in terms of probable outcomes for that particular flow event. In situations where the analyst wishes to construct a single event corresponding to a particular recurrence interval, Book VI of the Guidance Manual (USEPA 1984) describes a method for selecting flow, temperature, and pH. The method does not consider all variable inputs and may be restricted to single discharger situations.

With the 7Q10 (or similar) design convention, a level of protection decision is made automatically, grounded more on past precedent than on technical rationale. Its level of protection, however, may vary from site to site somewhat haphazardly, unrelated to use attainment. If such a conventional design condition is not used, the level of protection may become a technical question; that is, it must be determined what frequency (or other measure) of standards attainment will protect particular uses.

For protection of human health, the decision can often be based on readily available information. Many health criteria are based on long term (possibly life-time) average exposures. If the long term mean concentration were appropriate for the criterion, and if probabilistic or continuous simulation approaches were not used, specifying a design condition that produces the mean concentration is still not necessarily a trivial task. For example, it is the harmonic (not arithmetic) mean flow that produces the arithmetic mean concentration below a single discharger (because concentration is proportional to the inverse of dilution flow).

For the protection of aquatic life the allowable exceedance frequency is a particularly difficult technical question. As the criteria are based on laboratory tests with constant rather than time-variable concentrations, and because mobility for many species is less constrained

in the field than in the laboratory, relatively little technical data can be brought to bear on the question. In the past the question of exceedance frequency has probably not received the attention it deserved. It should be recognized that the uncertainty in the entire waste load allocation analysis is a combination of the uncertainty in the target concentration, the uncertainty in the target attainment frequency, and the uncertainty in the model predictions.

4.4 RESOURCE REQUIREMENTS

In this section, estimates are presented for conducting a water quality analysis for a hypothetical river. The estimates are based on the experience of the EPA Large Lakes Research Station at Grosse Ile, Michigan, in developing and applying a toxic substance model to heavy metals in the Flint River and PCB surveys and model development for Saginaw Bay, Lake Huron.

The estimates apply to setting up a model comparable to MICHRIV, using two intensive surveys for calibration/verification. The following presents the assumptions for which the costs were estimated:

1. Two major discharges.
2. 50-mile river reach.
3. Three metals and three organic compounds.
4. Sampling points at bridges.
5. Organic substances readily photolyze according to literature.
6. All capital equipment such as laboratory, field, and computer equipment is installed and available.

The estimates apply to an experienced WLA analyst, office support, and the laboratory and field personnel. The estimates exclude standards promulgation, permit negotiation, management, and overhead.

The resource estimates are summarized in Tables 4.3 and 4.4. It is obvious that the most costly component is for the chemical analyses for surveys, particularly the synoptic-type approach for Survey No. 1. These costs could vary widely depending on unit costs, analytical procedures, quality assurance, etc. The cost for organic analyses assumes that high resolution capillary column GC's are used. Metals are assumed to be analyzed using graphite furnace atomic adsorption.

There may be instances where the system is extremely complex, with nonpoint sources, complicated hydraulics, multiple and intermittent discharges, and multiple pollutants that would warrant surveys over a year's time frame including event sampling covering a range of conditions. In these cases, if the costs of the surveys are compared to the potential cost of remedial controls, they should be minor. In many situations, the regulatory agency may suggest or require that the permittee assist with the collection of the necessary data.

In summary, a waste load allocation project may vary from very simple to very complex. The resources estimates presented herein consider a typical problem setting. In the final analysis, the use of surveys and models depends on the site and chemical-specific problem.

TABLE 4.3 RESOURCE ESTIMATES FOR WASTE LOAD ALLOCATION ANALYSES[2]
(See Text and Table 4.3A for Assumptions and Related Costs)

Task[1]	WLA-Analysts Man-Days	Office Support Personnel Man-Days	Laboratory Personnel Man-Days	Field Personnel Man-Days	Computer[3] Costs ($)	Estimated[4] Man-Power Costs
PHASE 1						
Review Permit Application	0.3	0	0	0		
Retrieve Basic Basin Data	0.1	0.4	0	0	$ 50	
Summarize Input Data	0.5	0	0	0		
Review Stream Flow Data	0.5	0	0	0		
Calculate Dilution	0.3	0	0	0		
Prepare Decision Memo	0.3	0.1	0	0		
Total Phase 1	2.0	0.5	0	0	$ 50	$ 360
PHASE 2 (Assumes Phase 1 Completed)						
Retrieve and Compile Historical Data	1.0	2.0	0	0	$200	
Estimate Model Inputs	2.0	0.0	0	0		
Conduct Model Calculation and Sensitivity Analysis	2.0	0.0	0	0		
Prepare Decision Report	2.0	2.0	0	0		
Follow-Up Discussions, Presentation, etc.	2.0	1.5	0	0		
Total Phase 2	9.0	5.5	0	0	$200	$ 1000

TABLE 4.3 RESOURCE ESTIMATES FOR WASTE LOAD ALLOCATION ANALYSES[2] (Continued)
(See Text and Table 4.3A for Assumptions and Related Costs)

Task[1]	WLA-Analysts Man-Days	Office Support Personnel Man-Days	Laboratory Personnel Man-Days	Field Personnel Man-Days	Computer[3] Costs ($)	Estimated[4] Man-Power Costs
PHASE 3 (Assumes Phase 2 Completed)						
Design Monitoring Plan	5	1	3	2		$ 1400
Survey 1 (See Table 4.4)	5	2	1040	120	$100	$135360
Calibrate Model	10	10	-	-		$ 2400
Survey 2 (See Table 4.4)	5	2	186	12	$100	$ 29040
Verify Model	13	5				$ 2000
Monte Carlo Foreca ' ng	12				$400	$ 1920
Report	10	5			$200	$ 2480
Follow-Up	5					$ 800
Total Phase 3	65	25	1229	194	$800	$175,400
GRAND TOTAL	76	31	1229	194	$1050	$177,800

[1]See text for description of analysis phases and model levels.
[2]Not including initial capital expenditures for equipment, labs, vehicles, etc., or travel costs (no overhead).
[3]Time sharing for data retrievals - In-house computer for model calculations (no capital cost reported).
[4]Salaries including benefits, excluding overhead: Analyst $160/day; Support - $80/day; Lab - $120/day; Field - $80/day.

TABLE 4.4 RESOURCE ESTIMATES FOR MONITORING RESOURCES (MAN DAYS)

	No. Stations	No. Days	Frequency	No. Samples	Laboratory Man-Days: Metals 1 Total	Metals 1 Dis.	Organics 2 Total	Organics 2 Dis.	Misc. Analyses	Man Days Field
Survey 1 - 7 Days										
Monitoring - Water										
Master Stations	3	3	6/day	54	31	31	135	135	7	21
Regular	3	7	1/day	21	12	12	53	53	3	1
Effluents	2	7	1 Comp/day	14	8	8	35	35	2	7
	2	3	6/day	36	21	21	90	90	5	
Hydrology										
River Flow (2 persons)		2								4
Effluent Flow (1 person)		7								1
Time of Passage (8 Persons)		5								40
Sediment Related										
Sediment Samples (2 Persons - Sed. Sampling/Mapping/Characterization)	6	1	1/wk @ 4 depths	24	16	-	60	-	20	14
Process Related										
Photolysis Experiments	3	3	1/day	9	-	-	22.5			
(Dark-Light Bottles)										7
Sunlight Measurements (UV)										7
Bacteriological (Biolysis)										6
(Bottle-Sterile vs. Non-Sterile)	3	3	1/day	9			22.5			
Volatilization Experiments	3	3								6
TOTALS (Man-Days) Total Lab - 1038	Total Field - 120				76	72	418	313	37	126

TABLE 4.4 (Cont'd.)

	No. Stations	No. Days	Frequency	No. Samples	Laboratory Man-Days: Metals 1 Total	Metals 1 Dis.	Organics 2 Total	Organics 2 Dis.	Misc. Analyses	Man Day Fie
Survey 2 - 3 Days										
Monitoring (3 days x 2 persons/shift x 3 shifts/day)	6		3/survey	18	10	10	45	45	3	27
Effluents	2		3/survey	6	4	4	15	15	1	9
Dye Trace (3 days-9 persons/day 3 shifts)										27
Sediment	6		1	6	4	4	15	15	5	6
Process (Sunlight)										3
TOTALS (Man-Days)	Total Lab - 186		Total Field - 72		18	18	75	75	9	72

0.58 Man-Days/Sample - Including analysis, data mangement, miscellaneous.
20 Man-Hrs/Sample (2.5 Man-Days) (1 Man-Day = 8 hrs.).

SECTION 5.0

CASE STUDY: MODELING HEAVY METALS TRANSPORT IN THE FLINT RIVER

5.1 INTRODUCTION

The Flint River project, discussed in this section, was undertaken as a demonstration study for the development of procedures that can be used in regulating point source discharges of priority pollutants. The results of the one year study have served as a technical basis for the preparation of this document. Specifically, the field data aided considerably in the development of the MICHRIV model. This section contains the results of application of the MICHRIV model to the Flint River survey of zinc, cadmium, and copper. The emphasis will be on the calibration and, to a certain extent, the field testing of the model with the Flint data set. The project also serves as an example of data acquisition methods for the application of the model to a WLA problem.

Section 5.2 describes the study reach of the Flint River. Sections 5.3, 5.4, and 5.5 describe the application of the model to the August, 1981, the December, 1981, and the March, 1982, survey data.

5.2 DESCRIPTION OF FLINT RIVER STUDY SITE

The Flint River, located in Southeastern Michigan, is a major tributary to the Saginaw River, a major tributary to Saginaw Bay. The Saginaw watershed had been identified as one of several national priority sites. The Flint River is also considered a high priority site for development of toxicant WLA procedures by the Michigan Department of Natural Resources (MDNR).

The Flint River watershed occupies 3,500 square kilometers (Figure 5.2.1) and contains significant agricultural and urban development. The north and south branches of the river join in Lapeer County and flow in a

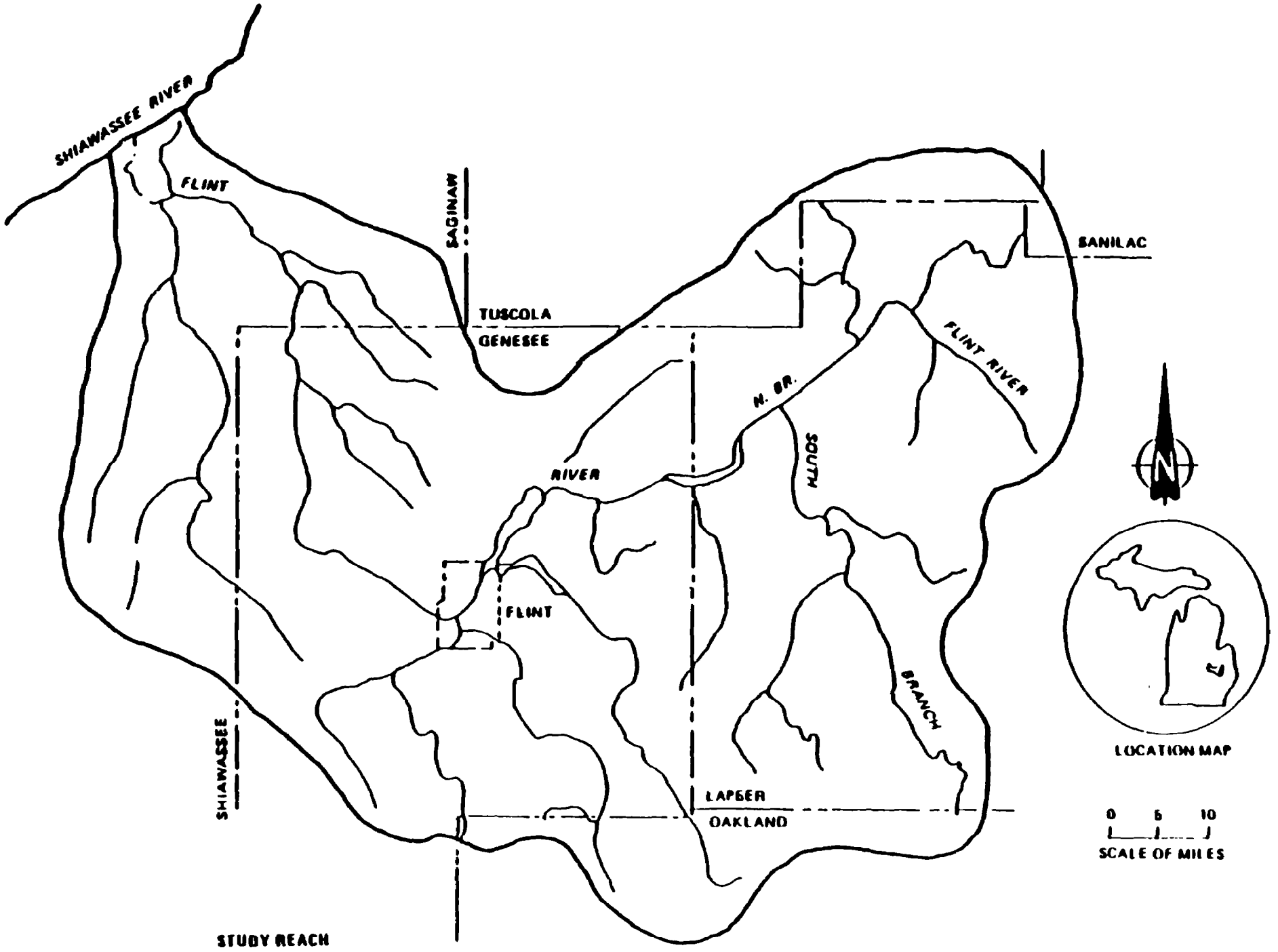


FIGURE 5.2. FLINT RIVER BASIN

southwesterly direction to the City of Flint. Within this reach are two impoundments, Holloway Reservoir and Mott Lake, which are used for recreation and occasionally for low flow augmentation in the summer months. Downstream from the City of Flint, the river flows northwest before joining the Shiawassee River in Saginaw County. Municipalities downstream of Flint include Flushing, Montrose, and Fosters.

Because the purpose of this project was to study a river system in enough detail to develop a metals transport model, and because there were insufficient resources to quantify all sources to the river in the city of Flint, the reach selected for the model application was the 60 kilometers from Mill Road (Km 71.9) to Cresswell Road (Km 11.0). This reach, shown in Figure 5.2.2, contains two major point discharges of metals - Flint wastewater treatment plant (Km 70.7) and Genesee Co. No. 2 (Ragnone) wastewater treatment plant (Km 41.1). Several tributaries, also monitored, join the river along the study reach.

5.3 FLINT RIVER AUGUST SURVEY

The Flint River August Survey, conducted during August 4-14, 1981, was intended to develop a quantitative cause-effect relationship between metals loadings and resulting concentrations during summer, low flow conditions. Thirteen river stations, four tributary streams, and five point source discharges were sampled during the two week survey. A list of the stations, their distance from the river mouth in kilometers and the sampling schedule for each station are presented in Table 5.3.1. The August survey is an example of a routine monitoring schedule. Most river stations were sampled daily; however, four "master" stations were sampled at more frequent intervals as a check on diurnal variations.

Temperature, dissolved oxygen, pH, alkalinity, and conductivity were measured in the field. Samples were also filtered and preserved in the

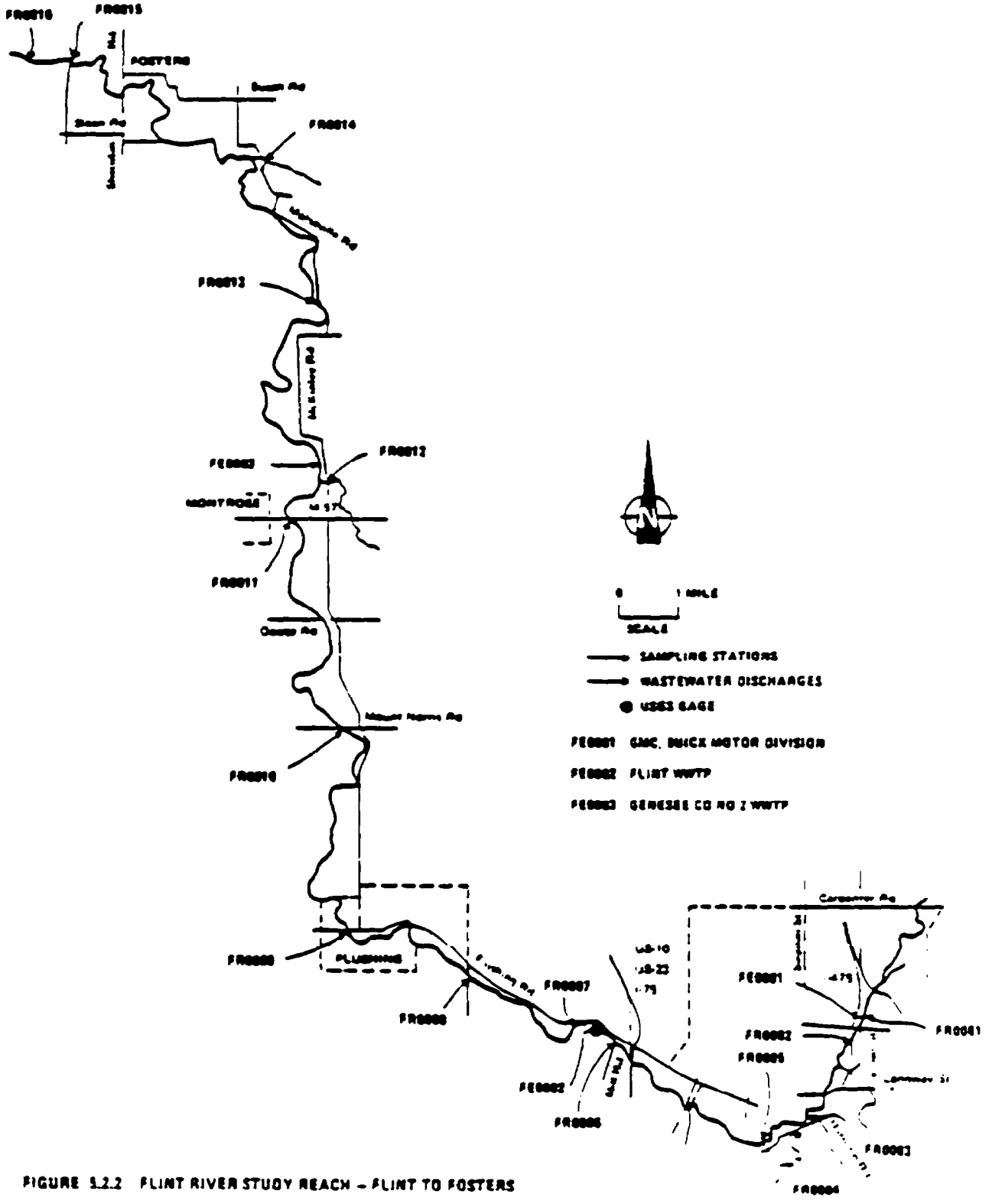


FIGURE 5.2.2 FLINT RIVER STUDY REACH - FLINT TO FOSTERS

TABLE 5.3.1 SAMPLING STATIONS FOR AUGUST, 1981 FLINT RIVER HEAVY METALS SURVEY

Station/Description	Km. Point	Sampling Schedule
FR0001/Utah Street river station	83.6	Grab - every 24 hours
FE0001/GM Plant discharge	83.4	24 hour composite
FR0002/Hamilton Street river station	81.9	Grab - every 24 hours
FR0003/Grand Traverse Street river station	79.3	Grab - every 24 hours
FR0004/Swartz Creek tributary	79.1	Grab - every 24 hours
FR0005/Chevrolet Street river station	77.9	Grab - every 24 hours
FR0006/Mill Road river station	71.9	Grab - every 24 hours
FE0002/Flint WWTP discharge	70.7	24 hour composite
FR0007/Linden Road river station	70.5	Grab - every 24 hours
FE00A1/Flint fly ash pond discharge	70.0	Single grab
FE00A2/Flint fly ash pond discharge	70.0	Single grab
FR0008/Elms Road river station	66.3	Grab - every 24 hours
FR0009/Main Street river station	61.2	Grab - every 24 hours
FR0010/Mt. Morris Road river station	52.6	Grab - every 24 hours
FR0011/Vienna Road river station	43.5	Grab - every 24 hours
FR0012/Brent Run tributary	41.6	Grab - every 24 hours
FE0003/Ragnone WWTP discharge	41.1	24 hour composite
FR0013/East Burt Road river station	32.1	Grab - every 24 hours
FR0017/Pine Run tributary	29.7	Grab - every 24 hours
FR0014/Silver Creek tributary	25.2	Grab - every 24 hours
FR0015/M-13 river station	14.9	Grab - every 24 hours
FR0016/Cresswell Road river station	11.0	Grab - every 24 hours

field. Hardness, suspended solids and total and filtrable zinc, cadmium and copper were analyzed at the Grosse Ile Laboratory. Field sampling and analytical work was the responsibility of Cranbrook Institute of Science. The USGS, Lansing Office participated in the field work and provided flow and time-of-travel information (Cummings and Miller 1981).

5.3.1 August Survey Data Summary

During the survey a precipitation event interrupted the steady-state conditions that existed for the first four days of the survey. The hydrographs from the USGS gaging stations near Flint and Fosters (Figure 5.3.1) illustrate the event. The water quality in the river responded predictably to the event, as illustrated by the hydrograph and various time profiles at Station FR08 (Figure 5.3.2). Suspended solids and particulate metals (as reflected in the total metals peaks with no change in dissolved phase concentrations) peaked in response to the flow event. As discussed later this phenomenon represented resuspension of sediments from the river bottom caused by higher shear stress. Also, dissolved constituents not particularly associated with sediment material were diluted by the increased flow. This process is illustrated by the conductivity and hardness profile.

Although the event phenomena are quite interesting, the model applied is steady-state. Consequently, the modeling described here is restricted to the first four days of the August survey. Observations at each station will be reported as four-day means plus or minus one standard deviation.

The necessary input data for the model include basic hydrological and morphological information on the river and loads of suspended solids and total metals to the system. Table 5.3.2 is a summary of the flows and river geometry from the Mill Road station (FR06) to the Cresswell Road station (FR16) for the four day steady-state, low-flow period in August. These values have been established primarily from measurements made by USGS (Cummings and Miller 1981) during the August survey.

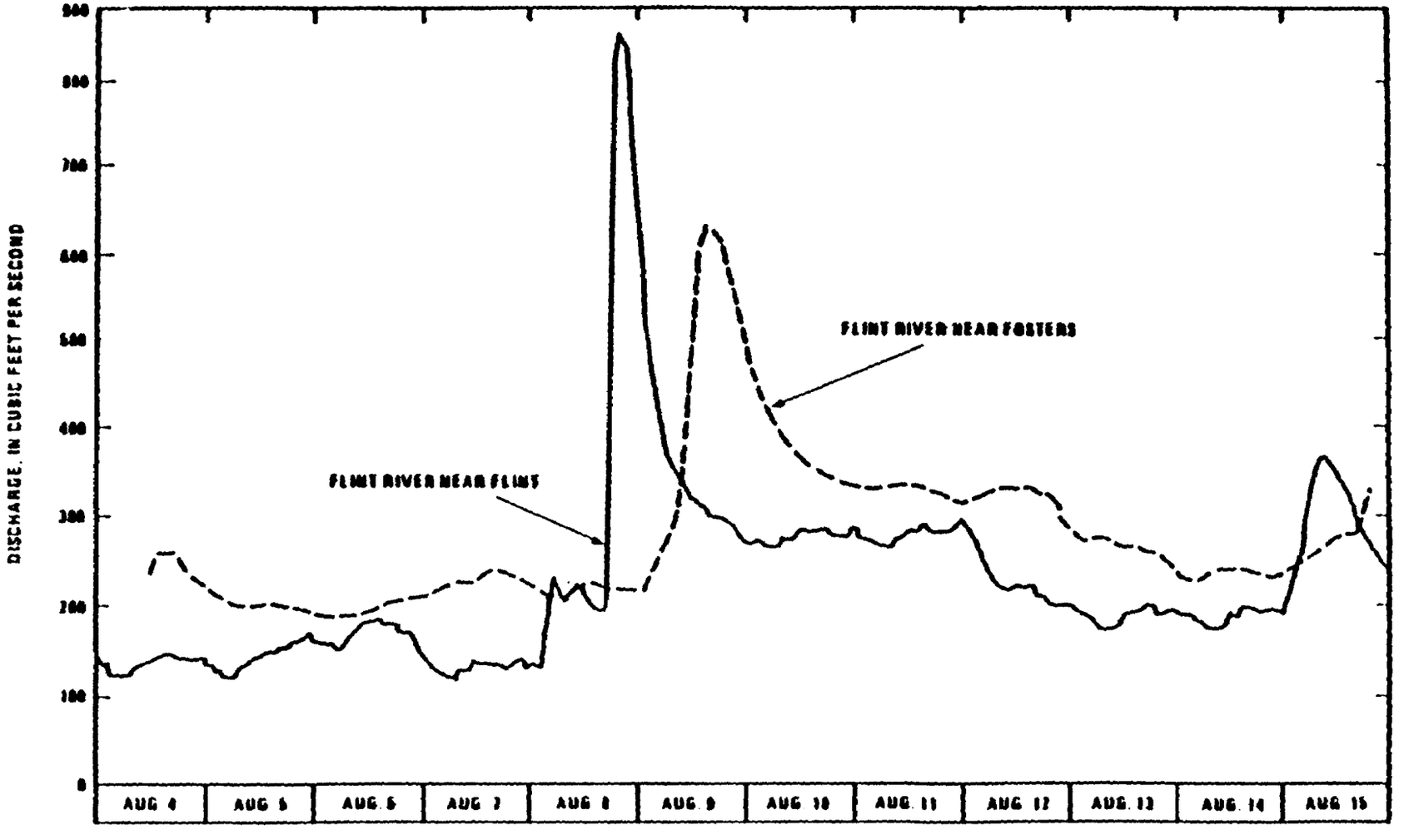


FIGURE 5 3 1 HYDROGRAPHS OF THE FLINT RIVER NEAR FLINT AND NEAR FOSTERS, AUGUST 4 - 15, 1981

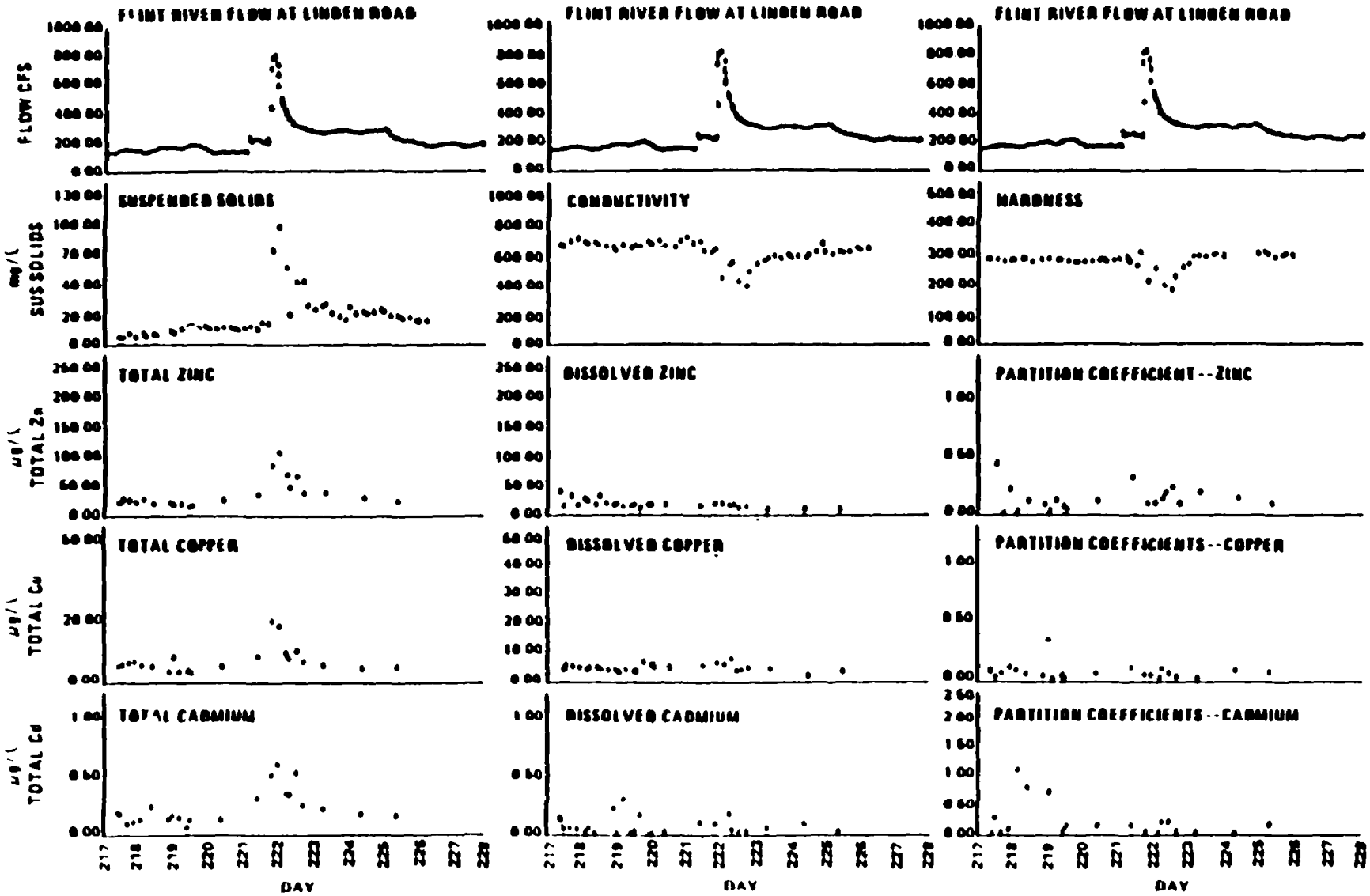


FIGURE 5 32 FLINT RIVER WASTE LOAD ALLOCATION SURVEY

TABLE 5.3.2 SEGMENTATION, FLOWS, AND GEOMETRY FOR FLINT RIVER DURING AUGUST 4-7, 1981

Segment No.	Boundary	Km. Point	Segment Flow (m^3/s)	Cross-Sectional Area (m^2)	Mean Depth (m)
	Mill Road	71.9			
1			2.66	14.5	0.45
	Flint WWTP	70.7			
2			4.34	20.5	0.64
	Flint fly ash ponds	70.0			
3			4.38	17.8	0.47
	Downstream of Elms Road	65.0			
4			4.38	15.7	0.34
	Brent Run	41.6			
5			4.53	22.8	0.47
	Ragnone WWTP	41.1			
6			5.22	24.5	0.64
	Upstream of E. Burt Road	36.0			
7			5.22	19.5	0.56
	Pine Run	29.7			
8			5.28	17.5	0.56
	Silver Creek	25.2			
9			5.36	17.8	0.70
	Cresswell Road	11.0			

For this model application the river reach from Mill Road to Cresswell has been divided into 9 segments. The segmentation was primarily governed by location of point sources and tributaries, although changes in river geometry also contributed to segment boundary selections. The segmentation is also presented in Table 5.3.2, where flows and geometry are given by segment.

The upstream boundary conditions and the effluent and tributary loads for the steady-state period are presented in Table 5.3.3. The two municipal plants represent the major source of metals to the river. Only total metal loads are reported, because equilibrium partitioning with solids is assumed. It should be noted, however, that in reality the metals discharged from the Flint plant were primarily in the dissolved phase while those from the Ragnone plant were primarily in the particulate phase. This information will be discussed further in the model calibration section.

5.3.2 August Survey Model Calibration

The model calibration was performed in two stages. First, the suspended solids simulation was calibrated to the existing data. This could be done independently of the metals calibration since the solids submodel does not depend on metals interactions or transport. The second stage consisted of calibrating the three metal predictions without altering the suspended solids calibration.

Given the input data presented in the previous section, the only parameters at one's disposal for calibrating the suspended solids submodel are suspended solids settling rate (w_s), solids resuspension rate (w_{rs}), and solids concentration in the bed (m_2). Since the solids entrainment rate or resuspension flux (g/m^2-d) is the product of w_{rs} and m_2, an extra degree of freedom exists in the model framework. This degree of freedom was eliminated by fixing the bed solids concentration based on d r:cl measurements.

TABLE 5.3.3. INITIAL CONDITIONS AND POINT SOURCES TO FLINT RIVER - MEAN LOADS FOR AUGUST 4-7, 1981

Source	Discharge Flow (m^3/s)	Discharge Concentration and Load							
		Suspended Solids		Total Zinc		Total Cadmium		Total Copper	
		(mg/ℓ)	(kg/d)	(μg/ℓ)	(gm/d)	(μg/ℓ)	(gm/d)	(μg/ℓ)	(gm/d)
Initial Boundary-Mill Road	2.66	13.5	3100.	7.7	1780.	0.067	15.5	2.9	672.
Flint WWTP	1.68	4.1	600.	55.	8000.	0.16	24.	8.3	1200.
Flint Fly Ash Ponds	0.04	39.5	150.	63.	240.	1.32	5.0	80.	304.
Brent Run	0.15	5.9	77.	3.8	49.	0.11	1.46	3.8	48.9
Ragnone WWTP	0.69	58.7	3500.	84.	5000.	5.4	32.2	28.5	1700.
Pine Run	0.06	7.0	33.	5.0	24.	0.04	0.18	3.8	18.5
Silver Creek	0.085	6.8	50.0	5.0	37.	0.04	0.27	3.8	28.1

The typical river bottom will have a water content between 60 and 95% by weight; therefore, if the solids have a specific gravity of 2.5, the solids concentration in the bed will vary from approximately 50,000 - 500,000 mg/ℓ of bulk sediment. Based on some bottom sampling conducted during the August survey, a value of m_2 = 200,000 mg/ℓ was selected for the river reach.

Since the August survey was during a relatively low flow period, the first solids calibration attempt was made assuming the resuspension rate (w_{rs}) was equal to zero. Furthermore, since there was no reason to suspect that the settling rate would vary along the river, a single value of w_s was used in all segments. It is possible that the solids settling rate would be a function of flow in the river; however, the flow differences along the river were not considered to be significant enough to justify segment-to-segment variation of w_s. The calibration with w_s = 0.25 m/d is shown in Figure 5.3.3a.

The calibration in Figure 5.3.3a is quite good until just downstream of the Ragnone treatment plant (about Km pnt. 35). From this point downstream it seems that the model underpredicts suspended solids. One possible explanation is that resuspension was occurring in the lower portion of the river. By applying a very small entrainment rate of 4.0 g/m^2-d in segment 7-9 (Km 36.0 11.0) on top of the settling rate of 0.25 m/d throughout the reach, the calibration shown in Figure 5.3.3b was obtained. The above entrainment rate corresponds to a resuspension velocity of 2.0×10^{-5} m/day.

Justification for applying a resuspension factor in segment 7-9 comes from a review of the experimental work of Lick (Lee et al. 1981; Fukuda and Lick 1980) and from a comparison of calculated bottom shear stresses among segments of the river. Lee et al. (1981) list five factors on which resuspension depends: (1) turbulent shear stress at the sediment-water interface; (2) water content of bottom sediments;

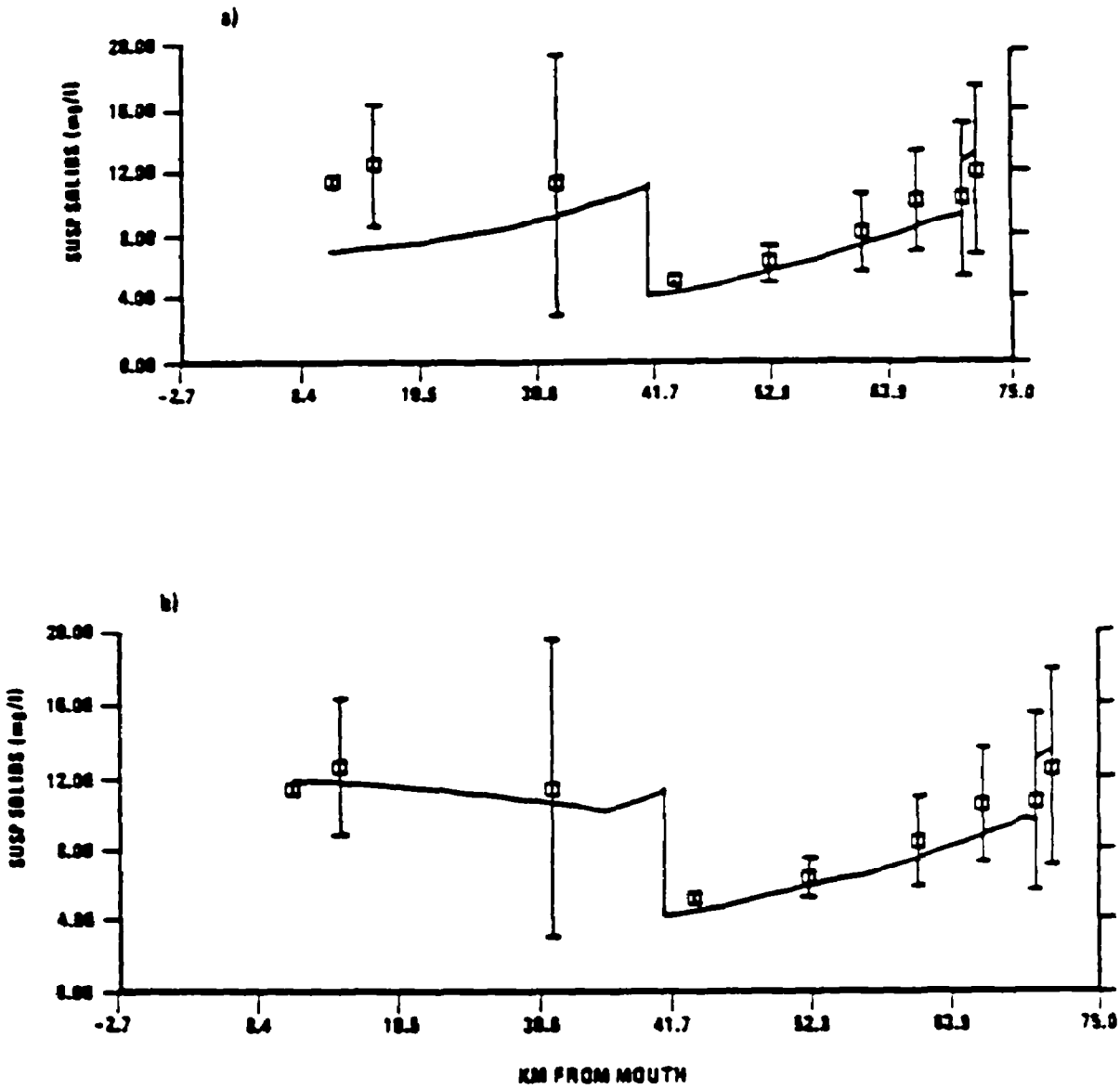


FIGURE 5.3.3 a & b

(3) composition (mineralogy, organic content, size distribution) of sediments; (4) activity of benthic organisms; and (5) vertical distribution of sediment properties, i.e., manner of deposition.

The effects of the first two factors are qualitatively understood. Lee et al. (1981) found that for the western basin of Lake Erie, bottom sediment resuspension rates were directly proportional to shear stress and water content. Sediments with a fine-grained (clay size) fraction deposited at the surface were more easily erodable than vertically well-mixed sediments with the same composition. These considerations suggest that resuspension in a particular river may be predicted from an empirical relationship between entrainment rate and shear stress.

In the case of the Flint River the best justification for increasing the resuspension velocity below Km 36 comes from comparing the bottom shear stress among various river segments, using Equation 3.6 (Graf 1971). For the August steady-state conditions, bottom shear stress values for several segments of the Flint River are presented in Table 5.3.4. Although the absolute values of shear stress are only estimates, the relative differences should be valid because of the consistent method of calculation. Note that the three downstream segments have greater shear values than the four upstream segments. There is typically a threshold value of shear for a given sediment condition above which entrainment rate increases rapidly. It is possible that for the Flint system the threshold value is in the neighborhood of 10 dynes/cm^2.

It should be noted, nevertheless, that resuspension is not the only possible explanation for increasing suspended solids profiles in rivers. Growth of phytoplankton biomasss can also produce this phenomenon, with each additional 5 µg/ℓ chlorophyll-a equivalent to 1 mg/ℓ suspended solids (Canale 1983). Unlike resuspension, phytoplankton growth should increase suspended solids concentrations without increasing total metals concentrations. While both interpretations seem compatable with the

TABLE 5.3.4. BOTTOM SHEAR STRESS IN SEGMENTS OF FLINT RIVER DURING AUGUST 1981 STEADY-STATE PERIOD

Segment	Segment Boundaries (Km. Points)	Shear Stress (dynes/cm_2)
1	71.9 - 70.7	3.91
3	70.0 - 65.9	6.92
4	65.0 - 41.6	9.87
6	41.1 - 36.0	4.70
7	36.0 - 29.7	10.54
8	29.7 - 25.2	13.4
9	25.2 - 11.0	12.5

August survey data, resuspension would be a more viable explanation during the winter surveys (described later). For the Flint River the model's overall results are not particularly sensitive to the question, however.

Once the suspended solids submodel was calibrated, only the metal partition coefficients were used to calibrate the metals predictions. Sediment-water diffusion of dissolved metals was considered to be insignificant.

Calibration of the metals system began with observed partition coefficients and adjusted these values within reason in order to match total and dissolved metal profiles. There are so many factors that can affect metals partitioning that insufficient information is available in this case for a priori establishment of partition coefficients. Plots of the observed partition coefficients for the three metals in question during the modeling period are presented in Figure 5.3.4. These field data indicate that the partition coefficient for zinc should fall between 0.1 and 0.3 ℓ/mg. There is a great deal of variation in observed cadmium partitioning; this variation, between about 0.05 and 0.45 ℓ/mg, is probably due to dissolved cadmium values being near the detectable limit. Finally, copper demonstrated the lowest partitioning with a range of approximately 0.02 - 0.10 ℓ/mg.

It is worthy of note that for all three metals the Linden Road samples, which are from a site just downstream from the Flint STP discharge, tended to have lower partition coefficients than the downstream sites. One possible explanation is that the Flint discharge contained metals primarily in a dissolved (filterable) state and that an equilibrium partitioning had not been attained in the first few kilometers downstream. The metals in the Flint discharge averaged 91%, 84%, and 75% dissolved phase for zinc, cadmium, and copper, respectively. As the MICHRIV model does not consider adsorption

COPPER
P(Cu) (L/mg)
CADMIUM
P(Cd) (L/mg)
ZINC
P(Zn) (L/mg)
CRESSWELL RD
M-13
EAST BURT RD
VIENNA RD
MT MORRIS RD
MAIN ST
ELMS RD
LINDEN RD
MILL RD
CHEVROLET ST
TRAVERSE ST
HAMILTON ST
UTAH ST
4-AUG-81 - 7-AUG-81
(L/mg)

FIGURE 5.3.4

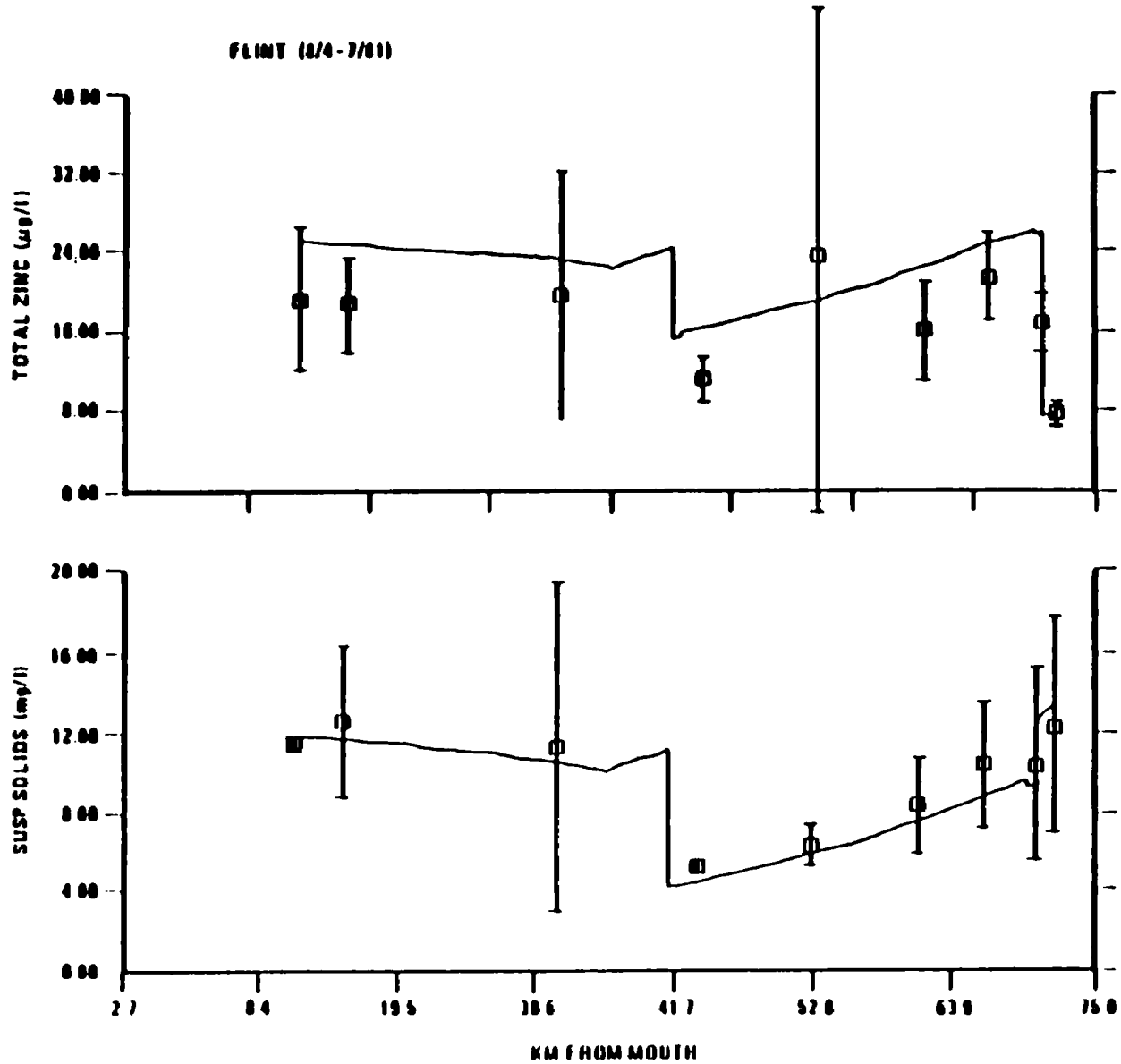

FLINT (8/4-7/81)
TOTAL ZINC (µg/l)
40.00
32.00
24.00
16.00
8.00
0.00
SUSP SOLIDS (mg/l)
20.00
16.00
12.00
8.00
4.00
0.00
2.7
8.4
19.5
30.6
41.7
52.8
63.9
75.0
KM FROM MOUTH

FIGURE 5.3.5

kinetics, the way to handle this phenomenon was to lower the partition coefficient for approximately four kilometers downstream of the Flint discharge.

The results of the model calibration for the three metals are presented in Figures 5.3.5-5.3.10. Table 5.3.5 summarizes the partition coefficients used for calibration. Recall that once the solids model had been calibrated, metals partitioning was the only remaining calibration parameter for the metals. For all three metals the lower partition coefficients in segments 2 and 3 downstream of the Flint discharge are necessary to simulate the higher proportion of dissolved metals in this region. Also, an increased partition coefficient for copper downstream of the Ragnone discharge was employed in the calibration. This was justified by the observed data (Figure 5.3.4) as well as the fact that an average of 83% of the Ragnone copper discharge was in a particulate phase.

It is encouraging to note that the relative magnitude of calibration partition coefficients among the three metals for the August 1981 Flint study is the same as was found in a Saginaw Bay modeling effort (Dolan and Bierman 1982). Even the absolute calibration values were quite similar. The calibration values for Saginaw Bay were 0.225, 0.145, and 0.05 L/mg for zinc, cadmium, and copper, respectively. The Flint River ultimately flows into Saginaw Bay via the Shiawassee and Saginaw Rivers.

5.3.3 August Survey Sensitivity Analysis

As indicated above, the main calibration coefficients for metals in the Flint River are the suspended solids settling (w_s) and resuspension (w_{rs}) rates and the partition coefficients for the respective metals. A sensitivity analysis on these model parameters would be instructive in determining the accuracy necessary in defining these parameters for a given model prediction accuracy. It would also confirm the need for the respective terms in the model framework.

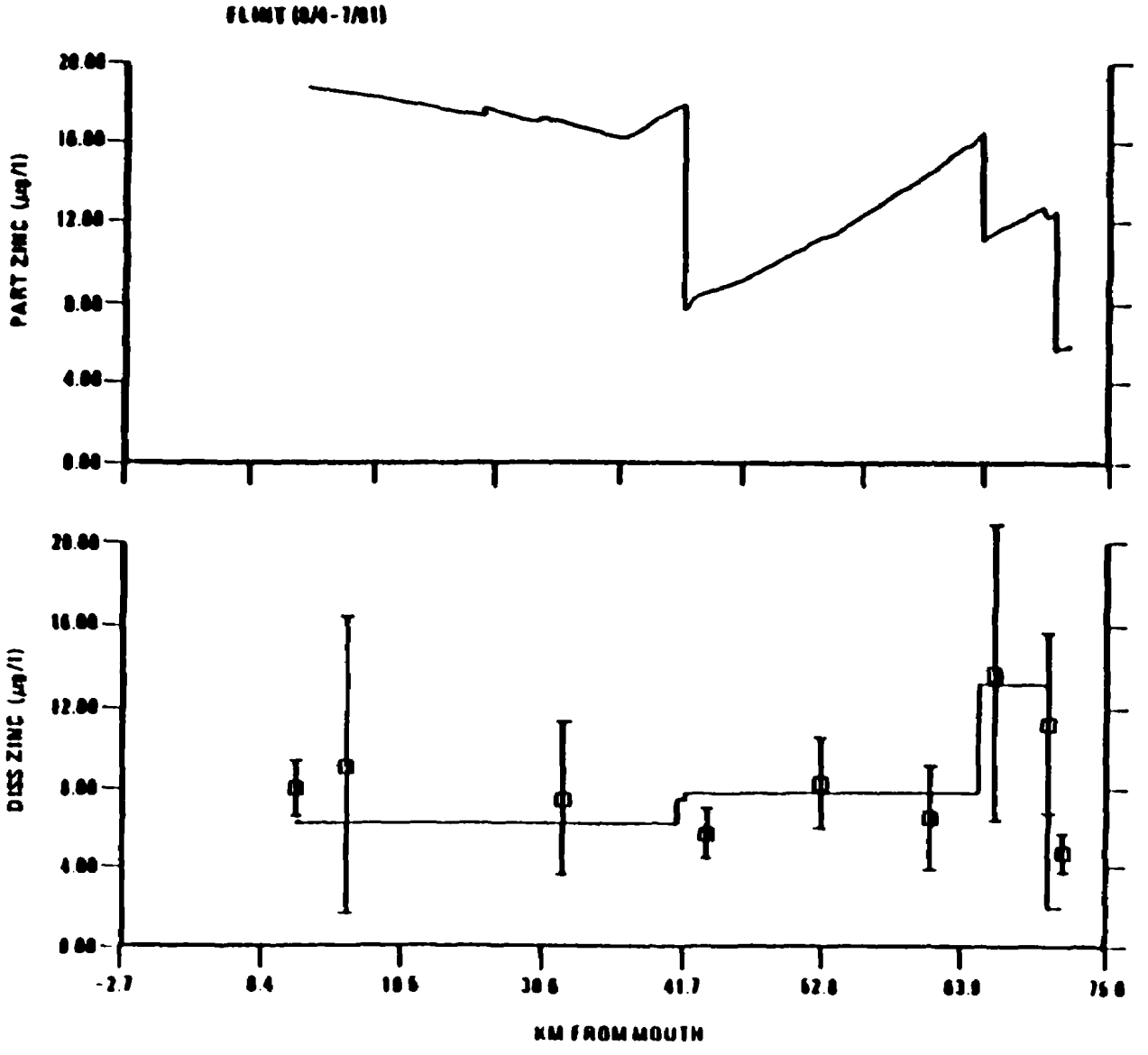

FLINT (8/4-7/81)
PART ZINC (µg/l)
20.00
16.00
12.00
8.00
4.00
0.00
DISS ZINC (µg/l)
20.00
16.00
12.00
8.00
4.00
0.00
-2.7
8.4
19.5
30.6
41.7
52.8
63.9
75.0
KM FROM MOUTH

FIGURE 5.36

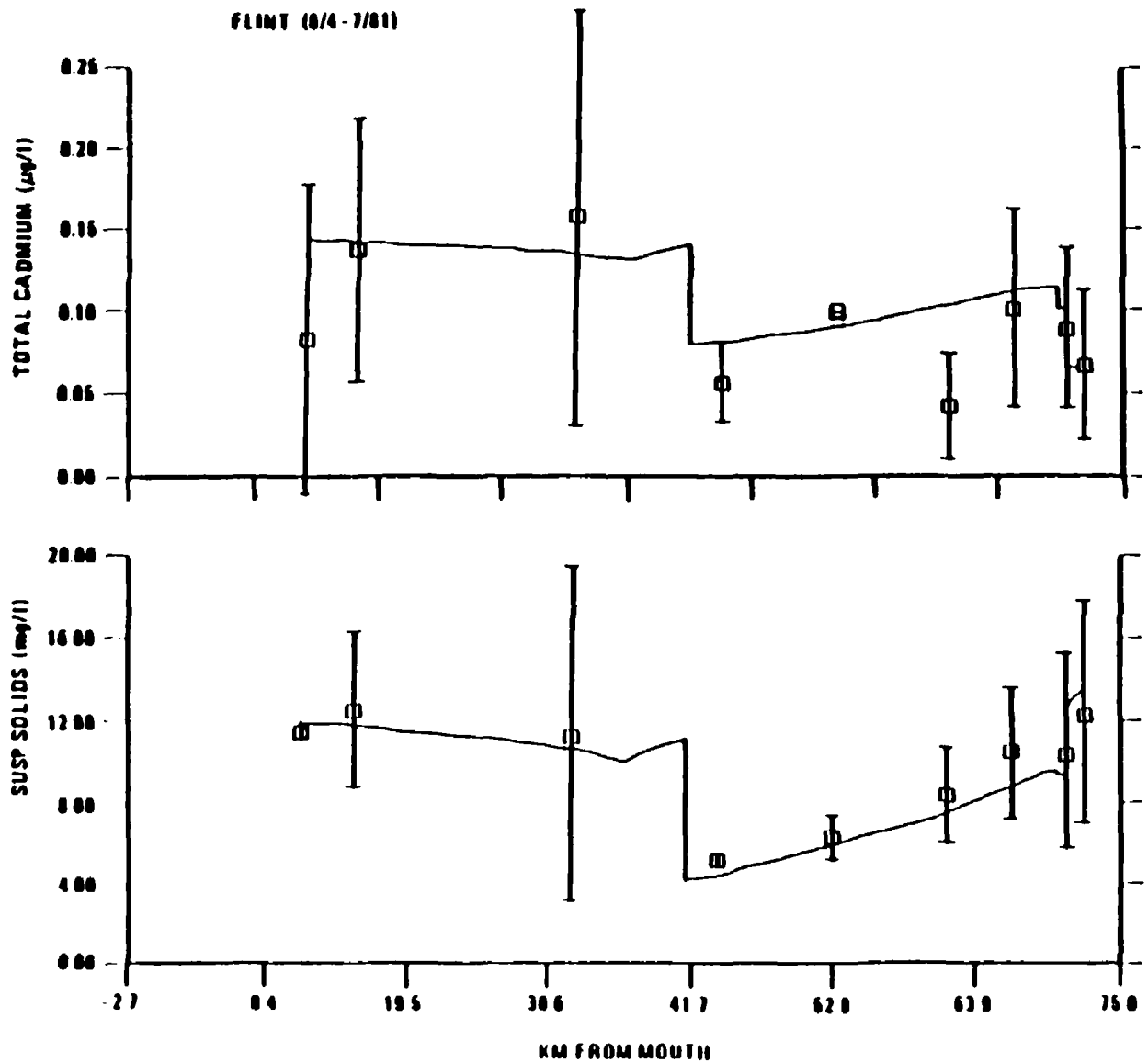

FLINT (8/4-7/81)
TOTAL CADMIUM (µg/l)
0.25
0.20
0.15
0.10
0.05
0.00
SUSP SOLIDS (mg/l)
20.00
16.00
12.00
8.00
4.00
0.00
-2.7
8.4
19.5
30.6
41.7
52.8
63.9
75.0
KM FROM MOUTH

FIGURE 5.3.7

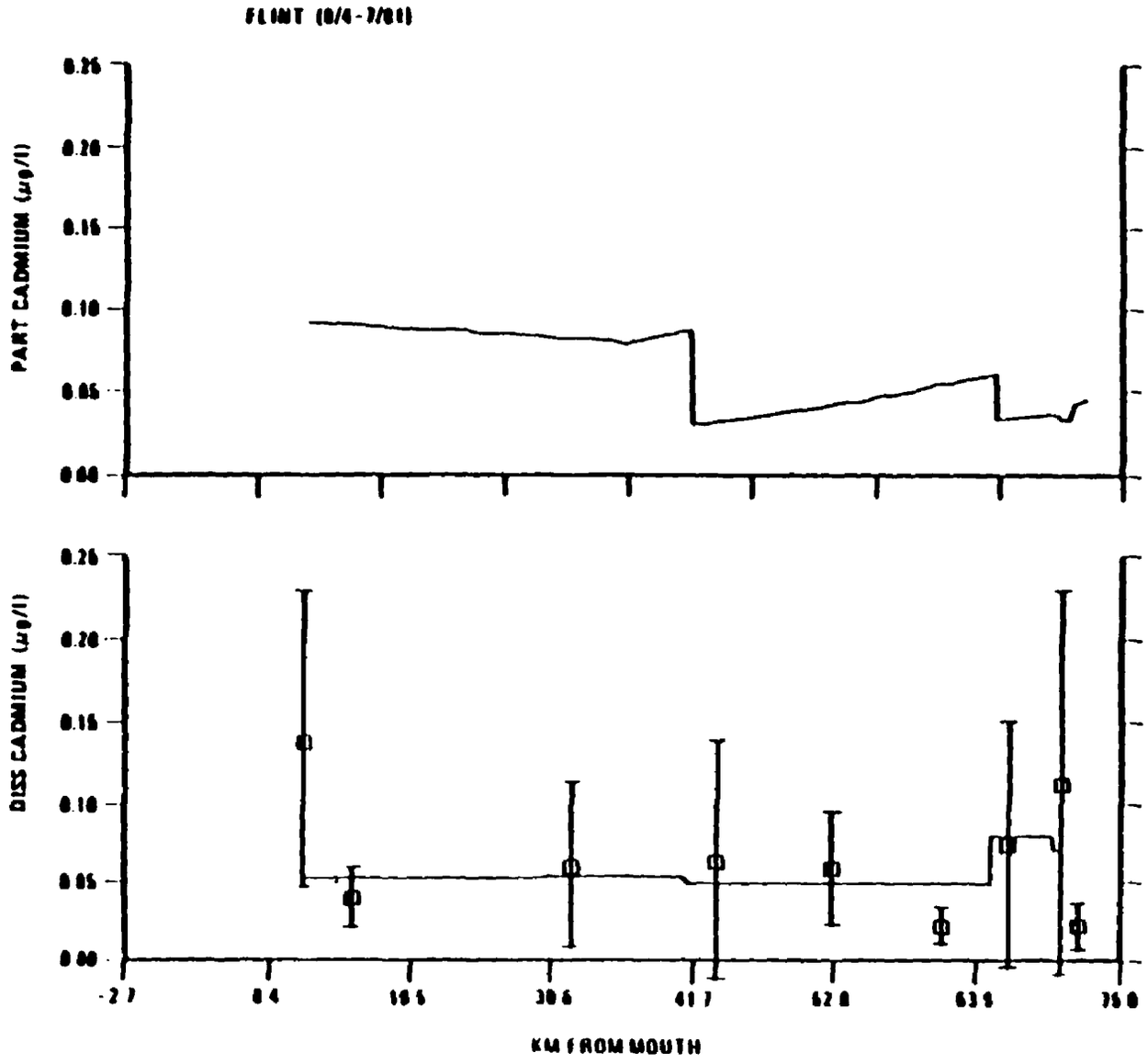

FLINT (8/4-7/81)
PART CADMIUM (µg/l)
DISS CADMIUM (µg/l)
0.25
0.20
0.15
0.10
0.05
0.00
-2.7
8.4
19.5
30.6
41.7
52.8
63.9
75.0
KM FROM MOUTH

FIGURE 5.3.8

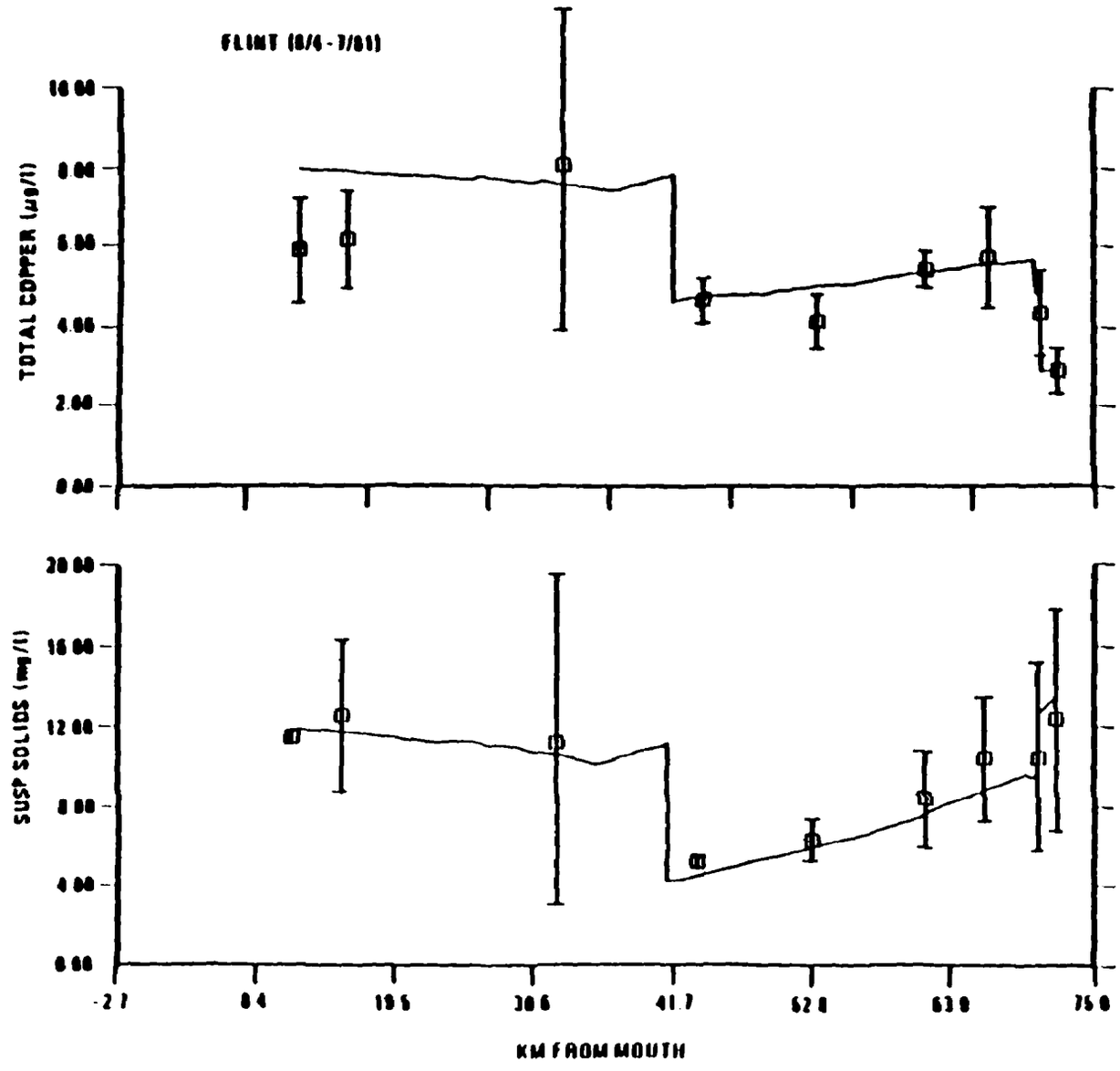


FIGURE 5 39

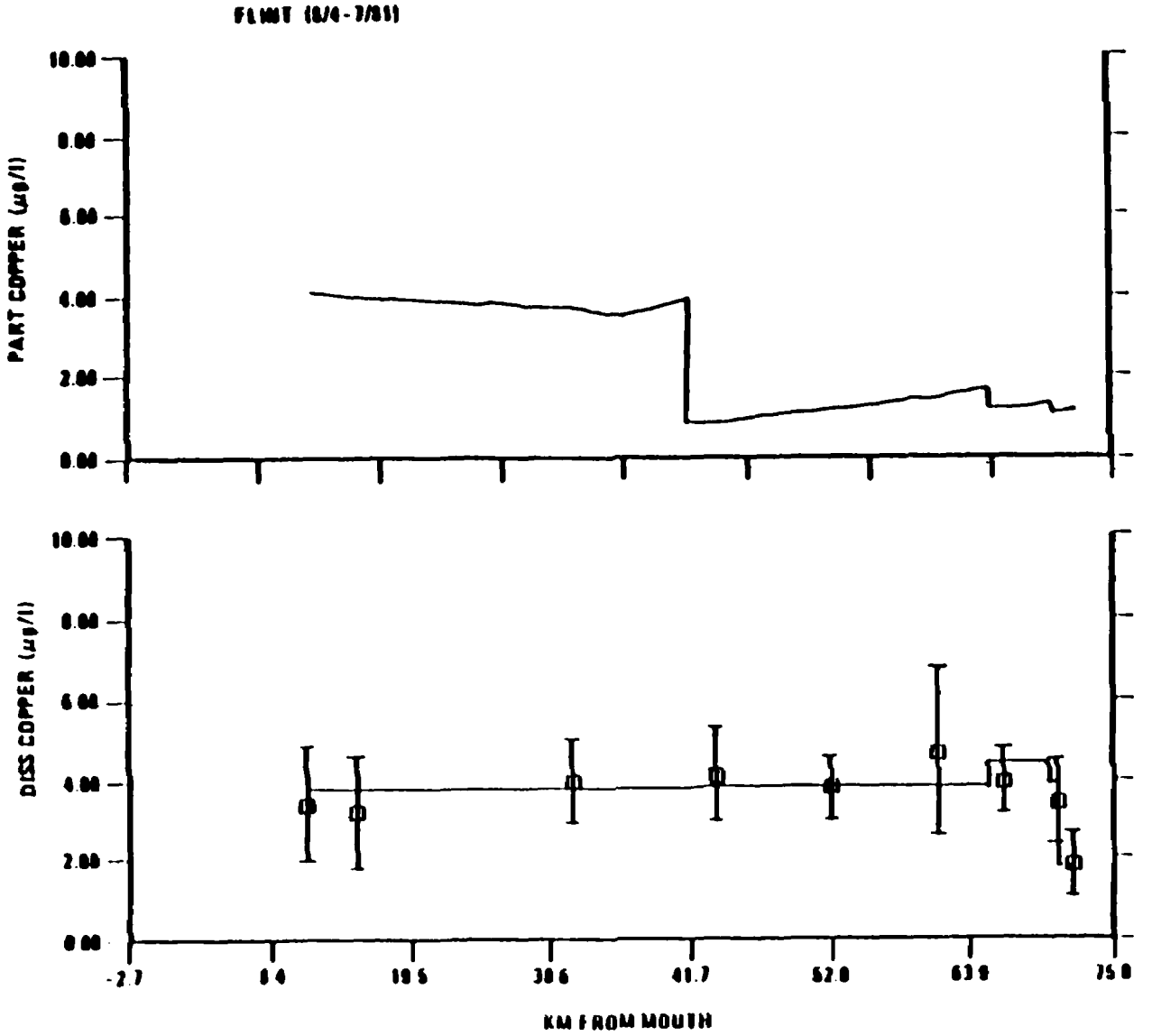

FLNOT (8/4-7/81)
PART COPPER (µg/l)
10.00
8.00
6.00
4.00
2.00
0.00
DISS COPPER (µg/l)
10.00
8.00
6.00
4.00
2.00
0.00
-2.7
8.4
19.5
30.6
41.7
52.8
63.9
75.0
KM FROM MOUTH

FIGURE 5.3.10

TABLE 5.3.5. CALIBRATION VALUES OF PARTITION COEFFICIENTS IN FLINT RIVER DURING AUGUST 1981 STEADY-STATE PERIOD

Segment	Metal Partition Coefficient (ℓ/mg)		
	Zinc	Cadmium	Copper
1	0.25	0.20	0.05
2	0.10	0.03	0.03
3	0.10	0.03	0.03
4	0.25	0.20	0.05
5	0.25	0.20	0.05
6	0.25	0.20	0.09
7	0.25	0.20	0.09
8	0.25	0.20	0.09
9	0.25	0.20	0.09

Results of varying the above model coefficients have been evaluated in terms of percent change of total and dissolved metal concentrations (and suspended solids when applicable) in the river for a given percent change of each parameter individually. Percent changes of both model coefficients and model output are related to the final calibration run presented in the previous subsection. Figure 5.3.11 presents the predicted response of suspended solids, and total and dissolved zinc at Km 45 to changes in the solids settling rate (w_s). (One hundred precent on the x-axis represents the calibration value of w_s for the August survey.) Suspended solids is the most sensitive state variable; with a value of $w_s = 0$ overpredicting the suspended solids concentration by a factor of 2. No solids settling would lead to an overprediction of total zinc by 50 percent; the extent of this variation depends on the partition coefficient. Dissolved zinc (and other dissolved metals) are relatively insensitive to vertical solids flux rates.

An example of the model response to the water column partition coefficient is presented in Figure 5.3.12. In this case the dissolved zinc is very sensitive to the choice of partition coefficient, with the sensitivity among metals depending upon the relative value of the calibration partition coefficient. Total metal levels are relatively insensitive to changes in water column partitioning, unless w is drastically underestimated or omitted altogether.

Since steady-state concentration profiles are not constant in the longitudinal direction, the percent change of model output depends on the distance along the x-axis over which the coefficient perturbation is applied. To demonstrate this concept, the sensitivity analysis results for the August survey are given at four different locations along the river: (1) kilometer point 65, 5 km downstream from the Flint discharge; (2) kilometer point 45, 25 km downstream of Flint; (3) kilometer point 35, about 5 km downstream from the Ragnon discharge; and (4) kilometer point 10, about 30 kilometers downstream of Ragnone. For the settling

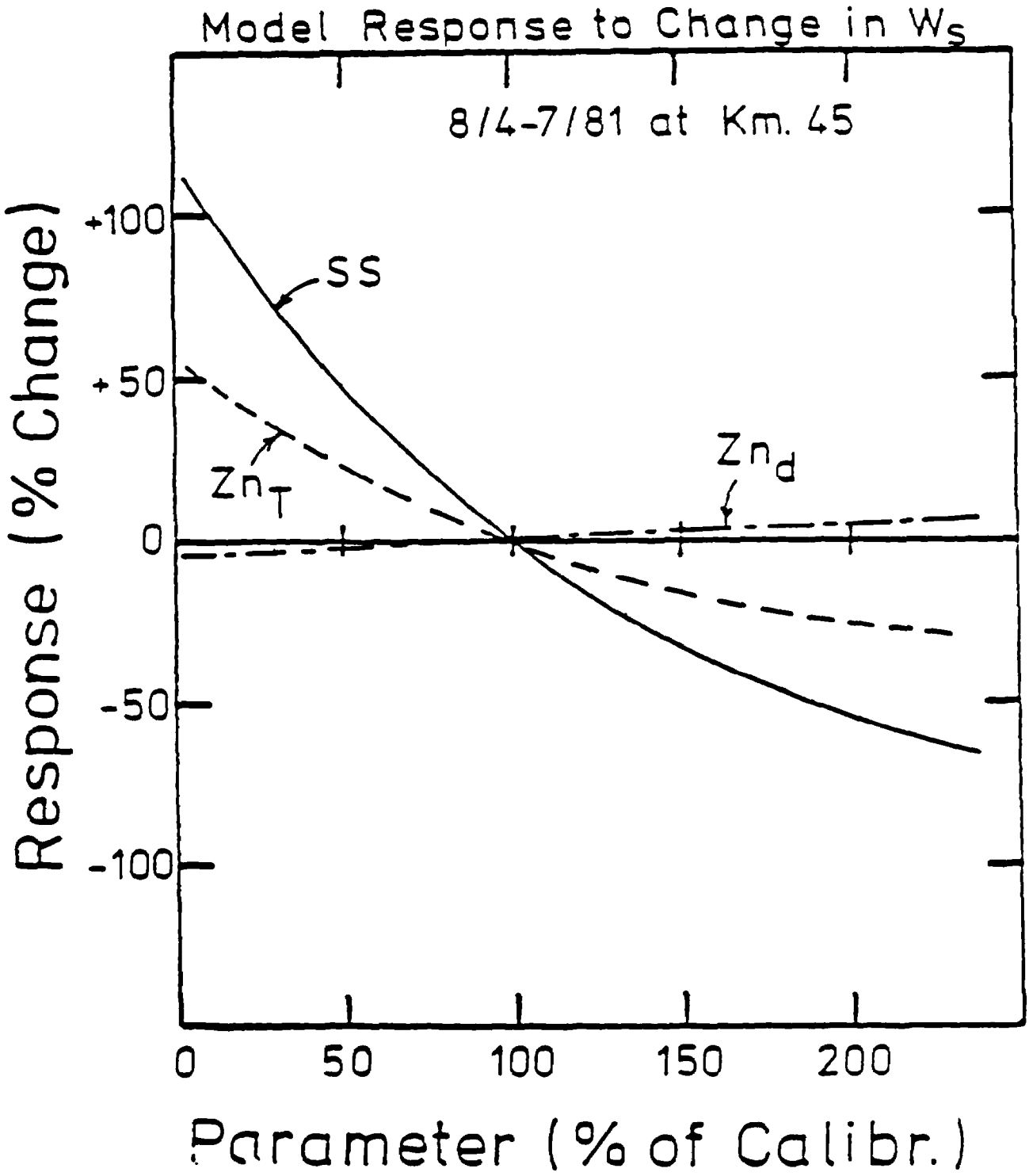

Model Response to Change in W_s
8/4-7/81 at Km. 45
+100
+50
0
-50
-100
SS
Zn_T
Zn_d
Response (% Change)
0
50
100
150
200
Parameter (% of Calibr.)

FIGURE 5.3.11

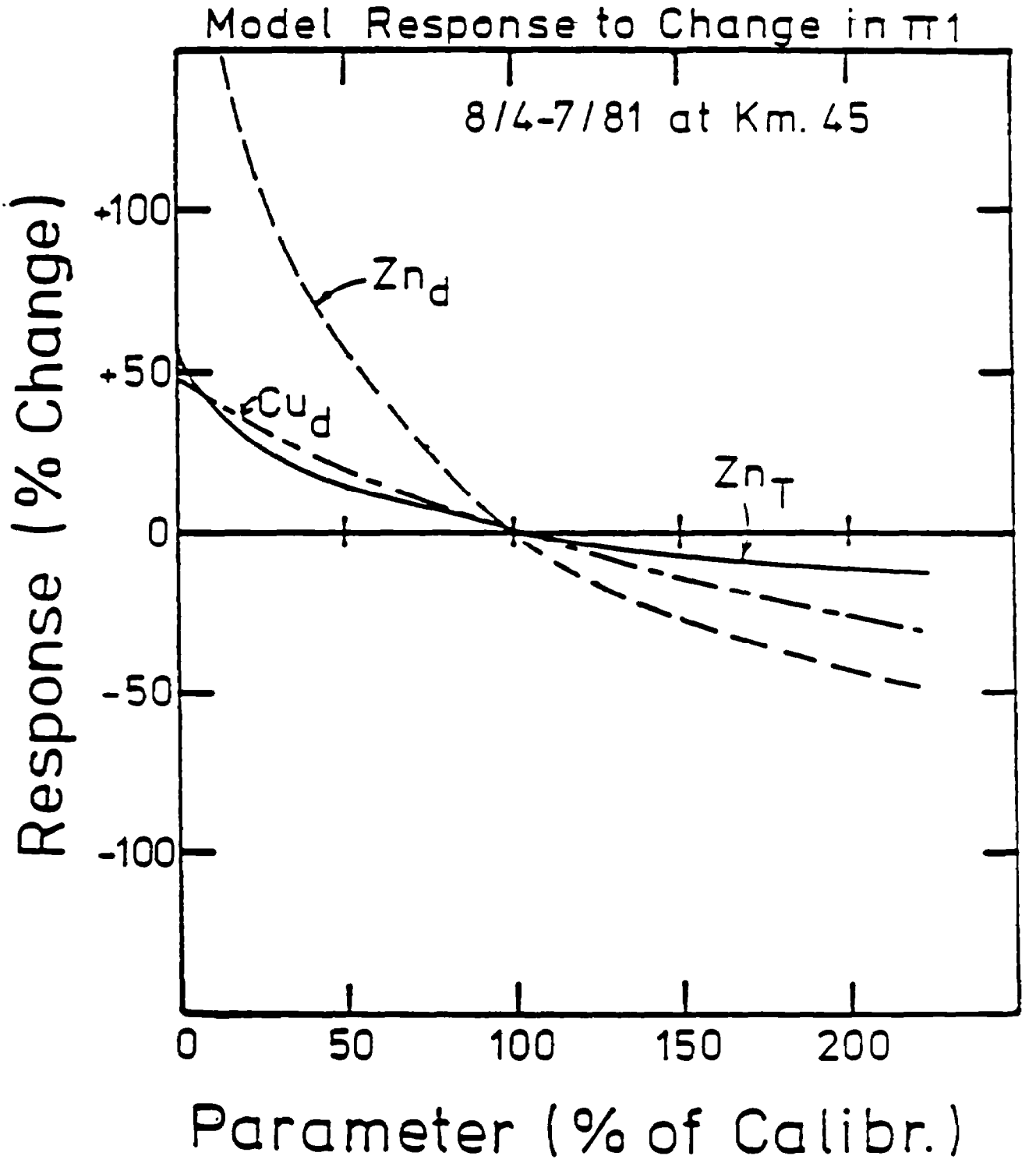

Model Response to Change in π1
8/4-7/81 at Km. 45
Zn_d
Cu_d
Zn_T
+100
+50
0
-50
-100
Response (% Change)
0
50
100
150
200
Parameter (% of Calibr.)

FIGURE 5.3.12

velocity and partition coefficient, the results are presented in Tables 5.3.6 and 5.3.7.

5.4 FLINT RIVER DECEMBER SURVEY

Another survey, conducted during the period December 1-4, 1981, studied metal profiles in the river during a relatively high-flow period. It was also felt that calibration of models for toxic substances in rivers under different flow regimes was an essential step in developing a model that could be applied to WLA problems with confidence.

Another benefit derived from the December survey was the demonstration of data collection for a steady-state system via the slug sampling method. In this sampling method a finite slug of river water is sampled periodically as it moves downstream. Any tributaries or point sources contributing materials to the slug are also sampled as the slug passes these points. This approach can provide an efficient (in terms of number of samples required) way to obtain a steady-state longitudinal profile of the river by eliminating much of the confounding influence of diurnal loading variations. Conducting the December survey in this manner provided model calibration data in a shorter period of time and with many fewer samples than the August data.

The parameters measured in the December survey were the same as those in the August survey, with the exception that dissolved oxygen analysis was omitted. The USGS once again participated in the field work. This time, in addition to providing discharge measurements, they conducted the dye dump and monitoring so as to coincide with the water quality sampling. By following the dye slug downstream, the sampling crew was assured of collecting water from the same slug as it passed the various sampling locations along the study reach. A list of the sampling stations for the December survey is presented in Table 5.4.1.

TABLE 5.3.6. MODEL SENSITIVITY TO VARIATION OF SUSPENDED SOLIDS SETTLING VELOCITY (w_s) FOR THE FLINT RIVER AUGUST 4-7, 1981 SURVEY.

Variation of w_s (% of calibration (value)	Km Pnt.	Model Response (% change) SS	Zn_T	Zn_d	Cd_T	Cd_d	Cu_T	Cu_d
200%	65	-15.9	-6.5	+0.8	--[a]	--	--	--
	45	-54.2	-25.8	+4.8	-21.8	--	-8.6	--
	35	-27.1	-19.3	+0.2	--	--	--	--
	10	-35.6	-26.9	-0.3	-23.7	--	-14.5	--
150%	65	-8.3	-3.4	+0.4	-2.4	0	-1.6	+0.1
	45	-32.4	-15.5	+2.3	-13.1	+2.9	-5.2	+0.9
	35	-16.1	-11.3	+0.03	-9.6	+1.3	-4.9	+3.0
	10	-21.1	-16.1	-0.2	-14.1	+1.0	-8.5	+2.8
50%	65	+9.0	+3.7	-0.4	+2.7	0	+1.7	-0.1
	45	+47.9	+22.9	-2.2	+19.6	-2.8	+8.0	-0.9
	35	+24.7	+17.6	+0.02	+14.6	-1.6	+7.3	-4.0
	10	+33.1	+25.2	+0.30	+21.8	-1.3	+12.8	-3.8
4%	65	+18.0	+7.5	-0.8	+5.5	--	--	--
	45	+112	+53.4	-4.2	+45.8	--	+18.9	--
	35	+58.6	+42.3	0	--	--	--	--
	10	+82.2	+62.7	+0.6	+53.9	--	+31.3	--

[a]Value not determined.

TABLE 5.3.7. MODEL SENSITIVITY TO VARIATION OF WATER COLUMN PARTITION COEFFICIENT FOR THE FLINT RIVER AUGUST 4-7, 1981 SURVEY

Variation of σ_1 for each metal (% of calibration value)	Km Pnt.	Model Response (% change) Zn_T	Zn_d	Cd_T	Cd_d	Cu_T	Cu_d
200%	65	-2.4	-33.2	--	-24.8	--	-19.1
	45	-10.9	-42.0	--	-40.2	--	-25.1
	35	-7.2	-46.1	--	-44.6	--	-37.8
	10	-5.4	-46.0	--	-44.5	--	-37.6
150%	65	-7.3	-19.3	-1.3	-14.2	-1.8	-10.8
	45	-6.1	-26.0	-7.0	-25.1	-6.5	-14.6
	35	-4.2	-29.6	-4.5	-28.5	-4.6	-23.1
	10	-3.0	-29.5	-3.2	-28.5	-3.0	-23.0
50%	65	+2.5	+33.2	+2.1	+20.1	--	+13.1
	45	+13.7	+55.6	+13.3	+49.1	+8.0	+19.4
	35	+9.6	+71.3	--	+64.2	--	+40.1
	10	+6.7	+70.9	+5.9	+63.8	+3.4	+39.8
0%	65	+7.8	+99.9	--	--	--	--
	45	+56.6	+238.	--	+187.	--	+48.0
	35	+42.8	+411.	--	--	--	--
	10	+26.0	+374.	--	+310.	--	+124.

*Value not determined.

TABLE 5.3.7. MODEL SENSITIVITY TO VARIATION OF WATER COLUMN PARTITION COEFFICIENT FOR THE FLINT RIVER AUGUST 4-7, 1981 SURVEY

Variation of σ_1 for each metal (% of calibration value)	Km Pnt.	Model Response (% change)					
		Zn_T	Zn_d	Cd_T	Cd_d	Cu_T	Cu_d
200%	65	-2.4	-33.2	--	-24.8	--	-19.1
	45	-10.9	-42.0	--	-40.2	--	-25.1
	35	-7.2	-46.1	--	-44.6	--	-37.8
	10	-5.4	-46.0	--	-44.5	--	-37.6
150%	65	-7.3	-19.3	-1.3	-14.2	-1.8	-10.8
	45	-6.1	-26.0	-7.0	-25.1	-6.5	-14.6
	35	-4.2	-29.6	-4.5	-28.5	-4.6	-23.1
	10	-3.0	-29.5	-3.2	-28.5	-3.0	-23.0
50%	65	+2.5	+33.2	+2.1	+20.1	--	+13.1
	45	+13.7	+55.6	13.3	+49.1	+8.0	+19.4
	35	+9.6	+71.3	--	+64.2	--	+40.1
	10	+6.7	+70.9	+5.9	+63.8	+3.4	+39.8
0%	65	+7.8	+99.9	--	--	--	--
	45	+56.6	+238.	--	+187.	--	+48.0
	35	+42.8	+411.	--	--	--	--
	10	+26.0	+374.	--	+310.	--	+124.

*Value not determined.

5.4.1 December Survey Data Summary

The December survey actually consisted of two distinct slug monitoring runs down the river. On December 1, 1981, at 7:00 a.m. the dye was dumped at Grand Traverse Street, a point 7.4 kilometers upstream of the initial water quality sampling station (Mill Road). This permitted the dye slug to adequately mix over the river cross-section by the time it reached Mill Road. At Mill Road and at all subsequent river stations and point source locations, estimates were made (based on average river velocity estimates) of the time of travel between samp'ing points along the river. These estimates were confirmed by following the dye slug along the river and sampling on-site at each location via fluorometric analysis when the leading edge and peak of the dye slug was passing. Three water quality samples were collected at each location, separated in time by about 1/2 hour, as the dye was passing. An attempt was made, in most cases successfully, to obtain one water quality sample prior to passage of the peak of dye, one at the peak, and one after passage of the peak. In this way a good representation of the water quality in the dye slug could be obtained.

Hydrographs of the Flint River at the M-57 (Vienna Road) and M-13 sampling locations during the week of the December survey are presented in Figure 5.4.1. These hydrographs indicate two major things. First, the discharge of the river during the December survey was an order of magnitude larger than the August low-flow survey. Second, the hydrographs are reasonably flat, indicating that the river flow was close to steady-state during the survey. There was a small peak in each hydrograph due to a brief rainfall late Tuesday afternoon; however, this event occurred between two sampling runs, as indicated in the figure.

A record of the dye slug time-of-travel and sampling times for both sampling runs has been reconstructed in Table 5.4.2. A very fortunate occurrence is evident from this table. The river flow conditions were

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A record of the dye slug time-of-travel and sampling times for both sampling runs has been reconstructed in Table 5.4.2. A very fortunate occurrence is evident from this table. The river flow conditions were

TABLE 5.4.2.. COMPARISON OF DYE CLOUDS TIME-OF-TRAVEL WITH SAMPLING SCHEDULE FOR DECEMBER, 1981 SURVEY OF FLINT RIVER

Site	Km. Point	Date	Arrival of Peak Dye Concentration*	Sampling Times	Time-of-Tra of Peak (hr
M111 Road	71.9	12/1/81	1005	0945;1005;1030	3.1
(R0006)		12/3/81	1010	0950;1010;1030	3.2
F int WWTP	70.7	12/1/81	1030	1005;1035;1105	3.5
(FE0002)		12/3/81	1035	1005;1025;1045	3.6
L nden Road	70.5	12/1/81	1045	1015;1045;1115	3.75
(R0007)		12/3/81	1050	1020;1040;1100	3.8
E ms Road	66.3	12/1/81	1220	1200;1230;1250	5.3
(FR0008)		12/3/81	1220	1200;1230;1300	5.3
4 in Street	61.2	12/1/81	1420	1400;1425;1455	7.3
R0009)		12/3/81	1430	1400;1430;1500	7.5
Mt. Morris	52.6	12/1/81	1745	1700;1730;1800	10.75
R ad (FR0010)		12/3/81	1800	1730;1800;1830	11.0
/ enna Road/-	43.5	12/1/81	2120	2020;2050;2145	14.3
M-57 (FR0011)		12/3/81	2150	2115;2145;2215	14.8
R gnone WWTP	41.1	12/1/81	2200	2120;2220;2250	15.0
0003)		12/3/81	2220	2215;2245;2315	15.3
ake Road	38.3	12/1-2/81	2345	2345;0020;0045	16.75
FR0018		12/4/81	0015	0000;0030;0100	17.25
Run	30.5	12/2/81	0330	0300;0330;0400	20.5
ad (FR0019)		12/4/81	0350	0315;0400;0445	20.8
M-13	14.9	12/2/81	1020	0930;1000;1030	27.3
0015)		12/4/81	1130	1015;1100;1145	28.5

Dye dumped at Grand Traverse Street (Km. Pt. 79.3) at 7:00 a.m. on 12/1/81 and 12/3/81.

very similar during the two sampling runs, effectively providing a replicate experiment that permitted a certain degree of field testing of the model. The table indicates the success attained in sampling river stations near the peak of the dye slug. The time-of-travel over the study reach from Mill Road to M-13 was 24.25 hours for run 1 and 25.33 hours for run 2. These travel times corresponded to average velocities through the study reach of 2.35 km/hr (0.653 m/s) and 2.25 km/hr (0.625 m/s) for runs 1 and 2, respectively.

Based on discharge measurements, time-of-travel data, and cross-sectional area data provided by USGS, the river reach from Mill Road to Cresswell Road was segmented and the hydrological and morphological input data were compiled by segment. This information is presented in Table 5.4.3. The same nine segments used in the August model application were sufficient for the December survey; however, a flow balance (based on available flow and gaging station measurements) showed that there were tributary or groundwater sources of water to some segments for which no accounting was available. The segments of concern are shown in Table 5.4.3 with two entries under the "segment flow" column; the first entry is the flow at the upstream boundary, and the second entry is the flow at the downstream boundary of the segment. The model was set up to handle this situation by distributing the flow increment of any given segment uniformly along the length of the segment.

The initial conditions at Mill Road and the point source loads at the time the dye cloud passed each point are presented in Tables 5.4.4 and 5.4.5 for runs 1 and 2, respectively. Once again the two municipal plants represented the major source of metals to the river. Both plants had higher discharge flows in December than in August, with correspondingly higher metals loads. It is worthy of note at this time that the suspended solids and metals loads from the Ragnone plant were almost an order of magnitude greater during run 2 than during run 1. This occurrence provided an excellent opportunity to determine how the

TABLE 5.4.3. SEGMENTATION, FLOWS, AND GEOMETRY FOR FLINT RIVER DURING DECEMBER 1981 SURVEY

Segment Number	Boundary	Km. Point	Segment Flow (m^3/s)	Cross-Sectional Area (m^2)	Mean Dep (m)
		Run 1 - 12/1-2/81			
	Mill Road	71.9			
1			26.3	39.5	1.2
	Flint WWTP	70.7			
2			28.5	44.0	1.2
	Flint Fly Ash Ponds	70.0			
3			28.6-29.3	41.3	1.0
	Downstream of Elms Road	65.0			
4			29.3-32.3	46.3	0.85
	Brent Run	41.6			
5			32.9	47.4	1.0
	Ragnone WWTP	41.1			
6			34.0-34.9	62.8	1.2
	Upstream of East Burt Rd.	36.0			
7			34.9-36.1	44.6	1.2
	Pine Run	29.7			
8			36.8	59.5	1.2
	Silver Creek	25.2			
9			37.4	60.9	1.3
	Cresswell Road	11.0			

TABLE 5.4.3. (Cont'd.)

Segment Number	Boundary	Km. Point	Segment Flow (m^3/s)	Cross-Sectional Area (m^2)	Mean D (m)
		Run 2 - 12/3-4/81			
	Mill Road	71.9			
1			26.4	39.5	1.2
	Flint WWTP	70.7			
2			28.6	44.0	1.2
	Flint Fly Ash Ponds	70.0			
3			28.7-29.0	41.6	1.0
	Downstream of Elms Road	65.0			
4			29.0-30.4	46.7	0.85
	Brent Run	41.6			
5			30.9	47.4	1.0
	Ragnone WWTP	41.1			
6			32.1-33.0	60.9	1.2
	Upstream of East Burt Rd.	36.0			
7			33.0-34.1	45.1	1.2
	Pine Run	29.7			
8			34.7	61.2	1.2
	Silver Creek	25.2			
9			35.2	60.5	1.3
	Cresswell Road	11.0			

TABLE 5.4.4. UPSTREAM CONDITIONS AND POINT SOURCES TO FLINT RIVER - FOR RUN 1 DECEMBER 1-2, 1981

Source	Discharge Flow (m^3/s)	Discharge Concentration and Load							
		Suspended Solids		Total Zinc		Total Cadmium		Total Copper	
		(mg/ℓ)	(kg/d)	(μg/ℓ)	(gm/d)	(μg/ℓ)	(gm/d)	(μg/ℓ)	(gm/d)
Upstream Boundary-Mill Road	26.35	7.40	16,800	4.0	9120.	0.05	114.0	2.0	4550.
Flint WWTP	2.19	7.8	1474.	54.3	10,300	0.18	34.0	16.0	3020.
Flint Fly Ash Ponds	0.10	23.5	203.	220.0	1900.	2.89	25.0	127.0	1100.
Brent Run	0.57	7.7	376.	7.67	375.	0.097	4.74	2.93	143.
Ragnone WWTP	1.14	40.7	4010.	75.0	7390.	0.21	20.4	18.5	1820.
Pine Run	0.67	5.5	318.	3.33	194.	0.043	2.50	2.10	122.
Silver Creek	0.62	3.5	188.	3.67	197.	0.040	2.15	1.80	96.8

TABLE 5.4.5. UPSTREAM CONDITIONS AND POINT SOURCES TO FLINT RIVER - FOR RUN 2 DECEMBER 3-4, 1981

Source	Discharge Flow (m^3/s)	Discharge Concentration and Load							
		Suspended Solids		Total Zinc		Total Cadmium		Total Copper	
		(mg/ℓ)	(kg/d)	(μg/ℓ)	(gm/d)	(μg/ℓ)	(gm/d)	(μg/ℓ)	(gm/d)
Upstream Boundary Mill Road	26.44	6.5	14,800	4.67	10,700	0.017	38.8	1.67	3810.
Flint WWTP	2.21	6.5	1240.	57.0	10,900	0.10	19.7	22.8	4350.
Flint Fly Ash Ponds	0.10	21.2	183.	212.	1830.	2.19	18.9	220.	1900.
Brent Run	0.51	3.9	171.	4.67	206.	0.02	0.88	3.13	138.
Ragnone Well	1.23	338.0	35,800	400.	42,500	1.47	156.	160.	17,000
Pine Run	0.64	4.9	268.	4.0	220.	0.007	0.38	1.57	86.4
Silver Creek	0.50	4.6	198.	4.0	171.	0.027	1.16	1.33	56.9

model would perform under similar river flow conditions with drastically different loads - an exercise often required in performing waste load allocations. Finally, it should be noted that once again the metals discharged from the Flint outfalls were primarily dissolved, while those from the Ragnone discharge were largely particulate.

5.4.2 December Survey Model Calibration

The procedure taken in calibrating the model to the December data was to first calibrate the model using data from run 1 only; then the calibrated model was applied to run 2 data as a field test of the model performance under similar flow conditions with very different loadings. As with the August survey, calibration of the suspended solids transport system was performed first by adjustment of w_s and w_{rs}; this step was followed by calibration of the metals system using the respective partition coefficients. Degradation and sediment-water diffusion of dissolved metals have again been considered insignificant.

In calibrating the suspended solids system one should not expect the sediment transport regime to be the same in December as it was in August. In the higher flow regime of the December survey, one might expect the river to have the capacity to carry larger particulate matter, which would have a larger intrinsic settling velocity (per Stokes formula). On the other hand, higher flows lead to higher stream velocities and depths, and thus result in greater bottom shear stress. Assuming that the other factors governing entrainment are the same, the December solids resuspension velocities (w_{rs}) should also be greater than those determined in August. Depending, of course, on the magnitude of change in w_s and w_{rs}, it is possible that the net flux of solids between bottom sediments and overlying water many not be significantly different from the August results. It is likely therefore, that because of the characteristically shorter detention time in the higher fl w river system, the longitudinal distribution of suspended

solids in December will not exhibit as great a variation as was observed in August.

The hypotheses presented in the above paragraph were largely confirmed by the calibration of the model to the December run 1 data. Calibration values for w_s and w_{rs} for each of the nine segments are presented in Table 5.4.6. Illustration of the suspected relative flatness of the solids longitudinal distribution and the comparison of model simulation with field data for run 1 are presented in Figure 5.4.2.

Once again the calibration was made without varying the settling velocity, w_s, among segments. Because of the greater uncertainty in ascertaining the factors governing sediment erosion, it was felt that there would more likely be intersegment variability in w_{rs} than in w_s. A settling rate of 0.6 m/d (as opposed to 0.25 m/d in August) does not seem unusually high for a river flowing at about five times the discharge rate. Assuming the river suspended solids had a specific gravity of 2.5, the effective Stokes diameter for 0.6 m/d settling velocity would be 3.0 μm compared with 1.8 μm for a settling velocity rate of 0.25 m/d.

The bottom shear stress in the various river segments calculated in the same manner as in the August survey ranged from 25 to 54 dynes/cm^2. Once again the lower segments (7-9) had slightly higher values than the upper reaches. All these shear stress values are considerably higher than the 4-13 dynes/cm^2 range calculated for the August flow conditions. In fact, both stream velocities and shear stresses in December are roughly three times the August values. It seems logical, therefore, that the calibrated resuspension values for December are greater in each segment (see Table 5.4.6) and greatest in the downstream segments again. There are other possible reasons for greater downstream erosion rates, related to some of the other governing factors mentioned by Lee _et al_. (1981). The downstream segments of the Flint River pass through an almost exclusively agricultural area, perhaps

TABLE 5.4.6. CALIBRATION COEFFICIENT FOR SOLIDS TRANSPORT SYSTEM USING FLINT RIVER, DECEMBER 1-2, 1981 (RUN 1) DATA

Segment	Settling Velocity (m/d)	Resuspension Velocity (m/d)
1	0.6	0.2×10^{-4}
2	0.6	0.2×10^{-4}
3	0.6	0.4×10^{-4}
4	0.6	0.4×10^{-4}
5	0.6	0.4×10^{-4}
6	0.6	0.2×10^{-4}
7	0.6	1.2×10^{-4}
8	0.6	1.0×10^{-4}
9	0.6	1.0×10^{-4}

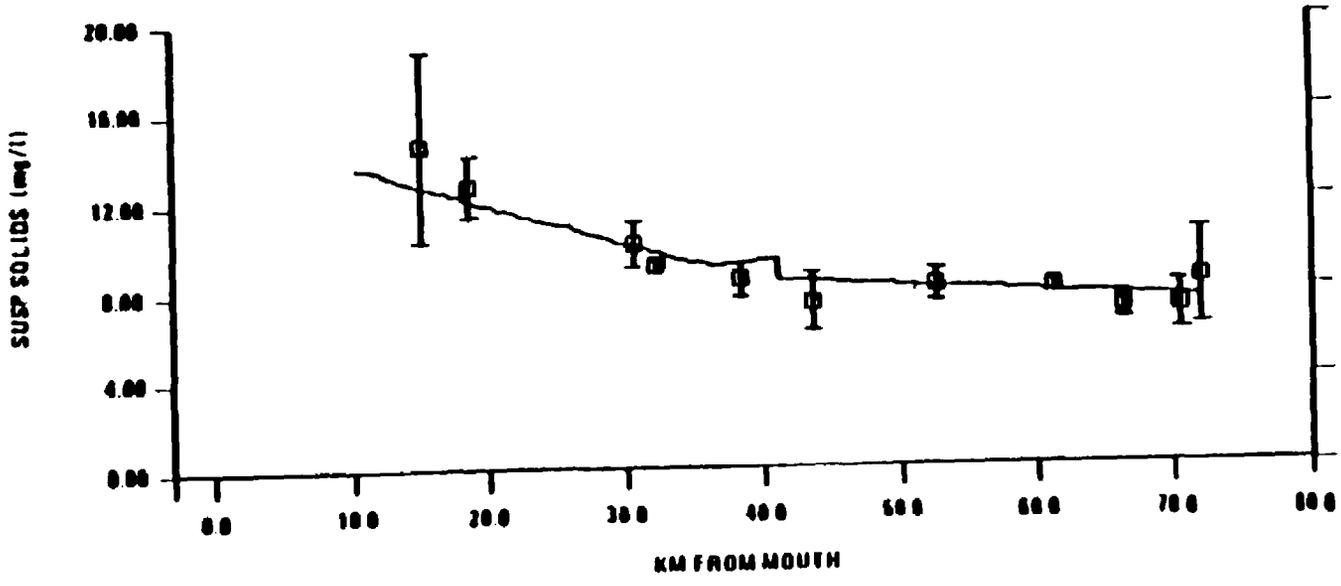
SUSP SOLIDS (mg/l)
20.00
16.00
12.00
8.00
4.00
0.00
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
KM FROM MOUTH

FIGURE 5.4.2

resulting in different bottom sediment characteristics. Furthermore, the downstream segments tend to have steeper, more loosely packed banks. It is also possible that the depositional pattern downstream of the Ragnone treatment plant, which tends to discharge high solids concentrations, might favor high erosion rates. Temporal variations in recent depositional history for any river reach may lead to variability in bottom sediment resuspension rates for a given flow regime.

Once the solids transport submodel has been calibrated, calibration for the metals is performed by adjustment of partition coefficients. The final calibration values for the three metals in each segment are presented in Table 5.4.7. A comparison of the model simulations using these coefficients with the run 1 field data is presented in Figures 5.4.3-5.4.7. The partition coefficients used to generate these simulations are very similar to those obtained in the August calibration. Where they do differ, such as for zinc and for copper downstream of the Ragnone discharge, they tend to be slightly lower for the higher flow case. This result might be expected, since the solids being transported in December are probably slightly larger, thus having a smaller surface area to mass ratio.

Once again the high fraction of dissolved solids in the Flint discharge forced a calibration with lower partition coefficients for all three metals in segments 2 and 3. Also, the copper in the high particulate metals load from Ragnone seemed to remain in a particulate phase through the end of the study reach. These necessary adjustments from segment to segment reflect a need to characterize the partitioning of metals in the effluent streams as well as in the river.

As indicated earlier, the second plug flow survey provided an excellent opportunity to field test the model for its ability to simulate variation in river solids and metals levels for different loading conditions under the same flow regimes. This test was performed by

TABLE 5.4.7. CALIBRATION VALUES OF PARTITION COEFFICIENTS IN FLINT RIVER DURING DECEMBER 1-2, 1981 SURVEY

Segment	Metal Partition Coefficient (ℓ/mg)		
	Zinc	Cadmium	Copper
1	0.20	0.20	0.05
2	0.08	0.05	0.03
3	0.08	0.05	0.03
4	0.20	0.20	0.05
5	0.20	0.20	0.05
6	0.20	0.20	0.07
7	0.20	0.20	0.07
8	0.20	0.20	0.07
9	0.20	0.20	0.07

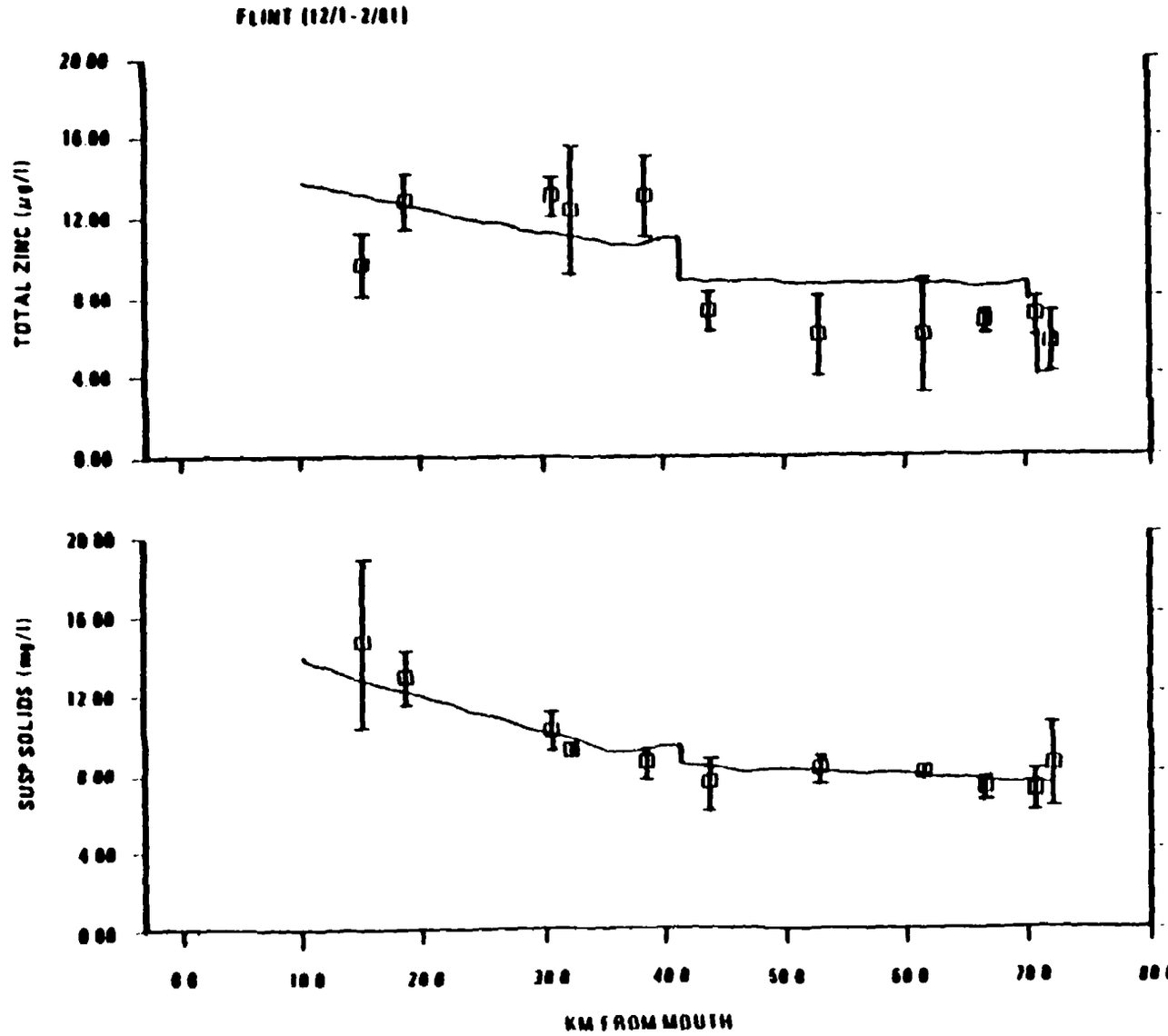
FLINT (12/1-2/81)
TOTAL ZINC (µg/l)
20.00
16.00
12.00
8.00
4.00
0.00
SUSP SOLIDS (mg/l)
20.00
16.00
12.00
8.00
4.00
0.00
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
KM FROM MOUTH

FIGURE 5.4.3

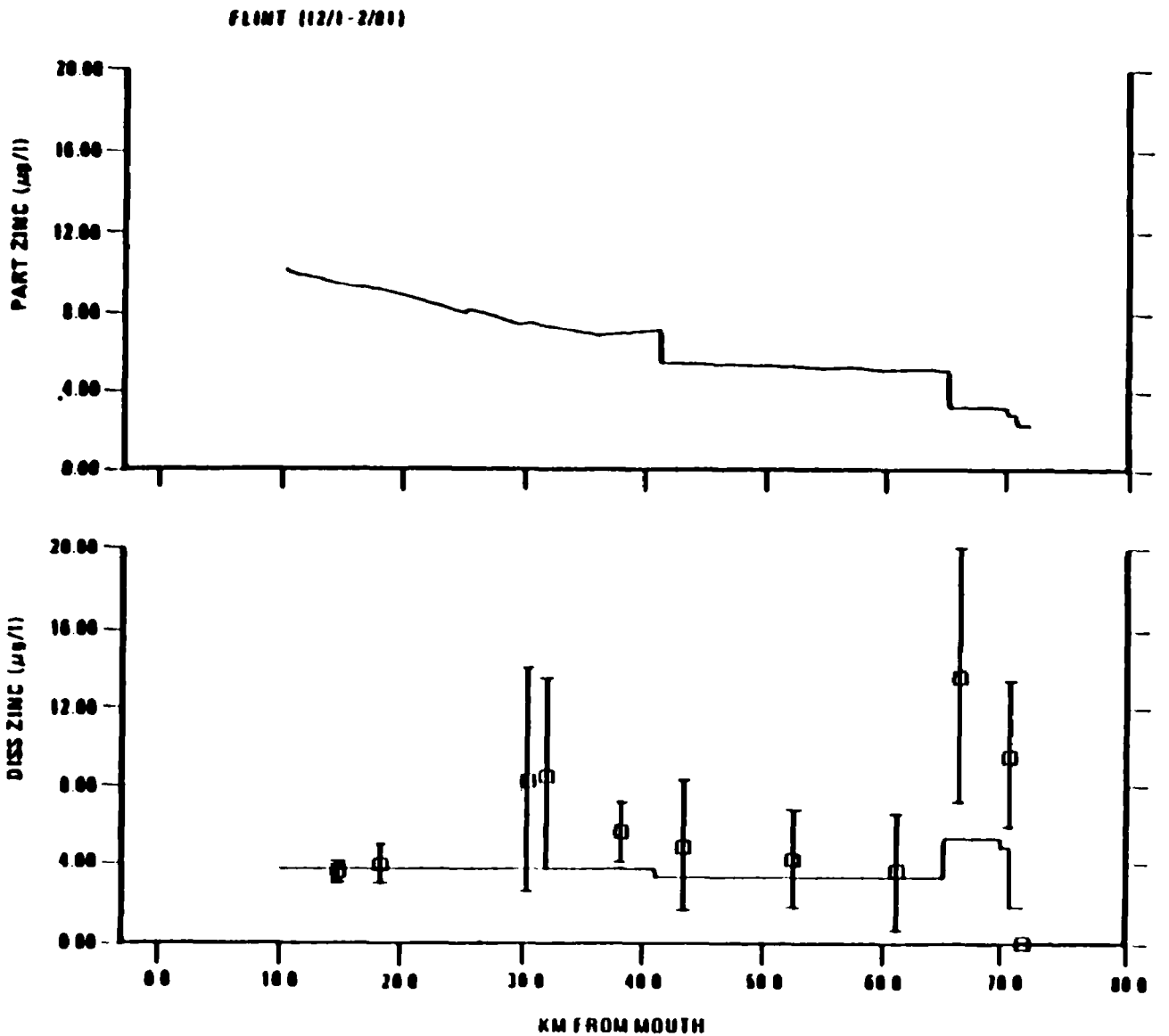
FLINT (12/1-2/81)
PART ZINC (µg/l)
20.00
16.00
12.00
8.00
4.00
0.00
DISS ZINC (µg/l)
20.00
16.00
12.00
8.00
4.00
0.00
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
KM FROM MOUTH

FIGURE 5.4.4

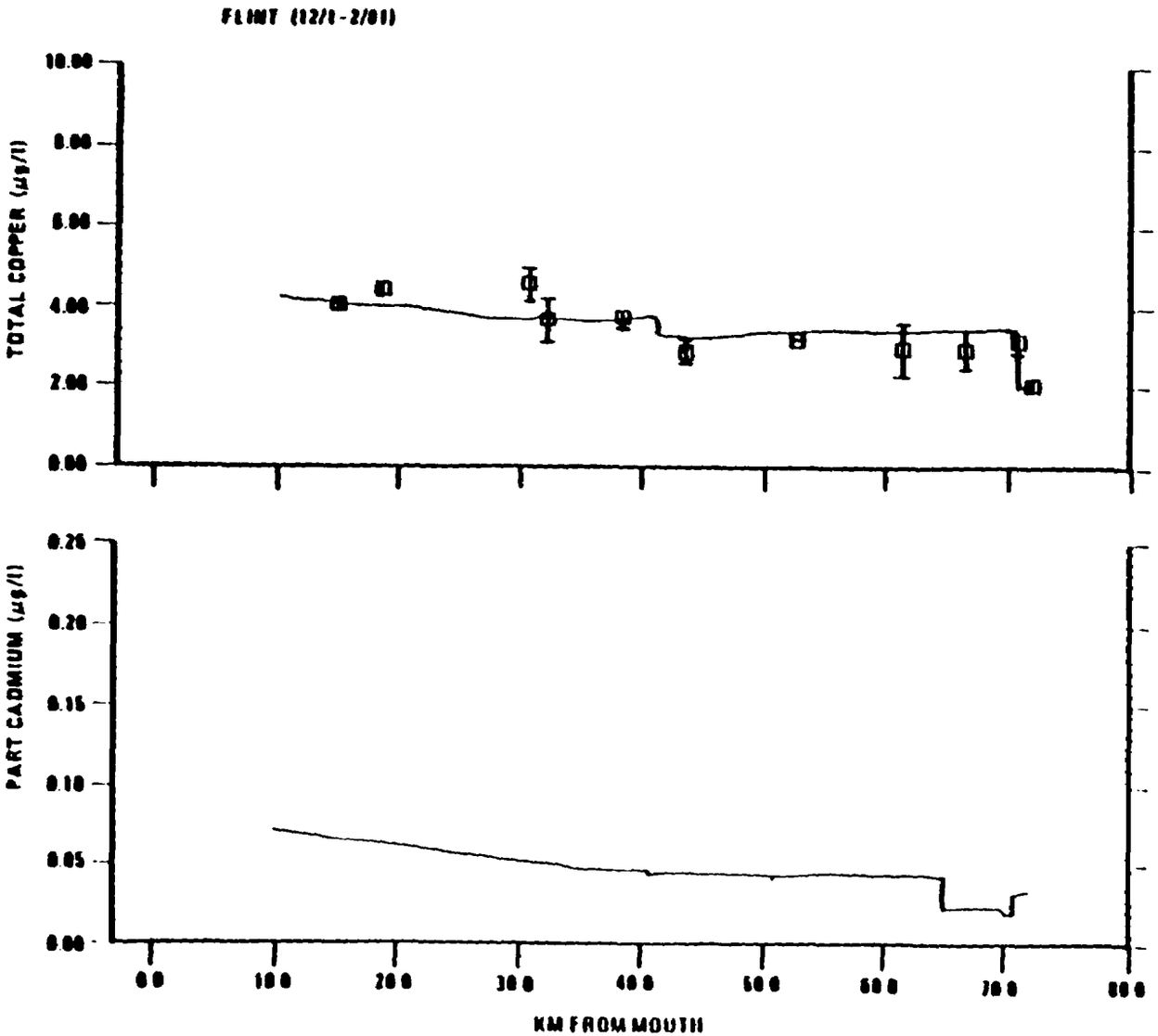
FLINT (12/1-2/81)
TOTAL COPPER (µg/l)
10.00
8.00
6.00
4.00
2.00
0.00
PART CADMIUM (µg/l)
0.25
0.20
0.15
0.10
0.05
0.00
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
KM FROM MOUTH

FIGURE 5.4.6

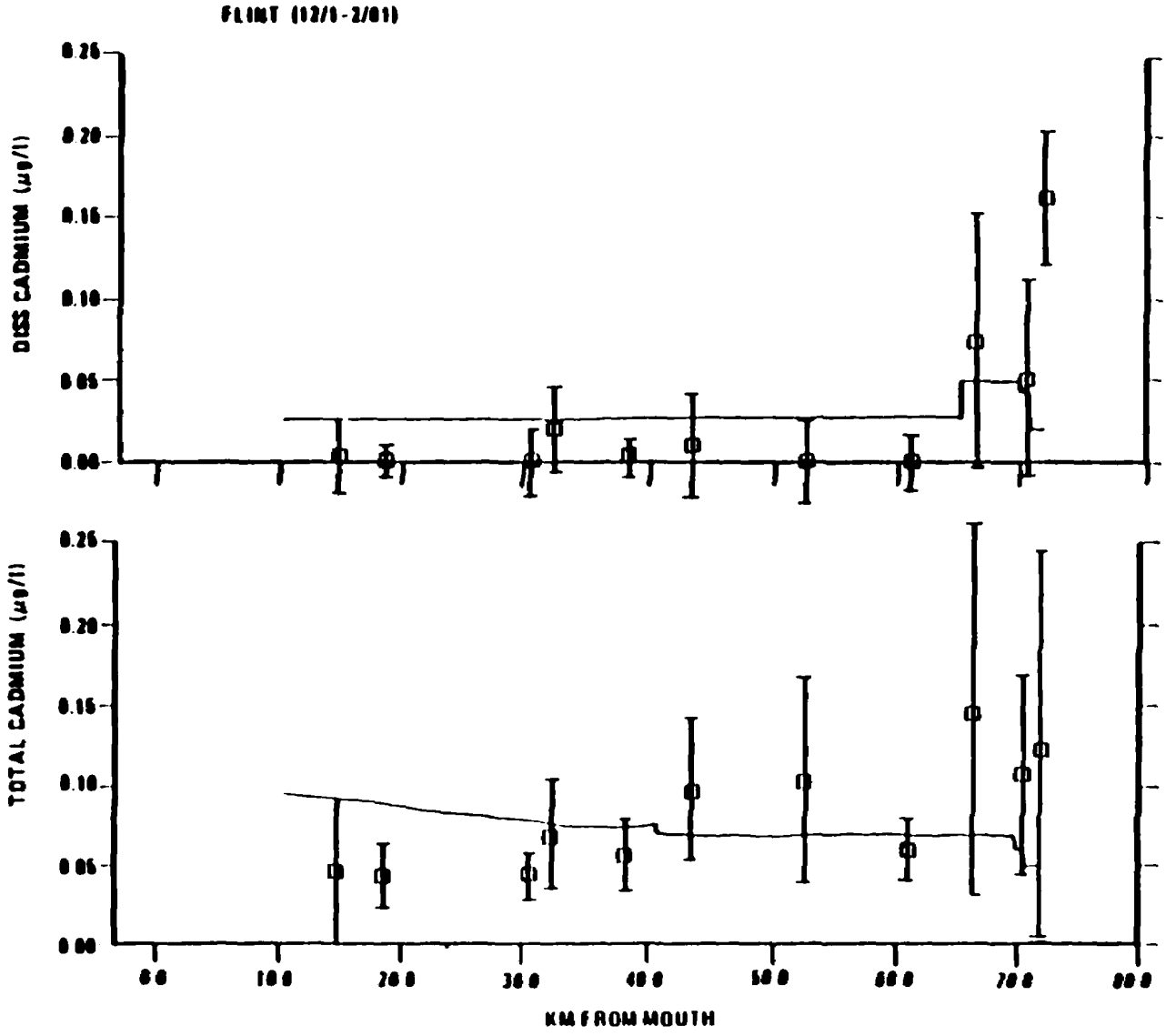
FLINT (12/1-2/81)
DISS CADMIUM (µg/l)
0.25
0.20
0.15
0.10
0.05
0.00
TOTAL CADMIUM (µg/l)
0.25
0.20
0.15
0.10
0.05
0.00
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
KM FROM MOUTH

FIGURE 5.4.5

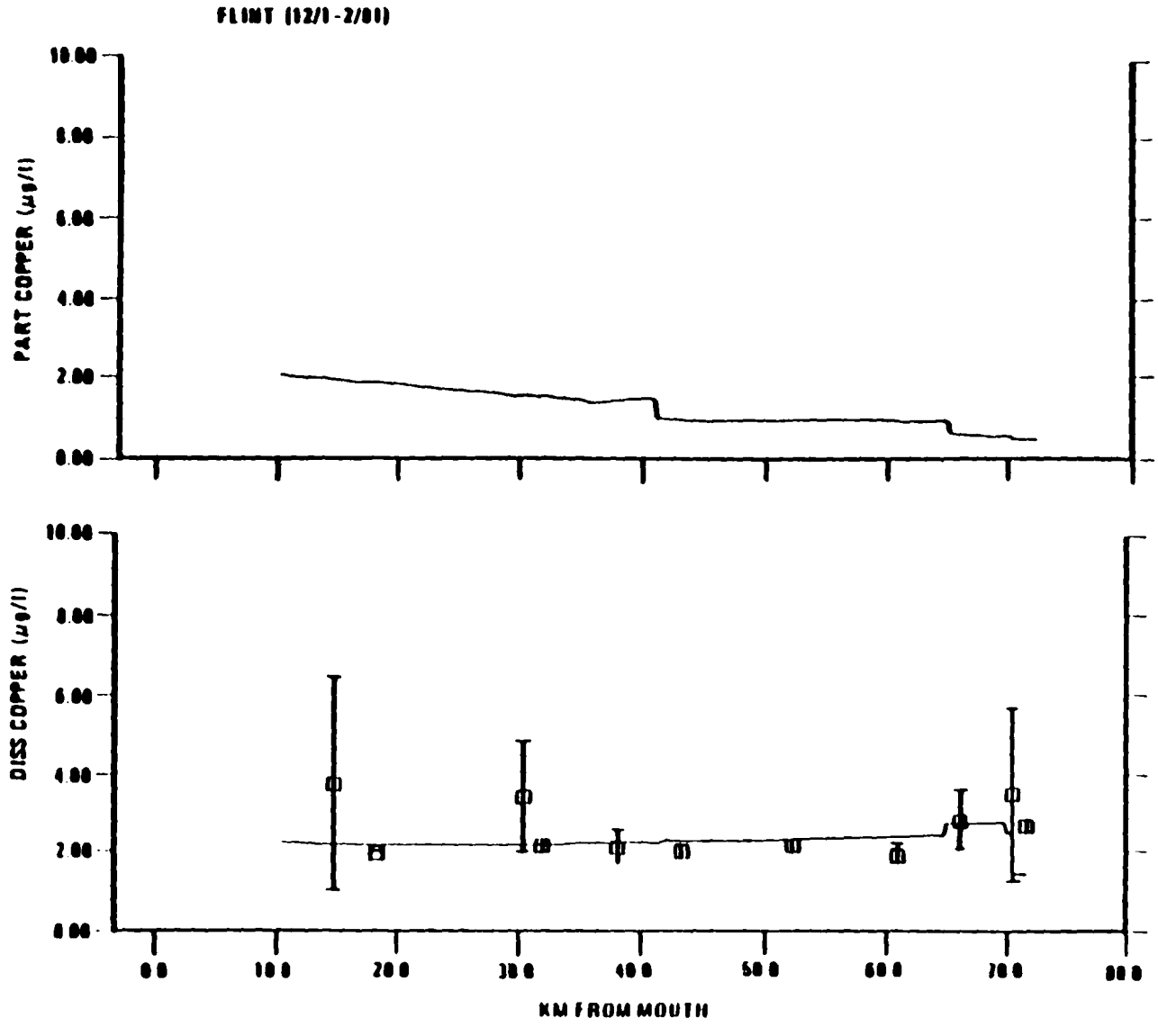
FLINT (12/1-2/81)
PART COPPER (µg/l)
10.00
8.00
6.00
4.00
2.00
0.00
DISS COPPER (µg/l)
10.00
8.00
6.00
4.00
2.00
0.00
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
KM FROM MOUTH

FIGURE 5 4 7

applying the model to the December 3-4, 1981 (run 2) loading data (Table 5.4.5) and hydrologic data (Table 5.4.3) without adjusting the calibration coefficients (w_s, w_{rs}, τ_{zn}, τ_{cd}, τ_{cu}) obtained using run 1 data. The results of this model run are presented in Figures 5.4.8 - 5.4.12. The main difference in the two data sets, of course, was the large increase in solids and particulate metals discharge from the Ragnone WWTP when the second dye cloud (run 2) was passing. Based on the comparison of model predictions with field data, the model performed quite well, without a need for recalibration. The only significant failing of the model was the over-prediction of dissolved copper downstream from the Ragnone discharge. Obviously, with particulate copper from the Ragnone discharge comprising over half of the total load of copper in segments 6-9, a higher partition coefficient would have helped to simulate the dissolved copper profile. In fact, if one were actually calibrating the model to the run 2 data, the only change from the run 1 calibration would be to raise the copper partition coefficients in segment 6-9 from 0.07 ℓ/mg to 0.12 ℓ/mg.

5.5 FLINT RIVER MARCH 1982 SURVEY

The primary goal of the Flint River March Survey (March 23-26, 1982) was to evaluate the status of metals and solids transport in the river during a period that would likely represent the highest discharge flow in an annual cycle. It was fortunate that the survey was scheduled about two weeks after a major snowmelt period in southeastern Michigan. At the time of the survey the study reach was discharging water which had previously collected in upstream reservoirs during the snowmelt. The flow in the study reach during the survey was about 4000 cfs (113 m^3/s), roughly 4 times the December flow and 20 times the August flow. Studying the river under this range of flow conditions provided a good idea of the range that is likely to exist in the values of those parameters, such as sediment settling and resuspension velocities and partition coefficients, that appear to be flow dependent.

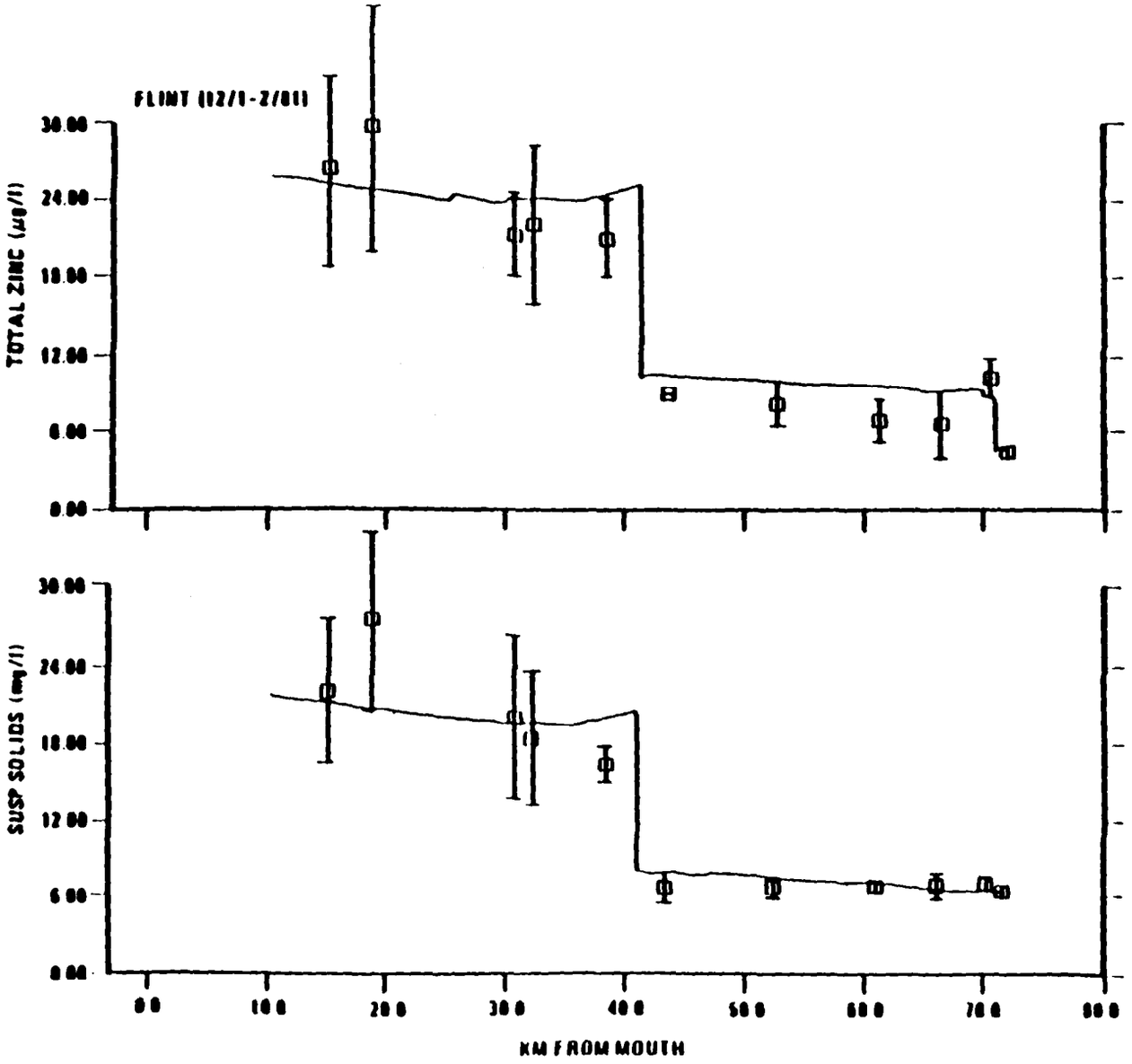
FLINT (02/1-2/81)
TOTAL ZINC (µg/l)
30.00
24.00
18.00
12.00
6.00
0.00
SUSP SOLIDS (mg/l)
30.00
24.00
18.00
12.00
6.00
0.00
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
KM FROM MOUTH

FIGURE 5.4.8

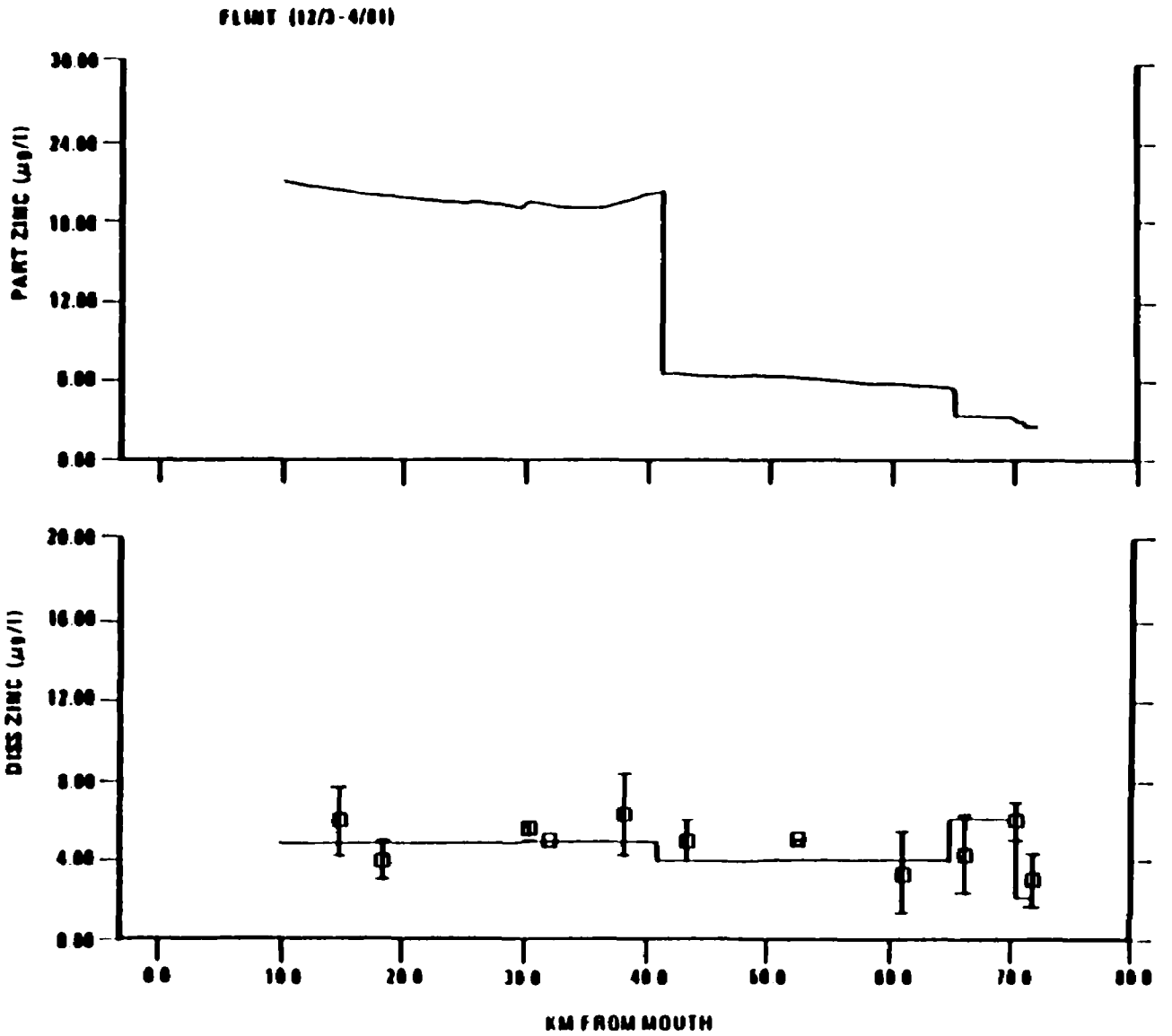
FLINT (12/3-4/81)
PART ZINC (µg/l)
30.00
24.00
18.00
12.00
6.00
0.00
DISS ZINC (µg/l)
20.00
16.00
12.00
8.00
4.00
0.00
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
KM FROM MOUTH

FIGURE 5.4.9

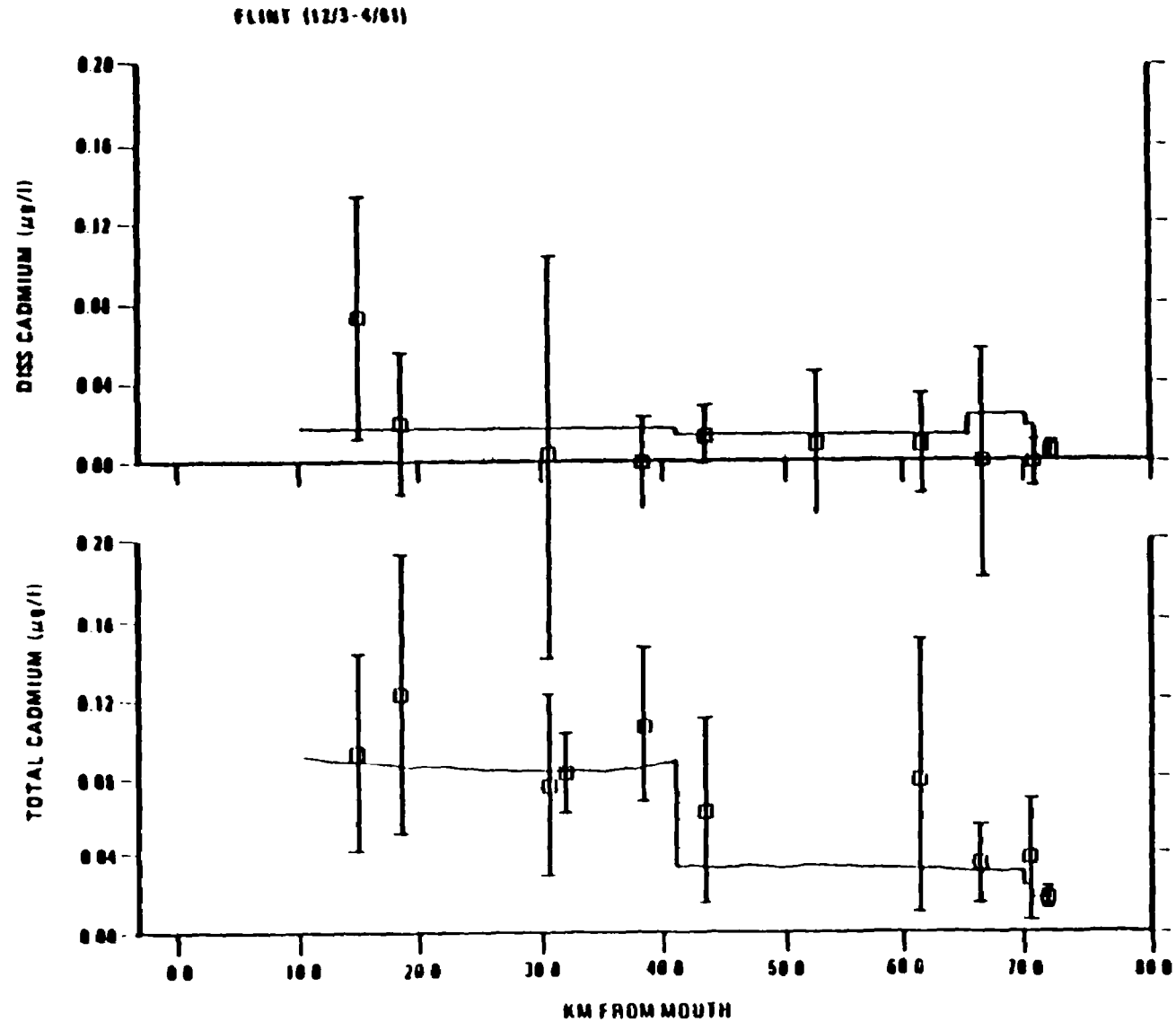
FLINT (12/3-6/81)
DISS CADMIUM (µg/l)
TOTAL CADMIUM (µg/l)
0.20
0.16
0.12
0.08
0.04
0.00
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
KM FROM MOUTH

FIGURE 5.4.10

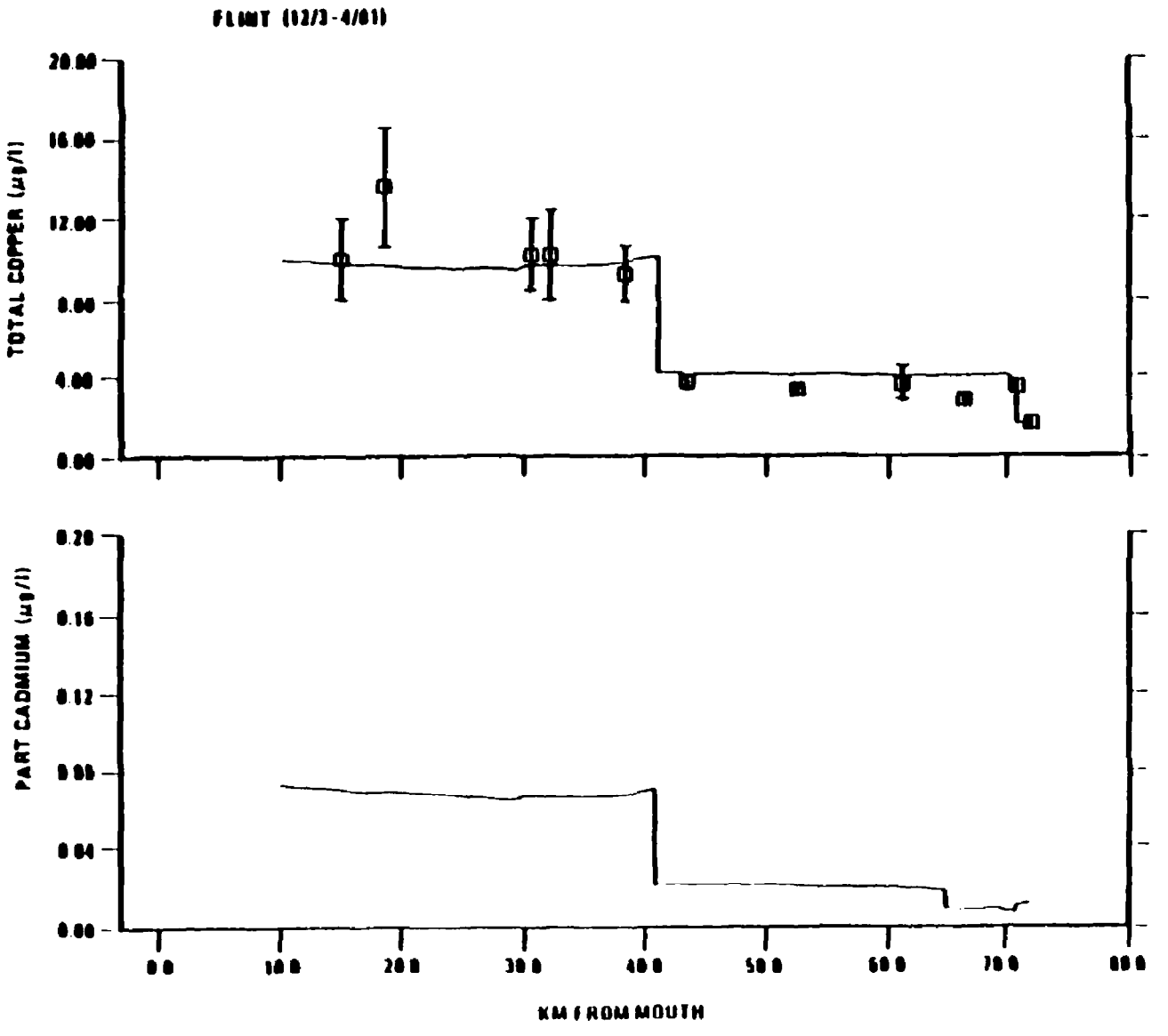
FLINT (12/3-4/81)
TOTAL COPPER (µg/l)
20.00
16.00
12.00
8.00
4.00
0.00
PART CADMIUM (µg/l)
0.20
0.16
0.12
0.08
0.04
0.00
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
KM FROM MOUTH

FIGURE 5.4.11

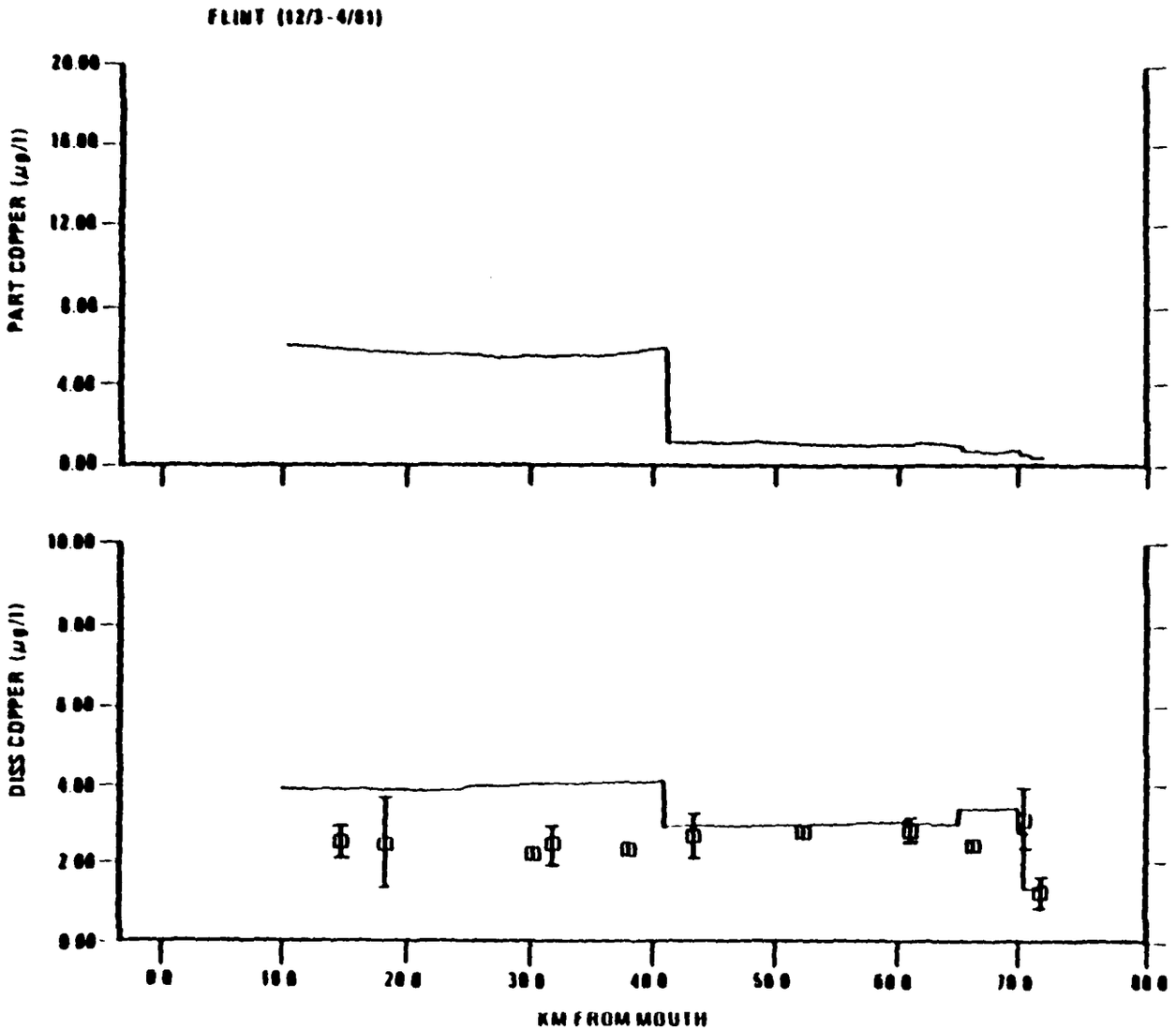
FLINT (12/3-4/81)
PART COPPER (µg/l)
20.00
16.00
12.00
8.00
4.00
0.00
DISS COPPER (µg/l)
10.00
8.00
6.00
4.00
2.00
0.00
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
KM FROM MOUTH

FIGURE 5.4.12

TABLE 5.5.1. SAMPLING STATION FOR MARCH 1981 FLINT RIVER HEAVY METALS SURVEY

Station/Description	Km. Point
FR0006/Mill Road river station	71.9
FE0002/Flint WWTP discharge	70.7
FE00A1/Flint Fly Ash Pond discharge	70.0
FE00A2/Flint Fly Ash Pond discharge	70.0
FR0008/Elms Road river station	66.3
FR0022/Mud Creek tributary	64.4
FR0023/Cole Creek tributary	60.2
FR0010/Mt. Morris Road river station	52.6
FR0024/Brent Creek tributary	50.6
FR0025/Armstrong Creek tributary	44.6
FR0011/Vienna Road (M-57) river station	43.5
FR0012/Brent Run tributary	41.6
FE0003/Ragnone WWTP discharge	41.1
FR0020/Birch Run Road river station	30.5
FR0017/Pine Run tributary	29.7
FR0014/Silver Creek tributary	25.2
FR0015/M-13 river station	14.9

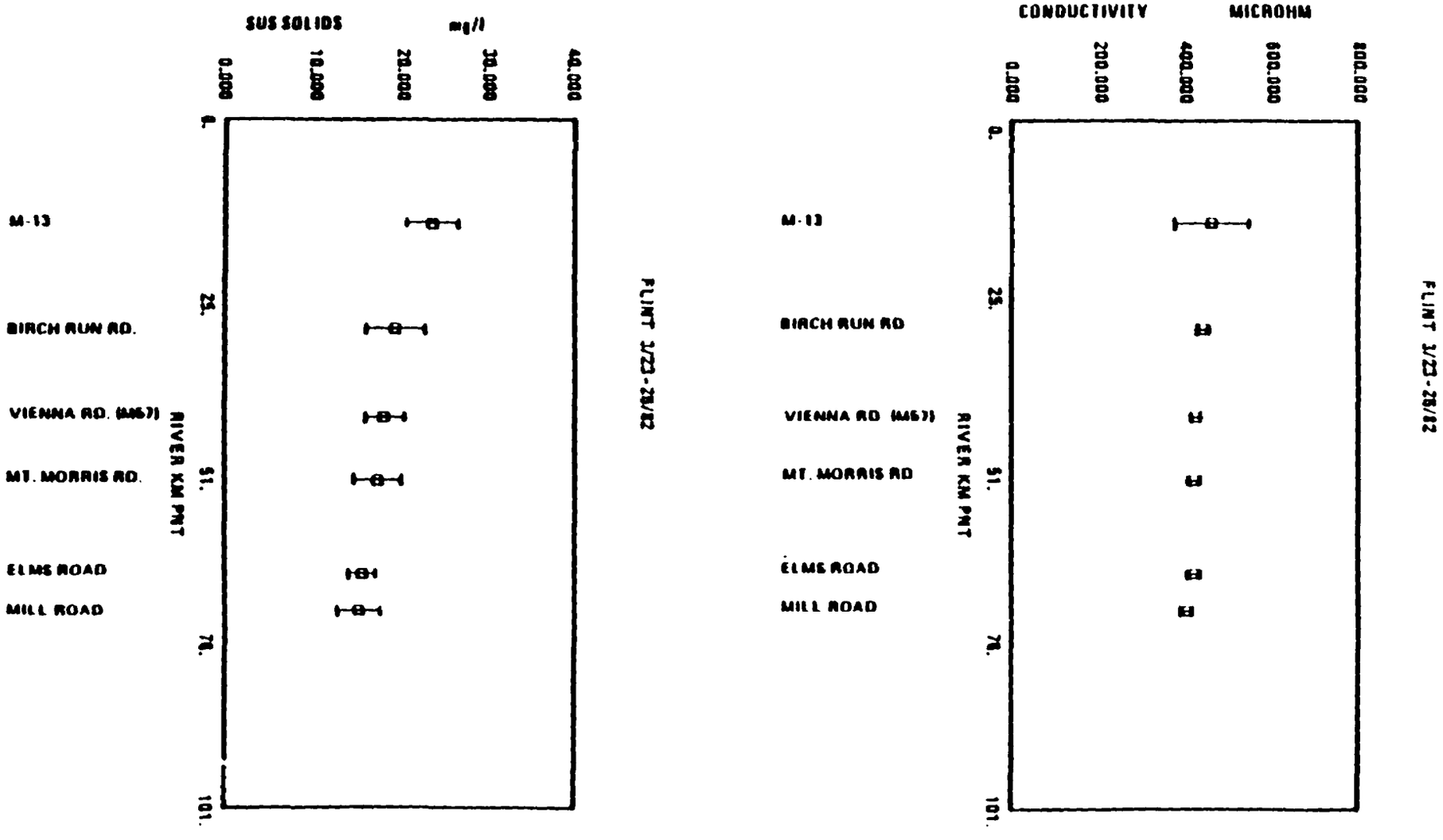
CONDUCTIVITY MICROHM
800.000
600.000
400.000
200.000
0.000
0.
25.
51.
76.
101.
M-13
BIRCH RUN RD
VIENNA RD (M57)
MT. MORRIS RD
ELMS ROAD
MILL ROAD
RIVER KM PNT
FLINT 3/23-28/82
SUS SOLIDS mg/l
40.000
30.000
20.000
10.000
0.000
0.
25.
51.
76.
101.
M-13
BIRCH RUN RD.
VIENNA RD. (M57)
MT. MORRIS RD.
ELMS ROAD
MILL ROAD
RIVER KM PNT
FLINT 3/23-28/82

FIGURE 5.5.1

TABLE 5.5.2. HYDROLOGIC AND MORPHOMETRIC INPUTS FOR FLINT RIVER MARCH 1982 HEAVY METAL MODELING APPLICATION

Segment Number	Boundary	Km. Point	Segment Flow (m^3/s)	Cross-Sectional Area (m^2)	Mean Dep (m)
	Mill Road	71.9			
1			93.4	97.5	1.8
	Flint WWTP	70.7			
2			96.1	95.0	1.8
	Flint Fly Ash Discharge	70.0			
3			96.25-99.9	90.0	1.5
	Cole Creek	60.0			
4			100.7-106.4	110.	1.5
	Armstrong Creek	44.6			
5			107.7	96.0	1.6
	Ragnone WWTP	41.1			
6			110.3-111.7	109.	1.6
	Upstream of East Burt Rd.	36.0			
7			111.7-113.5	85.0	1.8
	Pine Run	29.7			
8			115.5	115.	2.2
	Silver Creek	25.2			
9			117.5	120.	2.2
	M-13	14.9			

TABLE 5.5.3. UPSTREAM CONDITIONS AND POINT SOURCES TO FLINT RIVER
MEAN LOADS FOR MARCH 23-26, 1981

Source	Discharge Flow (m^3/s)	Discharge Concentration and Load							
		Suspended Solids		Total Zinc		Total Cadmium		Total Copper	
		(mg/ℓ)	(kg/d)	(μg/ℓ)	(gm/d)	(μg/ℓ)	(gm/d)	(μg/ℓ)	(gm/d)
Upstream Boundary Mill Road	93.4	15.5	125,000	7.24	58,400	0.025	202.	2.48	20,000
Flint WWTP	2.66	5.35	1220.	71.0	16,300	0.11	25.5	18.2	4190.
Flint Fly Ash Ponds	0.18	5.84	88.2	120.	1810.	0.93	22.5	71.4	1080.
Brent Run	1.51	13.4	1740.	10.6	1380.	0.032	4.16	5.14	668.
Ragnone WWTP	1.12	50.9	4920.	59.7	5780.	0.257	24.9	27.8	2690.
Pine Run	2.0	14.0	2420.	7.0	1210.	0.03	5.19	2.0	346.
Silver Creek	2.0	14.0	2420.	7.0	1210.	0.03	5.19	2.0	364.
Mud Creek	0.35	7.6	228.	7.0	211.	0.007	0.21	2.38	71.9
Cole Creek	0.46	9.0	359.	6.5	258.	0.007	0.28	2.07	82.2
Brent Creek	0.48	11.4	472.	6.0	249.	0.045	1.87	2.70	112.
Armstrong Creek	0.76	15.1	993.	7.0	460.	0.03	1.97	1.98	130.

Because of the expected short travel time for the study reach in March - it turned out to be about 16 hours - and because of the high possibility of encountering rapid time variations during the monitoring, the survey strategy was to sample fewer river stations more frequently. Also, more tributaries were added to the list in case surface runoff in the study reach was a significant source of solids and associated metals. All river stations were sampled every 4 hours, tributaries were sampled every 12 hours, and 4-hour composites were collected from point source effluents during the 72-hour survey. A list of the sampling stations for the March survey is presented in Table 5.5.1.

5.5.1 March Survey Data Summary

During the 72-hour March survey the Flint River flow was receding somewhat from the flood stage recorded during the rapid snowmelt. For example, the discharge at the furthest downstream station (M-13) dropped from approximately 4500 cfs to 3800 cfs during the survey. This roughly 15 percent flow decrease, however, did not appear to negate the possibility of applying the steady-state model to the data, as evidenced by the relatively narrow spread of conductivity and suspended solids values at each river station, as illustrated in Figure 5.5.1. Based on the hydrological and morphological data collected during the survey, therefore, the segmentation, river flow and geometry used as input for the steady-state model are given in Table 5.5.2.

Initial conditions and loads obtained for the March survey are presented in Table 5.5.3. It is apparent that flow and loads at the upstream boundary exceed the flow and loads of all point sources and tributaries combined.

5.5.2 March Survey Model Calibration

The results of calibration of the model to the March survey data are presented in Figures 5.5.2 - 5.5.6. The calibration was done using

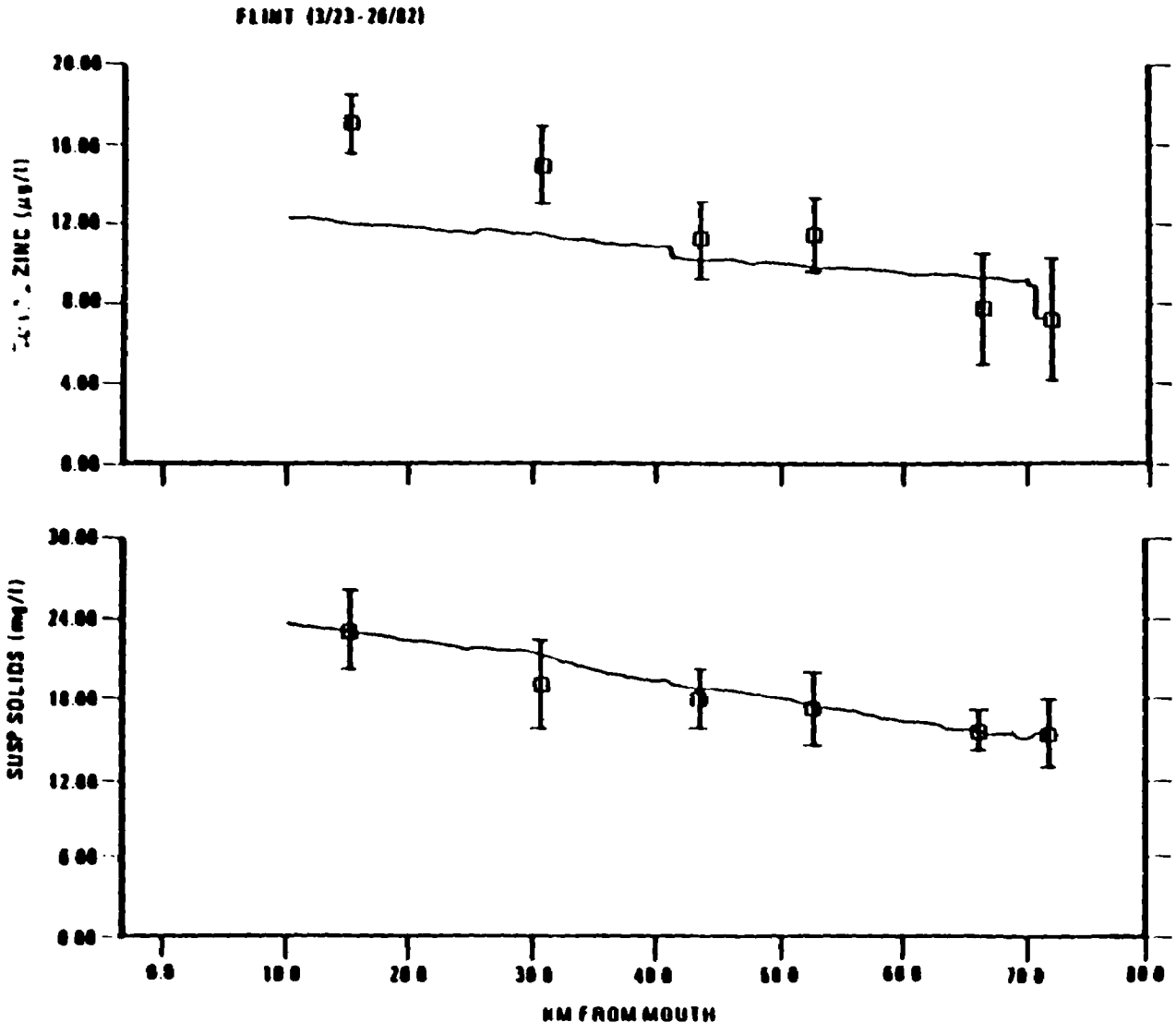
FLINT (3/23-26/82)
ZINC (µg/l)
20.00
16.00
12.00
8.00
4.00
0.00
SUSP SOLIDS (mg/l)
30.00
24.00
18.00
12.00
6.00
0.00
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
KM FROM MOUTH

FIGURE 5 5 2

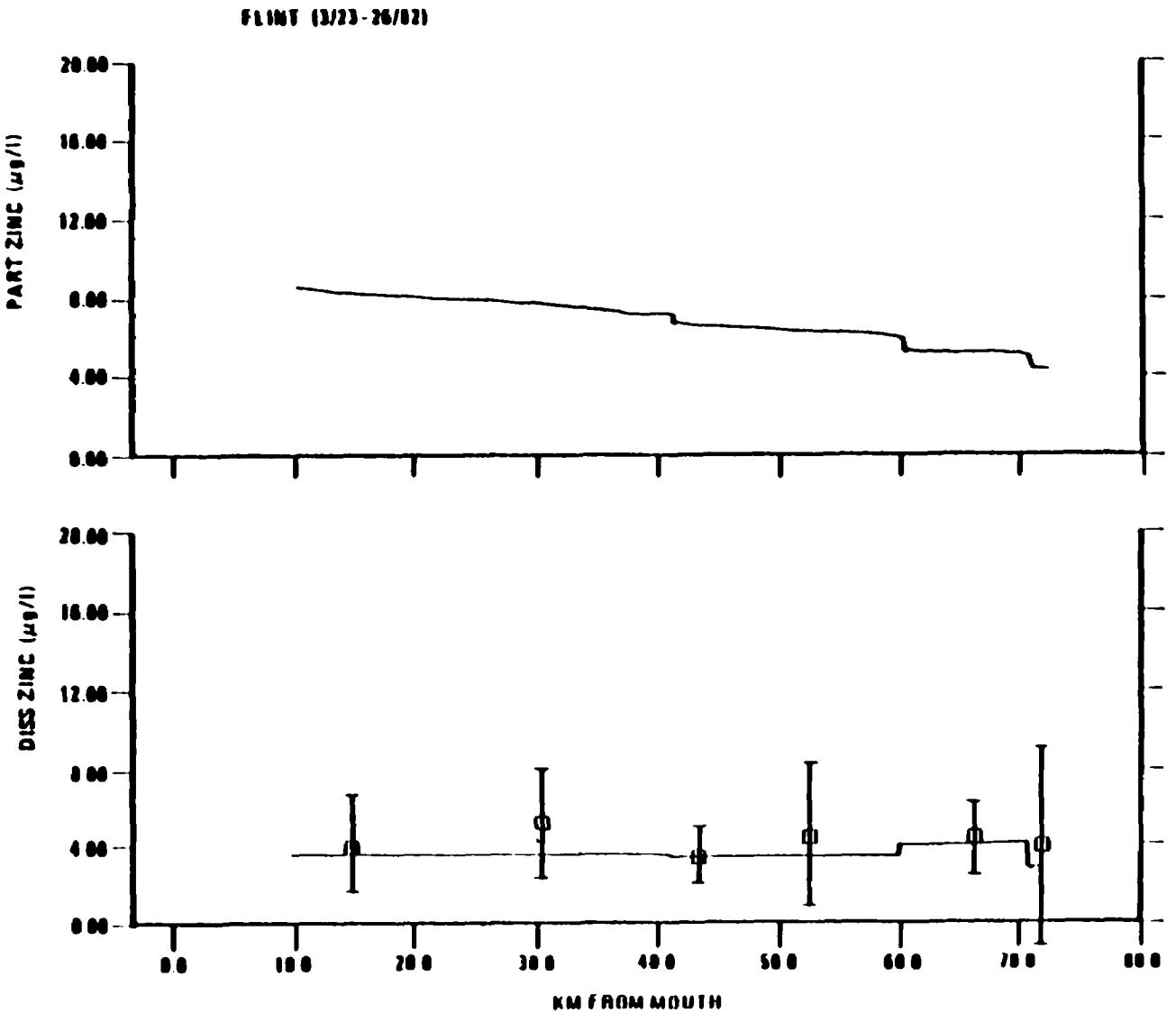
FLINT (3/23-26/82)
PART ZINC (µg/l)
20.00
16.00
12.00
8.00
4.00
0.00
DISS ZINC (µg/l)
20.00
16.00
12.00
8.00
4.00
0.00
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
KM FROM MOUTH

FIGURE 5.5.3

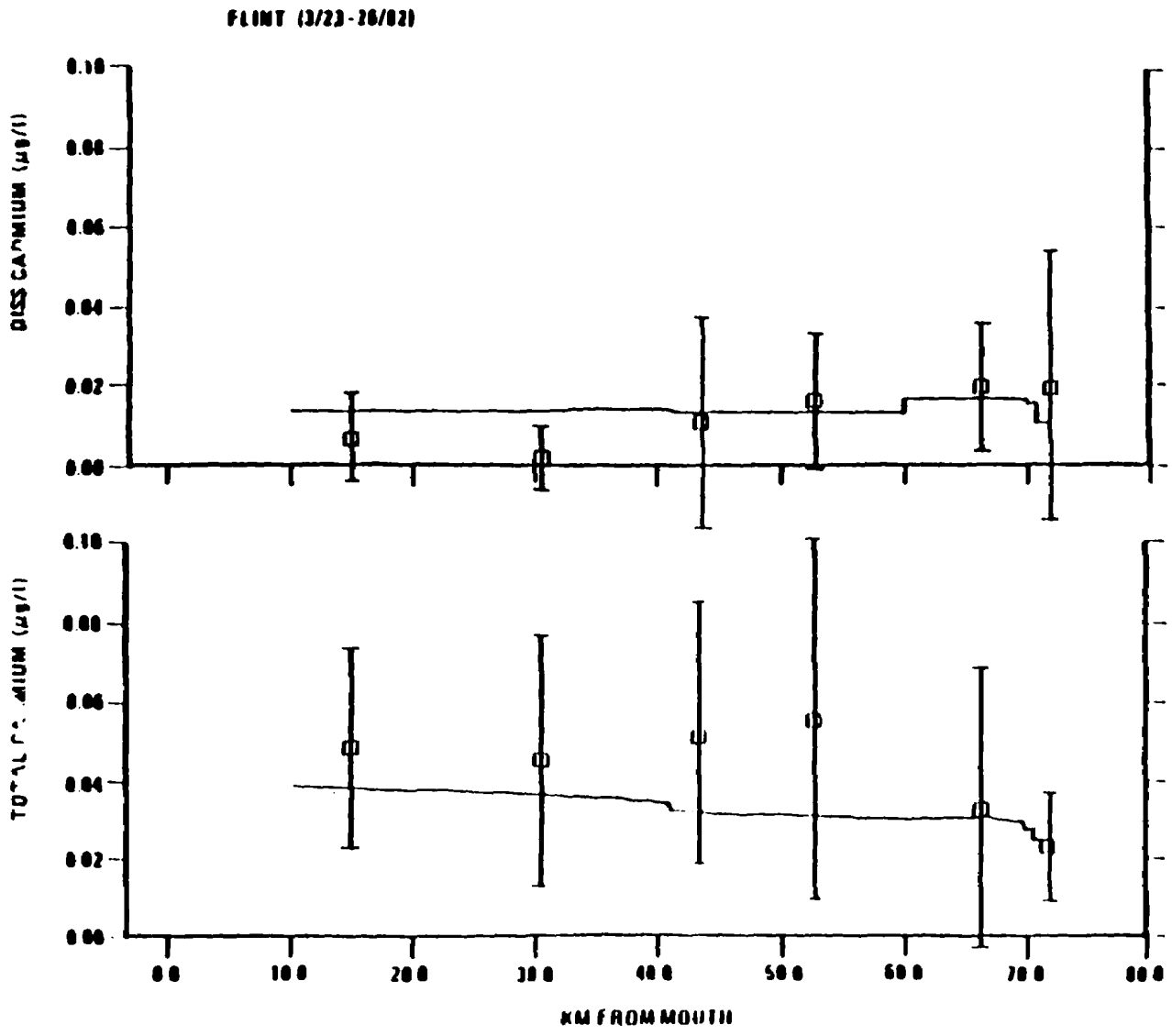
FLINT (3/23-26/82)
DISS CADMIUM (µg/l)
TOTAL CADMIUM (µg/l)
0.10
0.08
0.06
0.04
0.02
0.00
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
KM FROM MOUTH

FIGURE 5.5.4

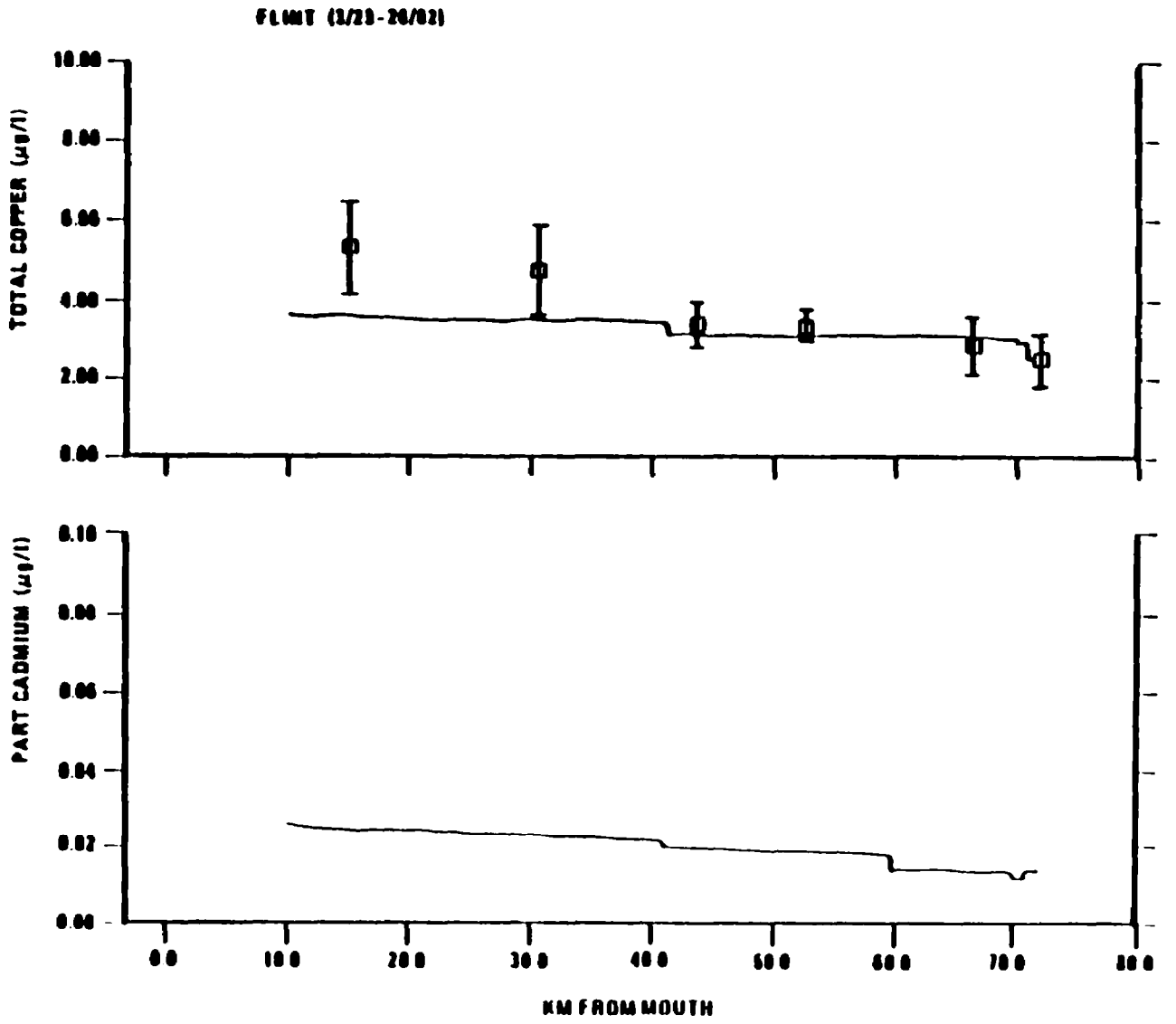
FLINT (3/23-26/82)
TOTAL COPPER (µg/l)
10.00
8.00
6.00
4.00
2.00
0.00
PART CADMIUM (µg/l)
0.10
0.08
0.06
0.04
0.02
0.00
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
KM FROM MOUTH

FIGURE 5.5.5

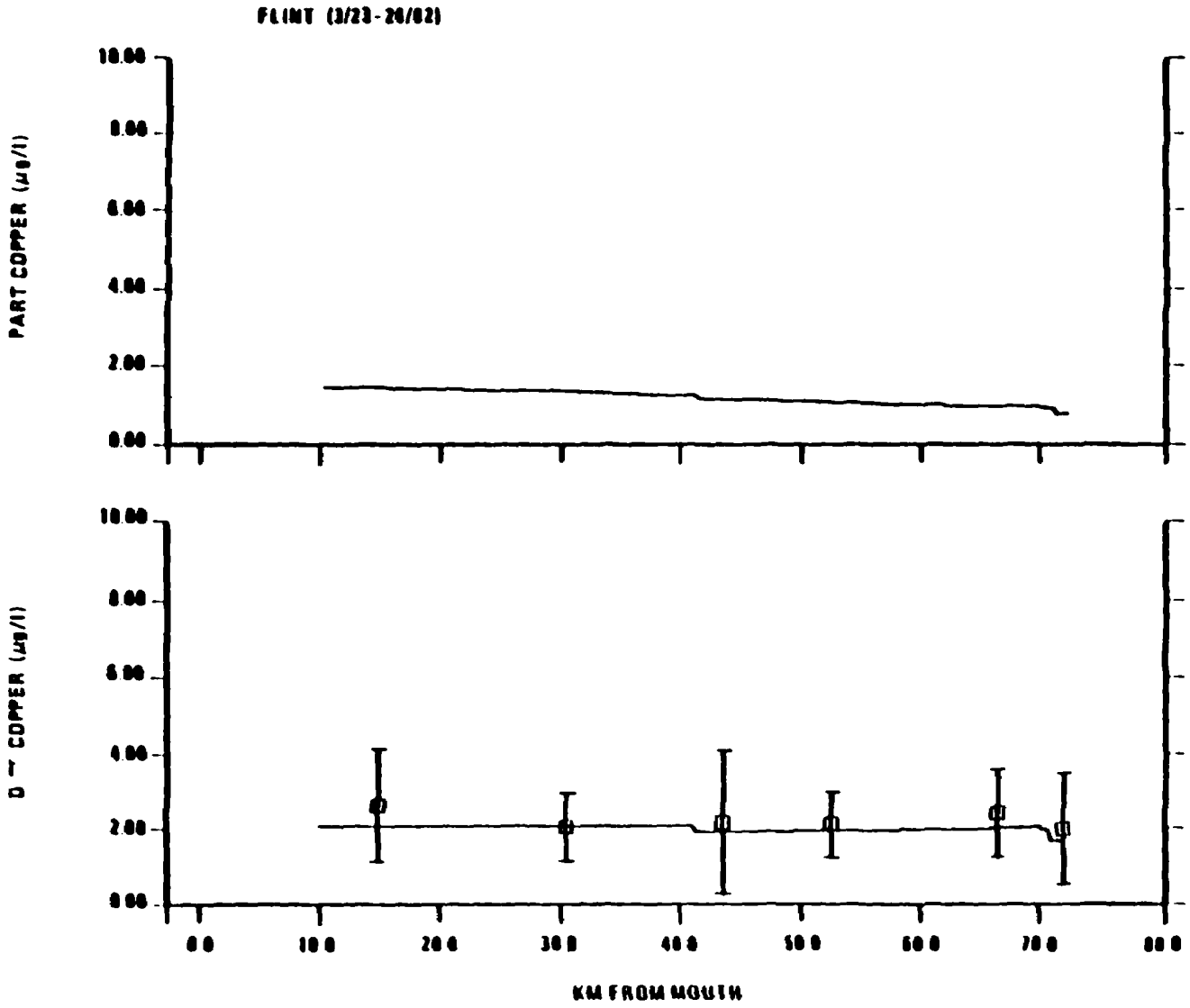
FLINT (3/23-26/82)
PART COPPER (µg/l)
D ~ COPPER (µg/l)
10.00
8.00
6.00
4.00
2.00
0.00
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
KM FROM MOUTH

FIGURE 5.5.6

larger settling and resuspension velocities than used in previous surveys. The more significant increase, however, was in the resuspension velocity, resulting in a net flux of solids from sediment to overlying water throughout the study reach.

The calibration coefficients for the solids transport submodel are given in Table 5.5.4. A large gross settling velocity would be expected in a system transporting larger particles. The increase in resuspension rates in all segments is justified by the large increase in calculated bottom shear stress over the December values, as shown in Table 5.5.4. In general, there is a reasonably good correlation between bottom shear stress and calibrated resuspension rate for a given river segment. Although only three data points were available (one for each survey), they did seem to follow a linear trend, as shown for three sample segments shown in Figure 5.5.7.

Calibration of the metals data by adjusting water column partition coefficients also produced reasonably predictable results. With presumably larger solids being transported with much of the material originating from the river bottom, one might expect to see slightly lower water column partition coefficients than were observed at lower flow conditions. This hypothesis was confirmed by comparing the final calibration partition coefficients to average observed values for each metal at each river station during the survey (Figure 5.5.8). The calibration values tend to be slightly lower then the measured values; however, this observation is often made in natural systems since measured values of total particulate metals tend to include a certain portion that does not readily exchange with the bulk solution.

TABLE 5.5.4. CALIBRATION COEFFICIENTS FOR SOLIDS TRANSPORT DURING MARCH 1981 FLINT RIVER SURVEY

Segment	Settling Velocity (m/d)	Resuspension Velocity (m/d)	Bottom Shear Stress (dynes/cm)
1	0.8	1.0×10^{-4}	92.5
2	0.8	1.0×10^{-4}	92.5
3	0.8	2.0×10^{-4}	127.
4	0.8	2.0×10^{-4}	94.3
5	0.8	2.0×10^{-4}	108.
6	0.8	2.0×10^{-4}	108.
7	0.8	4.0×10^{-4}	176.
8	0.8	3.0×10^{-4}	115.
9	0.8	3.0×10^{-4}	115.

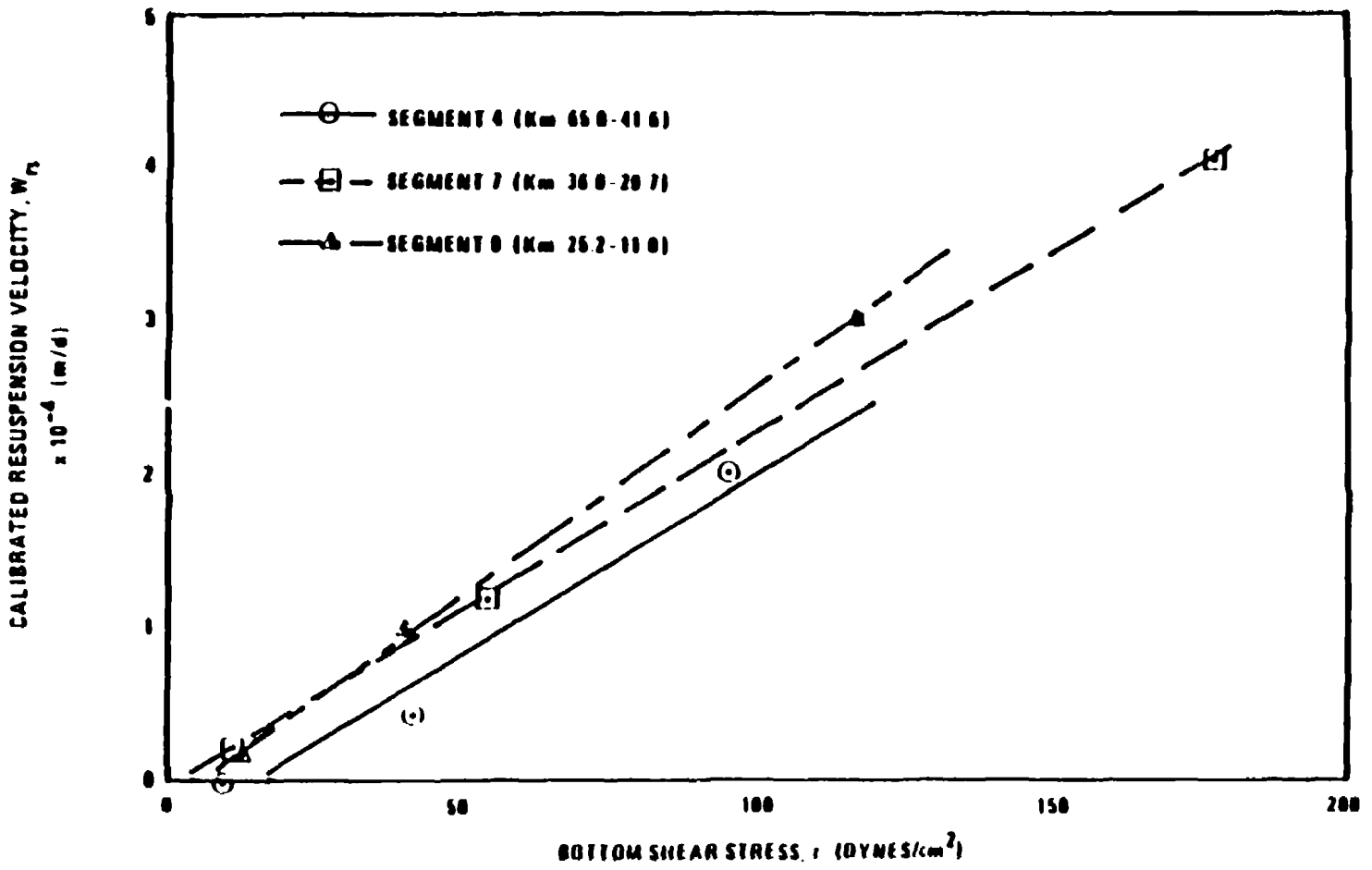

FIGURE 5.5.7 RELATIONSHIP BETWEEN CALIBRATED RESUSPENSION VELOCITY AND BOTTOM SHEAR STRESS UNDER THREE FLOW REGIMES IN THE FLINT RIVER

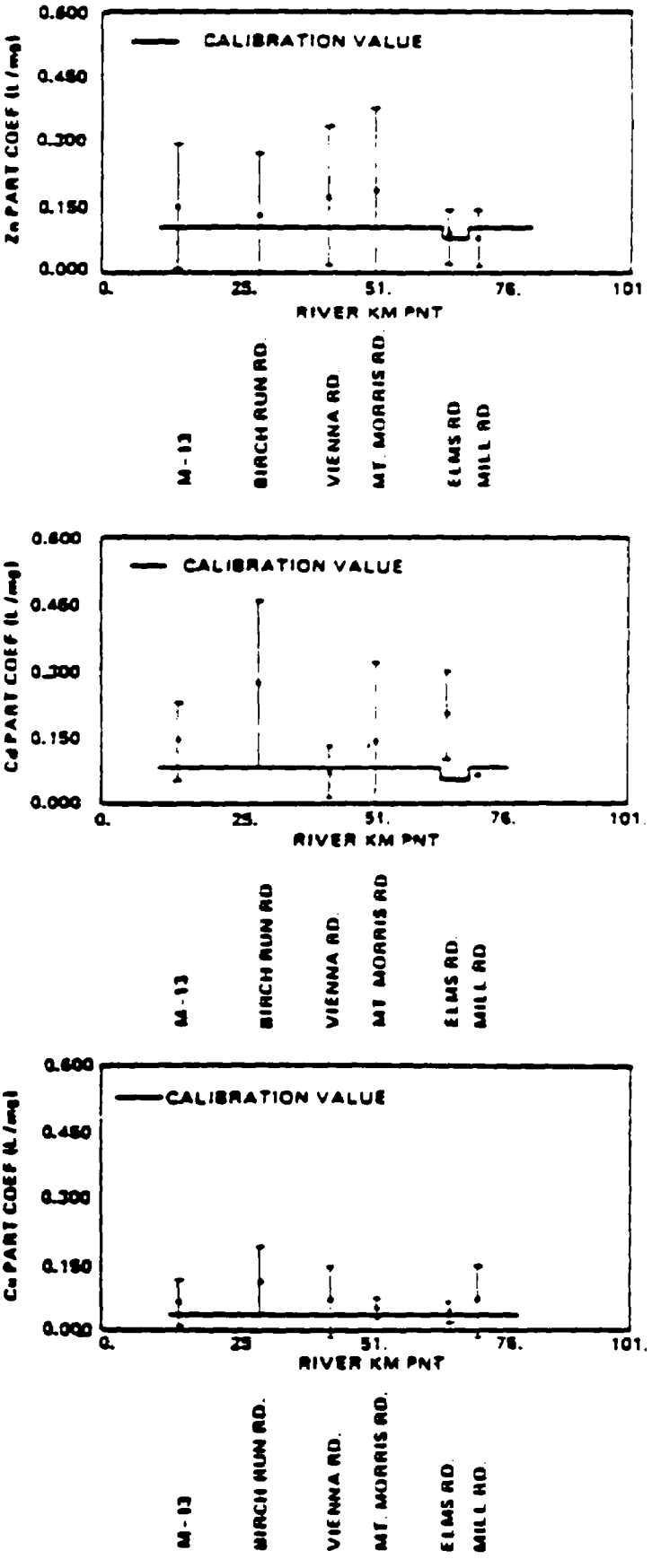
CALIBRATION VALUE
Zn PART COEF (L/mg)
0.600
0.450
0.300
0.150
0.000
0.
25.
51.
76.
101
RIVER KM PNT
M-13
BIRCH RUN RD.
VIENNA RD.
MT. MORRIS RD.
ELMS RD.
MILL RD.
CALIBRATION VALUE
Cd PART COEF (L/mg)
0.600
0.450
0.300
0.150
0.000
0.
25.
51.
76.
101.
RIVER KM PNT
M-13
BIRCH RUN RD.
VIENNA RD.
MT. MORRIS RD.
ELMS RD.
MILL RD.
CALIBRATION VALUE
Cu PART COEF (L/mg)
0.600
0.450
0.300
0.150
0.000
0.
25.
51.
76.
101.
RIVER KM PNT
M-13
BIRCH RUN RD.
VIENNA RD.
MT. MORRIS RD.
ELMS RD.
MILL RD.

FIGURE 5.5.8

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APPENDIX A

DEVELOPMENT OF MODEL EQUATIONS

August 1984

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DEVELOPMENT OF MODEL EQUATIONS

A.1 CONSERVATIVE POLLUTANT

The basic assumption in the conservative substance model is that there are no internal source/sink reactions that significantly affect the toxic substance concentration in the receiving water. Only external sources of the contaminant, or inflow of dilution water by advection or dispersion can alter the contaminant conconcentration, according to this conservative assumption.

Under the conservative substance assumption, and assuming that longitudinal dispersion is negligible relative to advective transport, the general river transport equation reduces to

$$\frac{dC}{dt} = \frac{1}{A} \frac{d(QC)}{dx} \tag{A1}$$

Furthermore, application of Equation A1 is almost always made under the assumption that the river reach in question is at steady-state with a constant, continuous point discharge of the contaminant in question. Also, flow is assumed to be constant over the reach. Under these assumptions, the solution for Equation A1 is simply

$$\begin{aligned} C(x) &= C_o; \quad x \geq 0 \\ C(x) &= C_u; \quad x < 0 , \end{aligned} \tag{A2}$$

where C_u = upstream river concentration of contaminant and C_o = river contaminant concentration at x = 0 after mixing upstream river water with point discharge. The concentration, C_o, is determined by performing a mass balance for C at x = 0, assuming instantaneous mixing at that point. Therefore, C_o is

calculated from C_u, the point source concentration (C_w), the point source flow (Q_w), and upstream river flow (Q_u) as follows:

$$C_o = \frac{[Q_u \cdot C_u] + [Q_w \cdot C_w]}{Q_u + Q_w} \qquad \text{(A3)}$$

Given the above assumptions, C_o is independent of x downstream of the effluent unless there is another downstream discharge of the substance or a dilution of the substance by inflow of uncontaminated diluting water. Multiple point discharges can be handled reapplying Equation A3 at each successive discharge point, using the result of the previous discharge mass balance as the upstream boundary conditions.

There is a large body of literature which suggests that most priority pollutants do not behave conservatively in water bodies. Recent results from dynamic mass balance modeling studies of heavy metals and several synthetic organics in the Great Lakes have indicated nonconservative behavior (Dolan and Bierman, 1981; Richardson, et al., 1983; and Rodgers, 1981). Flint River data (presented later in this section) collected by Michigan DNR in 1978 demonstrated that total zinc and copper did not behave conservatively in certain stretches of the river. Unless advective transport in a given reach is rapid relative to the transport and transformation processes discussed in Section 2.2 or unless relevant internal source/sink fluxes just balance, the instream concentration of a pollutant is likely to vary with longitudinal distance.

A.2 NONCONSERVATIVE POLLUTANT - SIMPLE WATER COLUMN ANALYSIS

Often the net result of the combined effects of transport and transformation forces acting on a chemical substance is a first-order die-off of the substance with distance (or time-of-travel) downstream from a discharge. This type of concentration profile can be simulated by lumping several processes into a single first-order loss term applied to the general river transport equation. Given this approach

$$\frac{dC}{dt} = E^2 \frac{d^2C}{dx^2} - \frac{Q}{A}\frac{dC}{dx} - K_T C \ . \qquad (A4)$$

where K_T [time^{-1}] is an aggregate first-order decay coefficient for the substance in question.

Several further assumptions are often involved in applying the above equation to a specific site. They are as follows:

1) The river is at steady-state with respect to flow and loads;

2) Concentration of the modeled substance is uniform over the cross-section of the river (i.e., one dimensional system); thus, any point discharge instantaneously mixes with the river flow at the point of discharge;

3) Dispersion is negligible in the longitudinal direction; that is, only advection is considered significant in the direction of flow; thus, E = 0 in equation A4;

4) Flow, cross-sectional area, and mean depth are constant over the reach in question.

Given the above assumptions, Equation A4 reduces to

$$0 = -\frac{Q}{A}\frac{dC}{dx} - K_T C \ . \qquad (A5)$$

The solution to Equation A5 is

$$C(x) = C(0)\exp\left(\frac{-K_T x}{U}\right) \qquad (A6)$$

where, U = Average river velocity in reach [length/time]

C(0) = Initial concentration of the modeled substance at x = 0 [mass/length^3].

This approach limits itself to only the water column and only one form of the pollutant.

There are two methods for applying Equation A6 to a problem of multiple discharges in a river system. Since Equation A5 is an ordinary,

linear differential equation, the independent solutions for individual point sources can be additively superimposed to obtain a total concentration profile along the river. Alternatively, the river reach in question can be segmented according to significant changes in river geometry or flow, or at locations of point sources. Then each segment is modeled sequentially moving downstream. The initial (upstream) concentration of each segment is determined by the concentration entering from the upstream segment, augmented by any effluent load entering at the segment boundary.

Great care must be taken in applying this type of model to a specific site without enough field data to confirm the validity of the aggregate decay coefficient. K_T for a particular pollutant may vary from site to site, or may vary over time due to changes in controlling parameters like flow or river cross-sectional geometry.

Application of Model to Flint River August 1978 Data--

As a brief example of analyzing a system with first-order decay model of the water column, metals and suspended solids data obtained during a preliminary survey of the Flint River will be compared to the model presented above. In this application the aggregate first-order coefficient, K_T, is assumed to be an apparent net settling velocity from the water column; therefore,

$$K_T = v_s/H \quad . \tag{A7}$$

where, K_T= First-order loss rate coefficient of total metal or suspended solids [time^{-1}],

v_s= Apparent net settling velocity [length/time],

H = Mean depth of river [length].

The study reach of the Flint River used in this investigation was from the Utah Street Dam in the city of Flint (Km 83.6) to the bridge at Crosswell Road (Km 11.0). Data on river metals and solids concentrations

and point source inputs were obtained from a Michigan DNR survey conducted in August of 1978 (Roycraft and Buda, 1979). Table A1 is a summary of the point discharges considered in this study, and Table A2 contains the river hydrology and geometry at the time of sampling. As indicated in Table A2, the river reach has been divided into four segments.

Figures A1 through A3 contain the survey data and model predictions for total zinc, total copper, and suspended solids, respectively. In attempting to simulate the data points in these figures, the only parameter that was varied was the net apparent settling velocity, v_s, which determines the stream concentration through Equations A7 and A6. Of course, when v_s is set equal to zero, it implies that the pollutant is transported conservatively down the river. All other parameters, those in Tables A1 and A2, and the initial upstream conditions were held constant.

It is apparent that none of the three substances behaved conservatively within the entire study reach; the conservative assumption considerably over-predicts the downstream concentrations. This type of error could be especially important in situations where a waste load must be allocated among multiple discharges along a river reach, since the conservative pollutant assumption omits the effect of depuration occurring between points of discharge.

In the segment between the Flint WWTP and the Ragnone plant (Km 70.7-41.1), total zinc appears to settle at an apparent rate of 1.0 m/d, while total copper is lost at a rate close to 0.5 m/d. The apparent settling rate for zinc in this segment may be slightly less than 1.0 m/d, or there may have been an unaccounted for source of zinc at about kilometer 46. The available data base did not permit this distinction. The suspended solids data and simulations (Figure A3) confirm the metal findings. In the segment between Flint and Ragnone plants, solids are settling at a rate between 1.0 and 1.25 m/d. The larger net settling rate observed for solids is consistent with the assumption that not all

TABLE A1. POINT DISCHARGES FOR AUGUST 1978 SURVEY

Source	Km	Flow (m /s)	Loadings (kg/d) Total Zinc	Total Cu	Suspended Solids
G.M./Buick	83.4	0.09	0.77	0.48	-
Flint WWTP	70.7	0.86	29.0	3.6	2,710
Ragnone WWTP	41.1	0.84	11.0	4.0	8,000

TABLE A2. FLINT RIVER HYDROLOGY AND GEOMETRY FOR AUGUST 1978 SURVEY

Segment	Starting Point (Km)	Segment Length (Km)	Mean Depth (m)	Cross-Sectional Area (m2)	Flow (m /s)
1	83.4	1.5	3.0	140	6.2
2	81.9	11.2	0.66	30	6.2
3	70.7	29.6	0.66	30	7.06
4	41.1	30.1	1.0	30.6	7.9

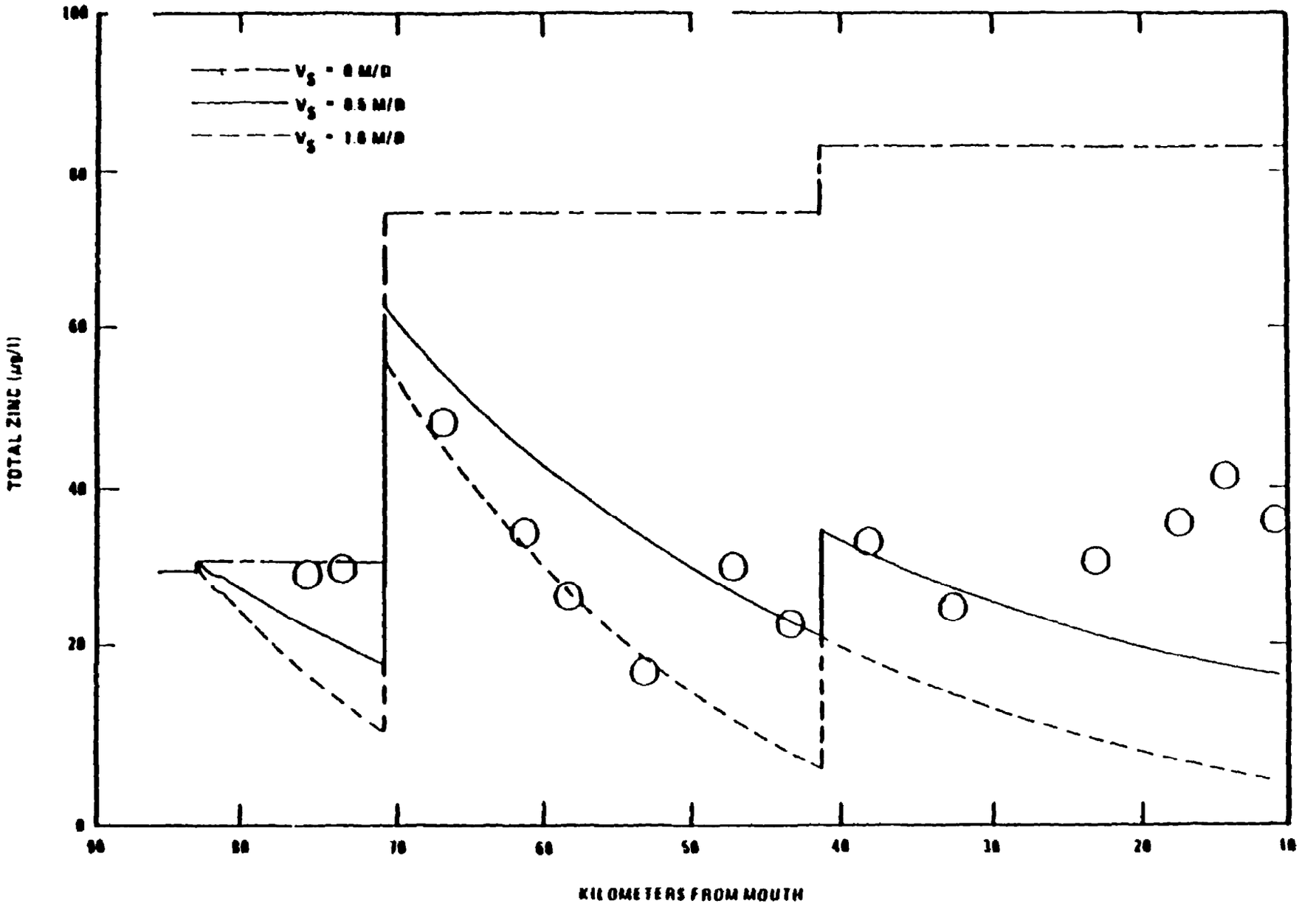

FIGURE A1 TOTAL ZINC CONCENTRATION IN FLINT RIVER VERSUS DISTANCE FROM MOUTH. DATA POINTS ARE FROM MICHIGAN DNR SURVEY OF AUGUST 1978.

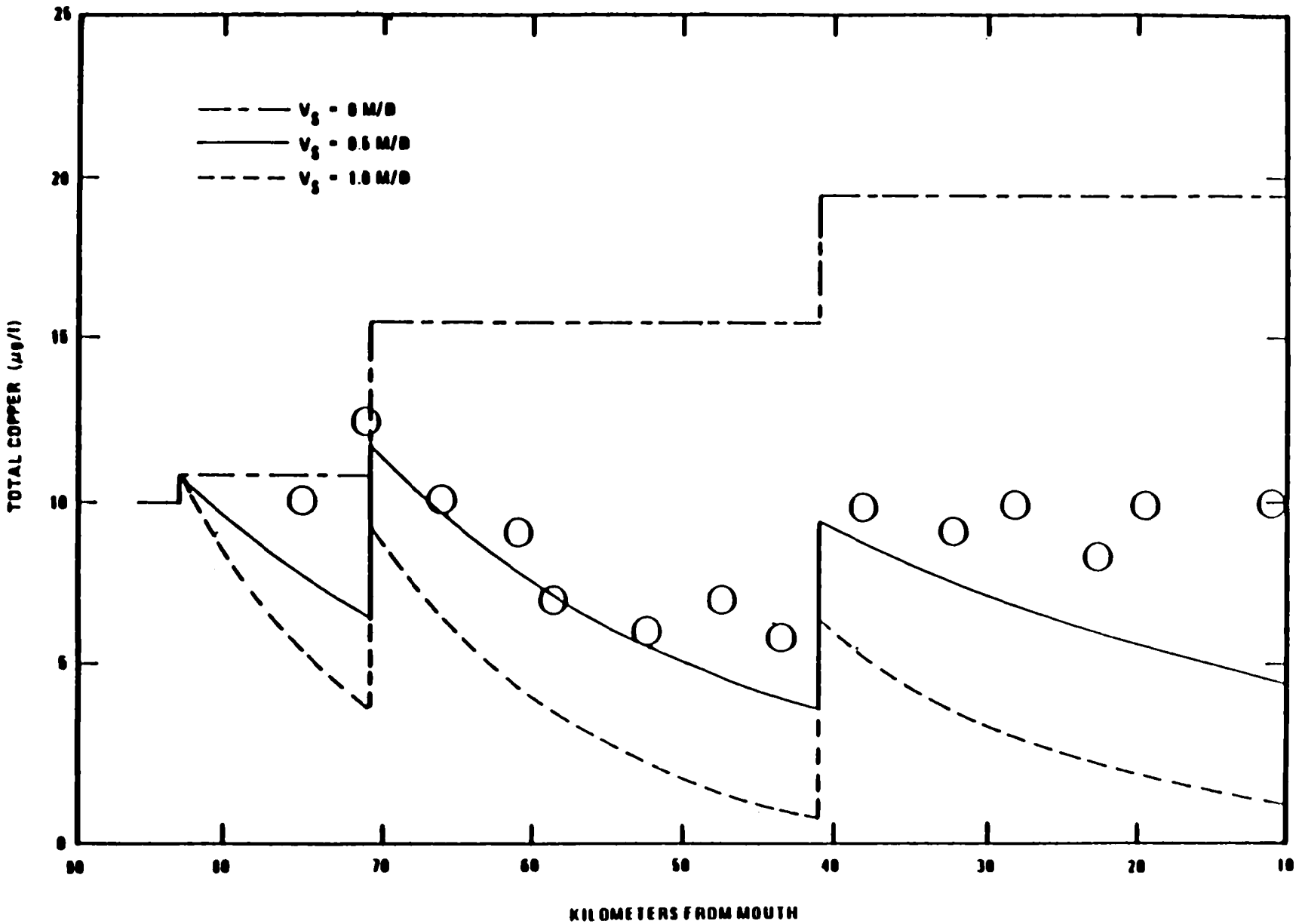

FIGURE A2 TOTAL COPPER CONCENTRATION IN FLINT RIVER VERSUS DISTANCE FROM MOUTH
DATA POINTS ARE FROM MICHIGAN DNR SURVEY OF AUGUST 1978.

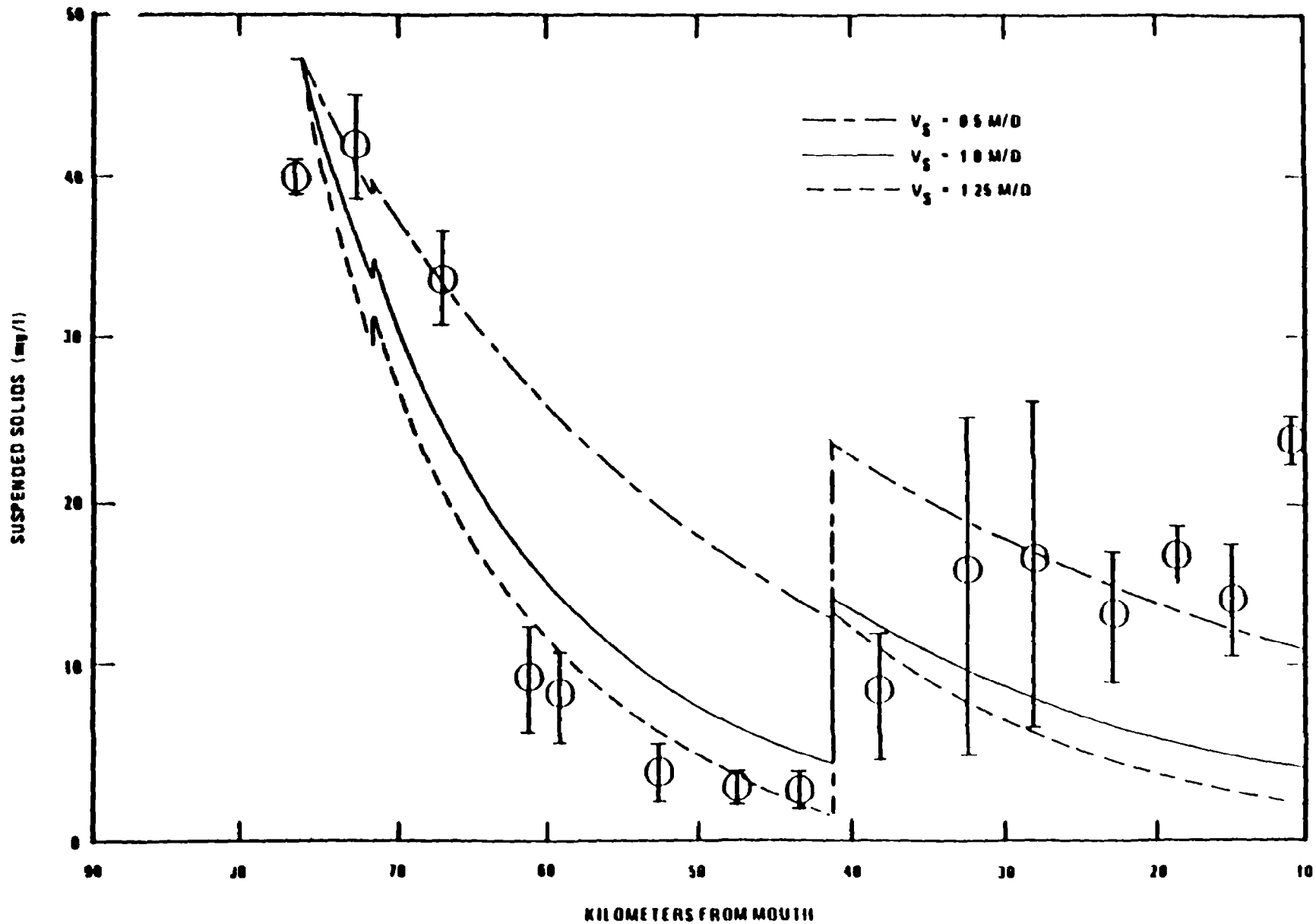

FIGURE A3 SUSPENDED SOLIDS IN FLINT RIVER VERSUS DISTANCE FROM MOUTH
DATA POINTS ARE TAKEN FROM MICHIGAN DNR SURVEY OF AUGUST 1978

the metals in the river are in a particulate form; therefore, the apparent settling rate for metals should be somewhat less than for suspended solids. Furthermore, the finer-grained, slower-settling particulates probably have a higher metals content than the larger, sand size particulates.

Some difficulty was encountered in simulating the data downstream of the Ragnone discharge for all three substances. If the data set is in fact representative of a steady-state condition in this segment (a fact which cannot be established from such a small sampling), then it appears that the net loss of metals and solids in this reach was close to zero. This could have been the result of sediment resuspension in this segment due to higher water velocities. This behavior is addressed further in Section 5.0, which is a case study of the more extensive 1981-82 Flint data.

Finally, it is quite apparent that the metals' behavior in the river is closely related to the suspended solids' behavior. This observation, coupled with the need to know the exposure of aquatic biota to dissolved contaminant concentrations, leads to the rationale for the somewhat more complicated approach described next.

A.3 WATER-SEDIMENT MODEL HAVING SEPARATE PARTICULATE AND DISSOLVED CONTAMINANT PHASES

One of the most significant mechanisms for the movement of pollutants through an aquatic environment is the adsorption or uptake of the chemical by both nonviable and viable particulate matter, followed by the transport of the interacting particulates. Association with suspended matter thus significantly alters the transport regime of a chemical by introducing additional transport processes, such as settling and resuspension. Furthermore, the association with suspended matter can indirectly affect the rate and extent of chemical transformations and biotic accumulations. For example, partitioning of a portion of a chemical in suspended solids could reduce the flux of the chemical's dissolved phase into the biota, thus potentially reducing its toxicity. Accordingly, determination of the fate and potential toxicity of

pollutants in aquatic systems requires knowledge of two important processes: 1) partitioning of metals between dissolved and particulate phases in aquatic systems, and 2) transport of particulate matter (i.e., settling and resuspension) as affected by hydraulics and particulate physical properties.

A conceptual diagram of the MICHRIV model is presented in Figure A4; nomenclature is presented in Table A3. Note that the calculation scheme permits the estimation of the equilibrium partitioning of total chemical between dissolved and solid phases in both the water column and the sediment bed. With this approach it is necessary either (a) to specify the (water column) suspended solids concentration as a parameter, or (b) to model suspended solids as a state variable. The former approach is used in the SLSA model; the latter approach, described below, is used in the MICHRIV model.

Settling, resuspension, and burial apply only to the particulate bound pollutant. Diffusion between the sediment pore water and water column applies only to the dissolved phase. The first-order decay coefficient represents the sum of a number of potential processes, most of which are insignificant for metals in streams. For organics, however, the loss rate can include volatilization, hydrolysis, photolysis, chemical oxidation, and biodegradation (described in Section 3).

In the current version of the MICHRIV model the decay coefficient applies only to the dissolved phase. Volatilization is a process that clearly applies only to the dissolved phase. While hydrolysis, photolysis, oxidation, and biodegradation may often be far more rapid in the dissolved than in the adsorbed phase, there seems to be no consensus that this is true in all cases. Consequently, to maintain generality the decay coefficient for total pollutant, K, has been formulated below as the weighted sum of dissolved and particulate phase decay coefficients, $K_d f_d + K_p f_p$ (with appropriate subscripts 1 or 2).

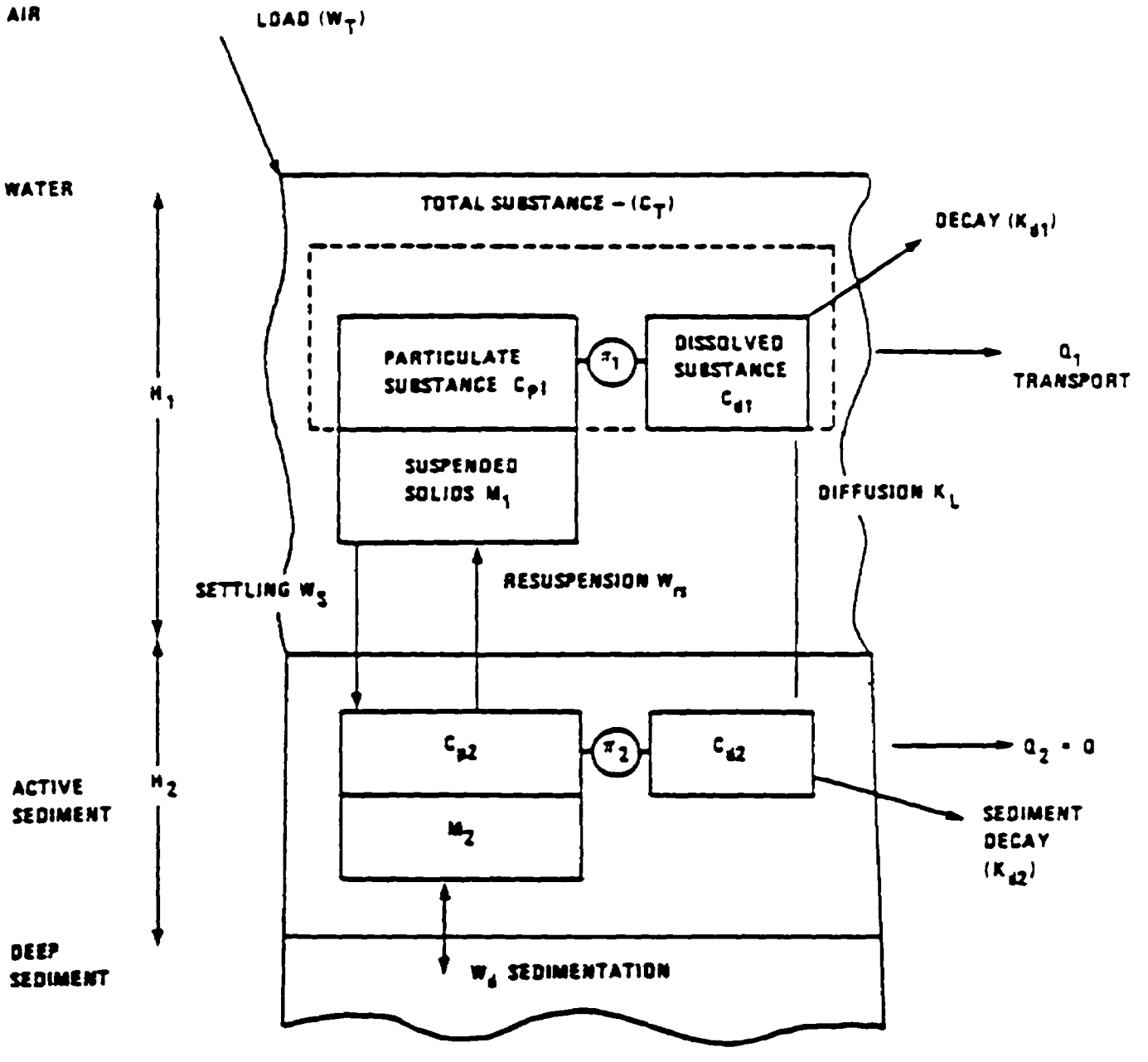

FIGURE A4. MICHRIV FRAMEWORK

TABLE A3: NOMENCLATURE FOR WATER-SEDIMENT MODEL

Parameters	Water Column	Sediment
<u>Concentrations</u>		
Total toxicant (μg/ℓ)*	C_{T1}	C_{T2}
Dissolved toxicant (μg/ℓ)*	C_{d1}	C_{d2}
Particulate toxicant (μg/ℓ)*	C_{p1}	C_{p2}
Particulate toxicant (g toxicant/ mg solids)	r_1	r_2
Total solids (mg/ℓ)*	m_1	m_2
Toxicant load (kg/day)	W_T	---
Sediment porosity	---	ϕ
<u>Partitioning</u>		
Dissolved fraction	f_{d1}	f_{d2}
Particulate fraction	f_{p1}	f_{p2}
Partition coefficient (ℓ/mg) ($\tau = r/C_d$)	τ_1	τ_2
<u>Channel Geometry</u>		
Downstream distance	x	x
Cross-sectional area (m^2)	A_1	---
Depth (m)	H_1	H_2
Flow (m^3/sec)	Q_1	---
Velocity (m/sec) ($U = Q/A$)	U_1	---

TABLE A3: NOMENCLATURE FOR WATER-SEDIMENT MODEL (Continued)

Parameters	Water Column	Sediment
<u>Rate Parameters</u>		
Aggregate decay rate coefficient (1/day)		
- for dissolved	K_{d1}	K_{d2}
- for particulate	K_{p1}	K_{p2}
- for total ($K = K_d f_d + K_p f_p$)	K_1	K_2
Settling velocity (m/day)	w_s	---
Resuspension velocity (m/day)	---	w_{rs}
Sedimentation (burial) velocity (m/day)	---	w_d
Sedimentation loss coefficient (1/day)	---	K_s
Diffusive exchange coefficient (m/day)	K_L	K_L

*In terms of bulk volume.

Within the conceptual framework of the model shown in Figure A4, the following assumptions are used to develop mass balance equations:

1. Constant hydrological and morphological conditions for each river segment;
2. Steady-state conditions exist: $\frac{dC_T}{dt} = \frac{dm}{dt} = 0$;
3. Vertical and lateral uniformity in water column and sediments; no mixing zones
4. Dispersion is negligible in the longitudinal direction;
5. No longitudinal (downstream) movement of the bed: $Q_2 = 0$;
6. No spatial variation of the solids content of the bed: m_2 is constant (although m_1 is not constant).
7. Partitioning between dissolved and solid phases is rapid relative to transport and other transformation kinetics.

The solution for pollutant concentrations in such a one-dimensional, steady-state system is developed below. The solution is based on four coupled differential equations representing mass balances for solids in the water column and in the bed, and for the toxicant in the water column and in the bed.

Using the subscript 1 for water column variables and the subscript 2 for sediment variables, the mass balance for solids suspended in the water column (m_1) takes the form:

$$0 = \underbrace{-\frac{Q_1}{A_1}\frac{dm_1}{dx}}_{\text{(advection)}} \underbrace{- \frac{w_s}{H_1} m_1}_{\text{(settling)}} \underbrace{+ \frac{w_{rs}}{H_1} m_2}_{\text{(resuspension)}} \qquad \text{(A8)}$$

Assuming that m_2 is not a function of x, and that w_s and w_{rs} are constant, this equation has the solution:

$$m_1(x) = \underbrace{m_1(0)e^{\frac{-w_s}{H_1}\frac{x}{U_1}}}_{\text{(initial solids)}} + \underbrace{\frac{w_{rs}\, m_2}{w_s}\left[1-e^{\frac{-w_s}{H_1}\frac{x}{U_1}}\right]}_{\text{(resuspended solids)}} \qquad \text{(A9)}$$

It can be seen that m_1 is a function of the travel time downstream (x/U_1), the settling velocity (w_s) or its associated depth-dependent rate coefficient (w_s/H_1), and the resuspension flux ($w_{rs}\ m_2$). When the resuspension velocity (w_{rs}) is zero, the second term drops out of Equation A9, and m_1 is no longer dependent on m_2. In comparing Equation A9 predictions with field data it is important to account for all external and internal sources of suspended solids. One potential internal source is phytoplankton growth: the concentration of phytoplankton solids may be 200 fold greater than the concentration of chlorophyll-a (Canale 1983).

A second mass balance equation, this one for solids in the bed, can be written:

$$0 = \underbrace{-\frac{Q_2}{A_2}\frac{dm_2}{dx}}_{\text{(advection)}} + \underbrace{\frac{w_s\ m_1}{H_2}}_{\text{(settling)}} - \underbrace{\frac{w_{rs}\ m_2}{H_2}}_{\text{(resuspension)}} - \underbrace{\frac{w_d\ m_2}{H_2}}_{\text{(burial)}} \qquad \text{(A10)}$$

It is assumed that the bed does not move ($Q_2 = 0$) and that m_2 is constant ($dm_2/dx = 0$). Either of these assumptions causes the advection term to drop out. Consequently, Equation A10 reduces to an algebraic equation:

$$\underbrace{w_s \frac{m_1}{m_2}}_{\text{(settling)}} = \underbrace{w_{rs}}_{\text{(resuspension)}} + \underbrace{w_d}_{\text{(burial)}} \qquad \text{(A11)}$$

The sedimentation velocity, w_d, represents the movement of material downward and out of the active sediment layer, the thickness of which (H_2) does not change with time. This velocity thus represents the rate of change in elevation of the surface of the bed, ignoring any effect of compression of the deep sediment. If the resuspending flux exceeds the settling flux, then w_d is negative, implying that channel downcutting is occurring. If the downward flux exceeds the upward flux, w_d is positive, implying that the chanrel bed is rising over time, for the conditions being modeled. Where chemical [illegible] within the bed is rapid, however, a positive w_d can approximate the situation where the settled solids are transported out of the system as a bed load.

The third mass balance equation is for the toxicant in the bed:

$$0 = \underbrace{-\frac{Q_2}{A_2}\frac{dC_{T2}}{dx}}_{\text{(advection)}} + \underbrace{\frac{w_s f_{p1} C_{T1}}{H_2}}_{\text{(settling)}} + \underbrace{\frac{K_L f_{d1} C_{T1}}{H_2}}_{\text{(diffusion in)}} \tag{A12}$$

$$\underbrace{-\frac{(w_{rs} + w_d)\ f_{p2} C_{T2}}{H_2}}_{\text{(resuspension and burial)}} \underbrace{-\frac{K_L\ f_{d2} C_{T2}}{H_2}}_{\text{(diffusion out)}} \underbrace{-K_2\ C_{T2}}_{\text{(decay)}}$$

The "diffusion out" term above assumes that the sediment porosity is high, such that dissolved concentrations are almost the same whether expressed in terms of bulk sediment volume or pore water volume. If sediment porosity ϕ is not high, f_{d2} in Equation A12 (as well as in A13 and A20) is replaced by ϕf_{d2}, in order to convert dissolved concentration from a bulk volume basis to an interstitual volume basis.

Since the advection term in Equation A12 is again zero, the equation reduces to an algebraic equation establishing the relationship between C_{T2} and C_{T1}:

$$\frac{C_{T2}}{C_{T1}} = \frac{w_s\ f_{p1} + K_L\ f_{d1}}{(w_{rs} + w_d)\ f_{p2} + K_L f_{d2} + K_2\ H_2} \tag{A13}$$

Before writing a fourth mass balance equation and solving for C_{T1}, it is worthwhile to express Equation A13 in other terms. Since:

$$C_T = \frac{rm}{f_p} \tag{A14}$$

thus,

$$\frac{C_{T2}}{C_{T1}} = \frac{m_2 f_{p1}}{m_1 f_{p2}}\ \frac{r_2}{r_1} \tag{A15}$$

If a term β, the "sediment capacity factor" (DiToro et al. 1982), is defined as:

$$\beta = \frac{m_2 H_2 f_{p1}}{m_1 H_1 r_{p2}}, \tag{A16}$$

then

$$\frac{C_{T2}}{C_{T1}} = \frac{\beta H_1 r_2}{H_2 r_1} \tag{A17}$$

Combining Equations A13 and A17, and solving for r_2/r_1,

$$\frac{r_2}{r_1} = \frac{(m_1/m_2)\ w_s f_{p2} + K_L f_{d1}(m_1 f_{p2}/m_2 f_{p1})}{(w_{rs} + w_d)\ f_{p2} + K_L f_{d2} + K_2\ H_2} \tag{A18}$$

The first term in the numerator is modified by noting the Equation A11 relationship between w_s, w_{rs}, and w_d. The second term is modified by noting that:

$$f_d = \frac{1}{1 + mw} \quad \text{and} \quad f_p = \frac{mw}{1 + mw} \quad \text{and} \quad f_p = mw f_d \tag{A19}$$

Consequently,

$$\frac{r_2}{r_1} = \frac{(w_{rs} + w_s)\ f_{p2} + K_L(w_2/w_1) f_{d2}}{(w_{rs} + w_s)\ f_{p2} + K_L\ f_{d2} + K_2\ H_2} \tag{A20}$$

The ratios C_{T2}/C_{T1} and r_2/r_1 thus depend on the water-sediment particle exchange rates, the water-sediment diffusion rate, and the decay rate within sediment. They do not depend on the decay rate within the water column.

The fourth mass balance equation is for the toxicant in the water column:

$$0 = \underbrace{-\frac{Q_1}{A_1}\frac{dC_{T1}}{dx}}_{\text{(advection)}} \underbrace{- K_1 C_{T1}}_{\text{(decay)}} \underbrace{- \frac{w_s f_{p1} C_{T1}}{H_1}}_{\text{(settling)}} \underbrace{- \frac{K_L f_{d1} C_{T1}}{H_1}}_{\text{(diffusion out)}} \tag{A21}$$

$$\underbrace{+ \frac{w_{rs} f_{p2} C_{T2}}{H_1}}_{\text{(resuspension)}} \underbrace{+ \frac{K_L f_{d2} C_{T2}}{H_1}}_{\text{(diffusion in)}}$$

Combining Equations A21 and A13 results in:

$$\frac{dC_{T1}}{dx} = \left[- K_1 - \frac{w_s f_{p1}}{H_1} - \frac{K_L f_{d1}}{H_1} + \frac{\beta r_2}{H_2 r_1}\left(w_{rs} f_{p2} + K_L f_{d2} \right) \right] \frac{C_{T1}}{U_1} \tag{A22}$$

All terms on the right side of the equation are constant for a particular reach except for C_{T1}, f_{d1}, and f_{p1} (and subsequently β). The fractions f_{d1} and f_{p1} are functions of m_1 per Equation A19; m_1 is a function of x per Equation A9. However, if the increments of x are small enough, then m_1, f_{d1}, and f_{p1} are essentially constant. Consequently within small increments of x, Equation A22 has a simple solution:

$$C_{T1}(x) = C_{T1}(0) e^{-K_T x/U_1} \tag{A23}$$

where

$$K_T = \underbrace{K_1}_{\text{(decay)}} + \underbrace{\frac{w_s f_{p1}}{H_1}}_{\text{(settling)}} + \underbrace{\frac{K_L f_{d1}}{H_1}}_{\text{(diffusion out)}} - \underbrace{\frac{\beta r_2}{H_2 r_1}\left(w_{rs} f_{p2} + K_L f_{d2} \right)}_{\text{(resuspension) (diffusion in)}} \tag{A24}$$

By stepping down the reach in small increments of x, C_{T1} can be computed from the input parameters w_s, w_{rs}, K_L, r_1, r_2, H_1, H_2, m_2, K_1,

K_2, and the input solids and toxicant loads using Equations A9, A19, A20, A23, and A24. Then C_{T2} can be computed from C_{T1} using Equation A13 or A15. For the solution to be valid, the increments of x must be short enough that the relative change in m_1 is small within each increment. That is, the increments Δx must be shortened until $\Delta m_1/m_1$ is small.

While Equation A24 is satisfactory as written, some simplification of it is helpful for better understanding the model. Using the relationships shown in Equations A19 and A16, the "diffusion in" term of Equation A24 can be put in terms of f_{d2} and combined with the "diffusion out" term. Using Equations A11 and A16, the "settling" term can be expressed in terms of resuspension and burial. The resulting equation is:

$$K_T = \underbrace{K_1}_{\text{(decay)}} + \underbrace{\frac{\beta(w_{rs} + w_d)f_{p2}}{H_2}}_{\text{(settling)}} - \underbrace{\frac{\beta r_2 w_{rs} f_{p2}}{r_1 H_2}}_{\text{(resuspension)}} + \underbrace{\frac{\beta K_L f_{d2}}{H_2}\left(\frac{r_2}{r_1} - \frac{r_2}{r_1}\right)}_{\text{(net diffusion)}} \quad \text{(A25)}$$

Meanwhile, Equation A20 can be solved in terms of K_L as follows:

$$K_L f_{d2}\left(\frac{r_1}{r_2} - \frac{r_2}{r_1}\right) = \frac{r_2}{r_1}(w_{rs} + w_d)f_{p2} + \frac{r_2}{r_1} K_2 H_2 - (w_{rs} + w_d)f_{p2} \quad \text{(A26)}$$

Substituting this relationship into the "net diffusion" term of Equation A25 causes several terms to cancel out; then, after defining the sedimentation or burial rate coefficient as $K_s = w_d/H_2$, the equation can be expressed as:

$$K_T = K_1 + \frac{\beta r_2}{r_1}\left[K_2 + K_s f_{p2}\right] \quad \text{(A27)}$$

This result expresses K_T, the overall rate coefficient for disappearance of the toxicant from the water column, in terms of the three avenues for elimination of the toxicant from the water-sediment system: decay in water, decay in sediment, and burial. The rates of sediment decay and burial are

modified by $\beta r_2/r_1$, which is a function of the water-sediment mass ratio, the partitioning parameters, the sediment-water exchange parameters, as well as the sediment decay rate itself. It might also be noted that for a condition where $\tau_1 = \tau_2$, $K_1 = K_2 = 0$, and $w_{rs} = 0$, this model reduces to the simpler model expressed by Equation A7.

APPENDIX B

SEDIMENT TRANSPORT CONSIDERATIONS

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SEDIMENT TRANSPORT CONSIDERATIONS

The pollutant fraction associated with particulate material is determined (at equilibrium) by the partition coefficient and the solids concentration. In many natural waters the particulate phase on average contains a small percentage of the alkali and alkali-earth metals such as sodium and calcium, 20-30% of the strontium and boron, 30-70% of the cadmium, zinc, copper, and mercury, 70-85% of the chromium and lead, and 98% of the aluminum and iron (Forstner 1977). The bulk of many pollutants is thus carried on particulate material.

Predicting the transport and fate of particulate-associated pollutants requires an understanding of the behavior of particles. Predicting particle behavior is, however, one of the most difficult and uncertain aspects of water quality modeling. Much of the existing knowledge pertains to the larger particles which control the configuration of the streambed rather than to the smaller particles likely to adsorb many of the toxic pollutants. Consequently, future findings in this area may significantly improve predictive abilities.

B.1 SEDIMENT PROPERTIES

An individual sedimentary particle may be characterized by its size, shape, density, fall velocity, mineral composition, surface texture, and other properties. Particle size can be described by a number of different measures, including but not limited to (a) nominal diameter - the diameter of a sphere having the same volume as the particle, (b) sieve diameter - size of sieve opening through which the particle will pass, approximately equal to the nominal diameter, and (c) fall diameter - diameter of a sphere with specific gravity 2.65 (quartz) that has the same fall velocity (Richardson 1971, Guy 1970). Table B1 and Figure B1 show the size ranges corresponding to particle classifications.

TABLE B1. KINDS OF SEDIMENT MATERIALS AND SIZE CLASS TRANSPORTED IN STREAM (from Culbertson 1977)

Sediment	Size Class	Mode of Transport
Boulders	>256 mm	Bed Load
Cobbles	64-256 mm	Bed Load
Gravel	2-64 mm	Bed Load
Sand	0.062-2 mm	Bed Load or Suspended
Silt	4-62 μm	Suspended
Clay	0.2-4 μm	Suspended
Organic Detritus		Bed Load or Suspended
Including leaves, trees biological remains, etc.		
Biota		Bed Load or Suspended
Including floating and bottom dwelling organisms		

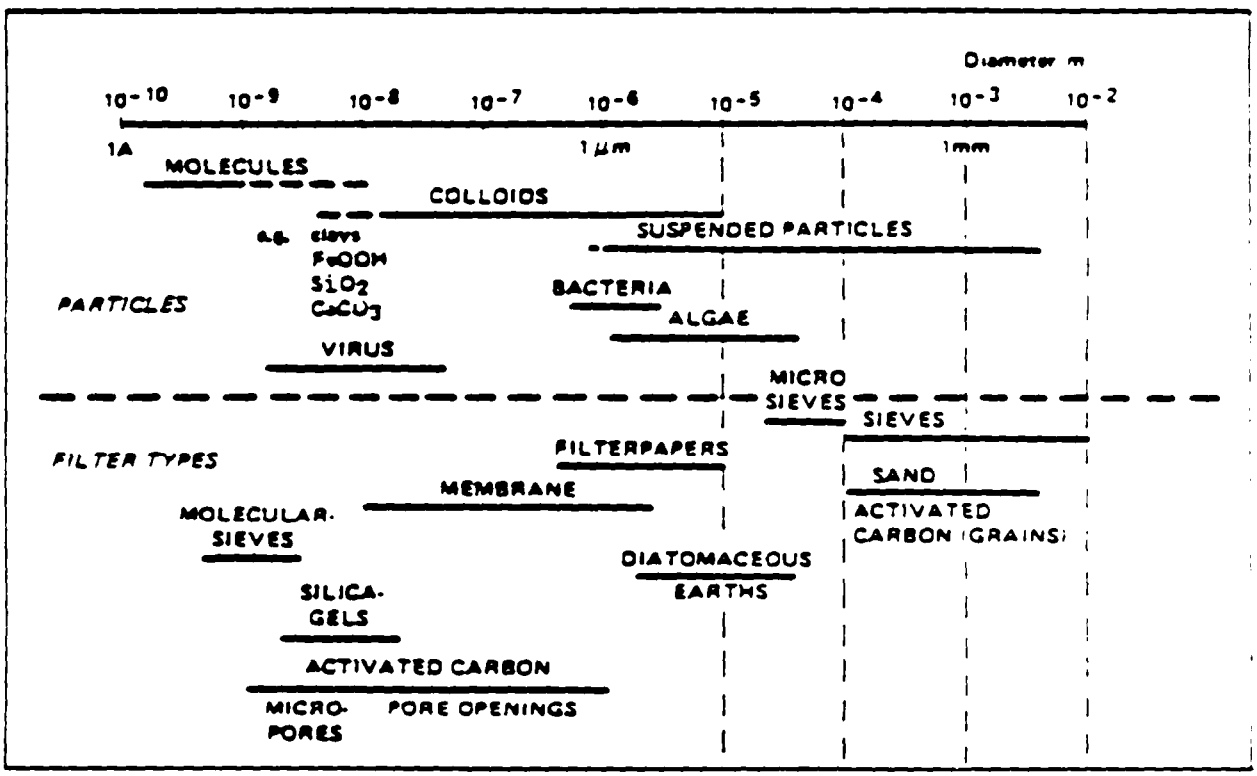


Figure B1. Size Range of Sediment Particles and Filter Pores (from Stumm and Morgan 1981).

Fall velocity is the average terminal velocity of a particle falling alone in quiescent distilled water. It is related to a number of particle and fluid characteristics including particle and fluid densities, fluid viscosity, and particle diameter, shape, surface texture, and tumbling frequency.

Mineral composition influences density, size, shape, and thus fall velocity. Most mineral sediments carried by stream flow have a specific gravity of around 2.65 (Culbertson 1977). Consequently, the fall velocity of quartz spheres having specific gravity 2.65 is used as somewhat of a benchmark. Nevertheless, substantial variations in density may be observed, with organic particles especially tending toward lower density.

For sediment transport the most useful expression of particle shape is given by the Corey shape factor, $c/\sqrt{ab}$, where a, b, and c are the lengths of the longest, intermediate, and shortest mutually perpendicular axes, respectively (McNown and Malaika 1950).

Bulk sediment is a complex mixture of differing individual particles. Bulk properties are related to the above individual properties and to the way they are distributed. Bulk properties of particular importance may be the size distribution, specific gravity, porosity, and cohesiveness.

Measured size distributions may be expressed in a number of different ways. Frequency distribution histograms show the prevalence of material within given class intervals. Cumulative distribution plots show the total percentage of material with size smaller than particular values. Cumulative distribution plots can be used to specify quartile values, d_{25}, d_{50}, and d_{75} (where d_x is the diameter greater than x percent of the particles). Table B2 shows particle size distributions observed in raw sewage, primary effluent, and secondary effluent of one municipality (Eganazountas and Mathias 1984). Figure B2 shows the size distributions observed in stream beds of 11 rivers (Guy 1970). Mills et al. (1982) also presents some sediment data for several rivers.

TABLE B2. MASS DISTRIBUTION OF FILTRABLE SUSPENDED SOLIDS IN RAW AND TREATED SEWAGE

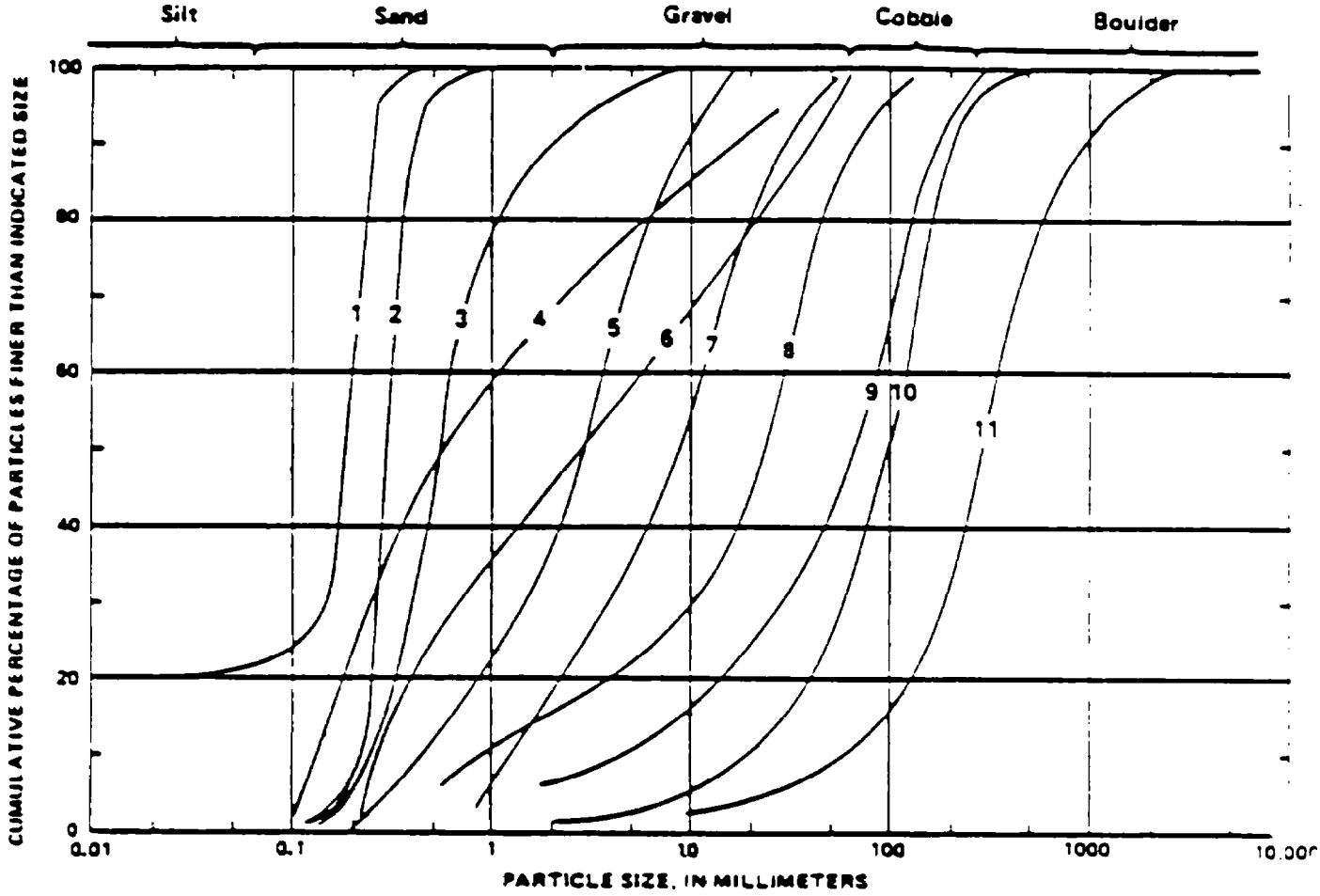
Sample[a]	Conc.[b] mg/L	Percent of mass retained in µm size range						
		>0.1 <1.0	>1.0 <3.0	>3.0 <5.0	>5.0 <8.0	>8.0 <12.0	>12.0	>35
Influent wastewater	220 (150-400)	10 (4-12)	8 (6-10)	2 (1-6)	1 (1-4)	3 (2-8)	16[c] (12-24)	60 (50-70)
Primary effluent	90 (60-120)	22 (10-30)	20 (16-25)	4 (2-12)	3 (2-8)	8 (4-16)	43 (30-60)	-- -
Trickling filter effluent	42 (30-50)	40 (35-55)	5 (2-10)	6 (2-10)	3 (0-5)	1 (0-2)	45 (30-55)	-- --

[a]All samples from the University of California, Davis wastewater treatment plant.

[b]Based on the total mass of filtrable suspended solids retained on an 0.1 micron filter.

[c]Size range between 12-35 µm.

Source: Tchobanoglous et al. (1983) as reported by Bonazountas (1984).



1 — Mississippi River at Head of Passes, La.
2 — Mississippi River at Cairo, Ill.
3 — Missouri River at Omaha, Nebr.
4 — Republican River at Clay Center, Kans.
5 — South Platte River at South Platte, Colo.
6 — Pembina River at Walhalla, N. Dak.
7 — Seneca Creek near Rockville, Md.
8 — Brandywine Creek at Lenape, Pa.
9 — Brandywine Creek at Cornog, Pa.
10 — Yellowstone River at Billings, Mont.
11 — W. Fork Rock Creek near Red Lodge, Mont.

Figure B2. Particle-size Distribution of Streambed Material Typical of Indicated Streams in the United States (from Guy 1970).

The size distribution of natural sediment is ordinarily expected to plot as a straight line on log probability paper. If this is the case, then the median will equal the geometric mean, and the ratio d_{50}/d_{16} and d_{84}/d_{50} will equal the geometric standard deviation or "gradation coefficient." The complete distribution can thus be described by the median (or geometric mean) and the geometric standard deviation.

For a given shape, texture, and density, particle size is inversely proportional to the particle surface-to-mass ratio. As discussed in Section 3.2, the partition coefficient of organic contaminants can be related to the quantity of organic solids (i.e., the product of solids concentration and percentage organic material) without regard for the solids surface-to-mass ratio. For metals, however, the partition coefficient is likely to be related to the mineral composition and surface-to-mass ratio of the solids. Tada and Suzuki (1982) and to some extent Dossis and Warren (1980) observed higher particulate metal concentrations in smaller particles. Hayter and Mehta (1983) present similar data, as shown in Figure B3. Thus, the smaller size fractions, particularly the readily transported silt and clay fractions, are expected to more strongly affect contaminant behavior.

The porosity of bed sediment is a measure of the interstitial volume per unit of bulk volume in place. Porosity may vary between 0 and 1, with 0 signifying 100% solid and 1 signifying 100% water in the bed. Porosity affects the shear strength of the bed, which in turn affects the rate of resuspension under various shear stresses or current velocities. Bed porosity must be distinguished from individual particle porosity.

Cohesiveness describes the attraction the individual particles have for each other. Noncohesive sediments are composed primarily of sand and gravel. Cohesive sediments consist of silts and clays. The behavior of cohesive sediments differs from that of noncohesive sediments in some important ways.

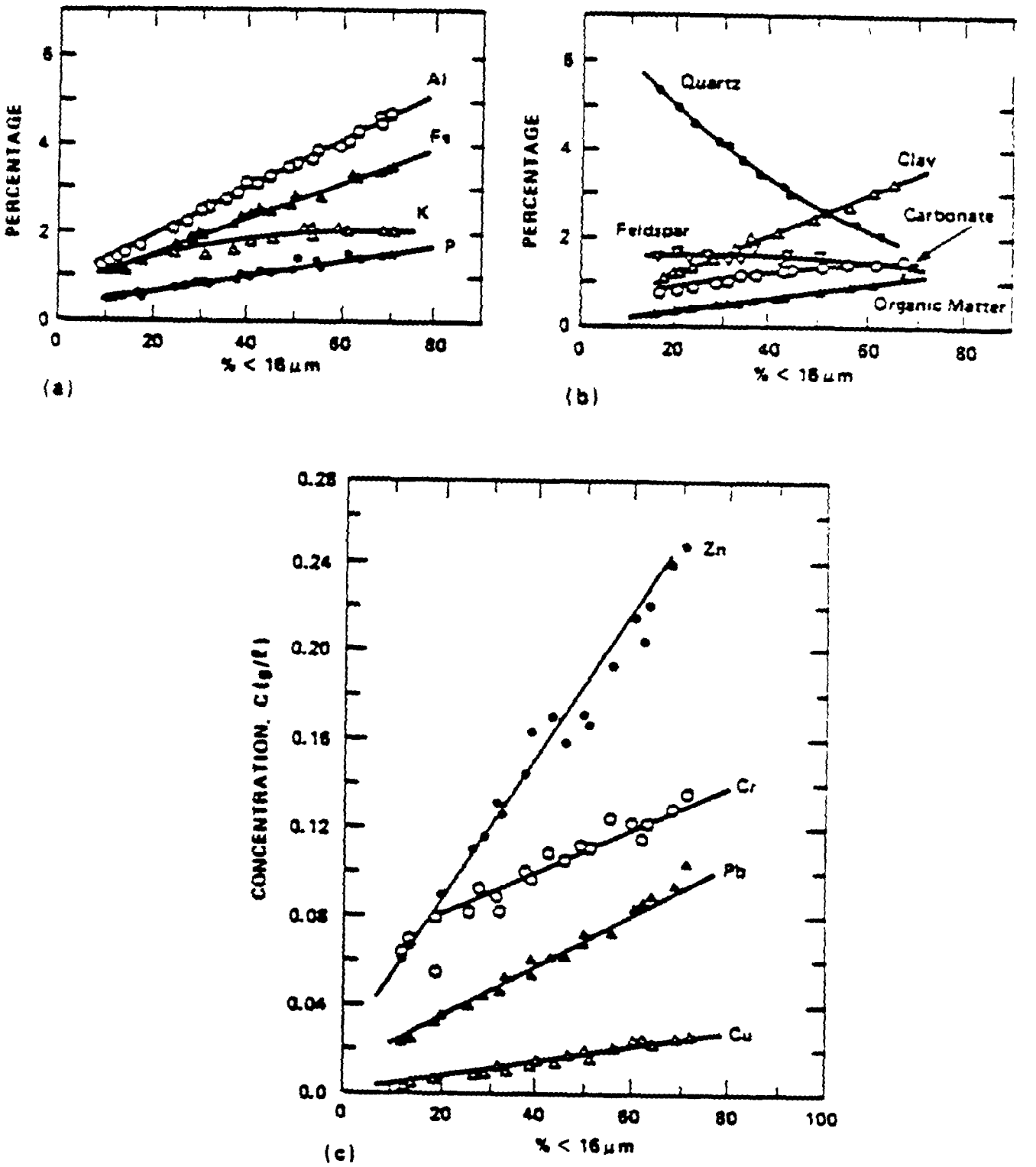


Figure 83. Variation of Metal Concentration with Sediment Particle Size (from Hayter and Mehta 1983).

In suspensions of noncohesive material the basic settling unit is the individual grain. Particle interactions are strictly mechanical, such as momentum transfer between colliding grains. Noncohesive sediment beds resist erosion by the submerged weight of the individual grains, which may provide mutual support by interlocking or by friction (Partheniades 1971).

Cohesive sediments consist of particles small enough, with surface-to-mass ratio large enough, that their surface physico-chemical forces may become much more important than their weight. These forces may include (a) van der Waals forces, (b) surface electric charges, (c) chemical bonds, and (d) interactions of the double layer (counter-ions attracted from the solution). These forces are only partially understood and may vary with the water environment (Partheniades 1971).

For clay particles in distilled water the net effect of these forces may be repulsion, allowing enormous concentrations to be suspended at small current velocities. However, even small amounts of dissolved salt will bring about particle attraction (through double layer compression), resulting in the aggregation of colliding particles into flocs having size and fall velocity much larger than those of the individual clay particles. The basic settling unit is thus the floc, the size distribution of which may depend on the flow conditions and on the physico-chemical properties of the water and sediment: Cohesiveness provides a sediment bed with additional shear strength to resist erosion. Partheniades (1971) notes that fresh waters ordinarily contain enough salt to bring about clay particle flocculation. Nevertheless, Edzwald et al. (1974) and Hayter and Mehta (1983) found estuarine salinity to measurably increase fall velocity over that in ordinary fresh water.

B.2 TRANSPORT OF SEDIMENT LOADS

The gravity-driven downhill movement of stream flow is resisted by the friction of the fluid passing over the stream bed. This results in a variation of velocity with depth: velocity decreases near the bottom of

the water column. For the stream flow to keep particles in suspension the flow turbulence must counter the tendency of the particles to settle. Consequently, the stream flow tends to carry heavier particles near the bed, while it is likely to carry fine particles more uniformly throughout the water column, as illustrated in Figure B4.

The total sediment load (mass/time) passing a river cross section can be split into two parts using any of three related but nonequivalent schemes (Thomas 1977):

Based on Mode of Transport:

The suspended load consists of sediment particles that are transported entirely within the body of fluid with very little contact with the bed. The bed load consists of particles either rolling and sliding along the bed as surface creep or intermittently leaping into the flow, settling to the bed, and resting on the bed (Shen 1971; ASCE 1975). Such intermittant movement is called saltation. As there is no sharp distinction between saltation and suspension, there is likewise no sharp boundary between suspended load and bed load. The bed load is usually a small fraction of the suspended load (Thomas 1977). The suspended load plus the bed load equals the total sediment load.

Based on Sampling Capabilities:

The term measured load refers to that portion of the sediment load that can be measured with sampling equipment. The unmeasured load is the portion that would escape detection. Current equipment can sample over the entire range of depth to within inches of the bed. All but a small percentage of the total load is usually measurable (Thomas 1977).

Based on Availability in the Stream Bed:

This division is based on particle sizes. Wash load is that portion of the total load comprised of grain sizes finer than those found i..

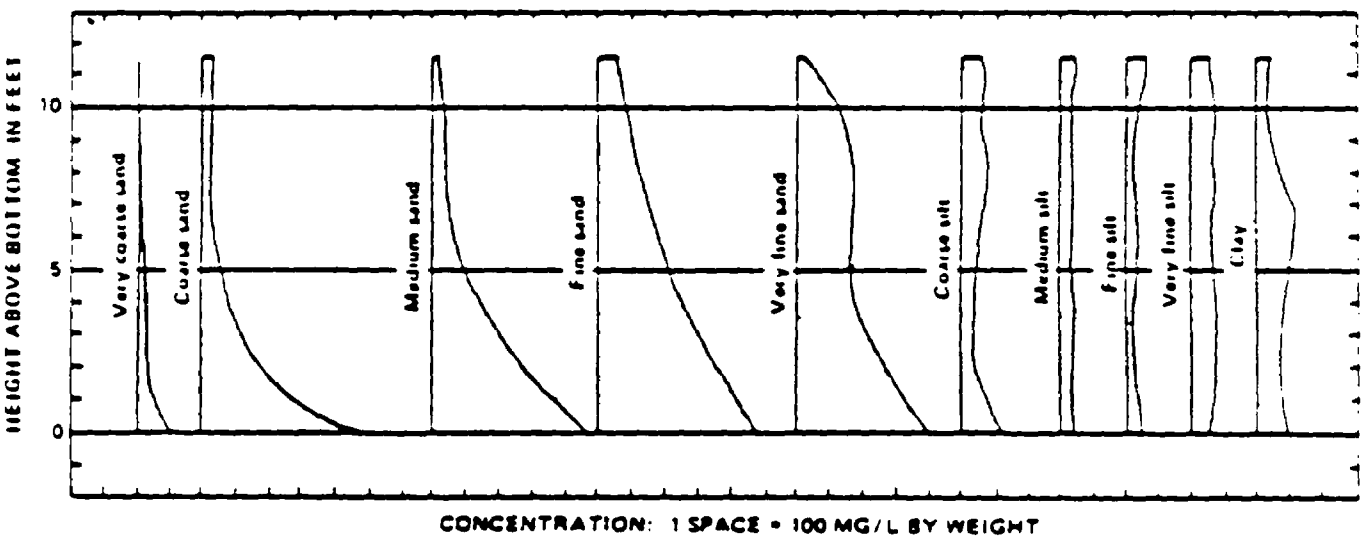


Figure B4. Flow-weighted Concentrations of Different Particle Sizes for the Missouri River at Kansas City (Guy 1970).

significant quantities in the stream bed. The magnitude of the wash load is controlled by the rate of entry of these particles from the terrestrial watershed. The bed material load consists of coarser particles, readily found in the bed; the magnitude of this load is determined by the ability of stream flow to move the bed particles. H.A. Einstein (1964) describes this distinction as follows:

> Either the availability of material in the watershed or the transporting ability of the stream may limit the sediment load at a cross section. In most streams the finer part of the load, i.e., the part which the flow can easily carry in large quantities, is limited by its availability in the watershed. This part of the load is designated as wash load. The coarser part of the load, i.e., the part which is more difficult to move by flowing water, is limited in its rate by the transporting ability of the flow between the source and the section. This part of the load is designated as bed material load.

Wash load is often considered to be silt and clay, while bed material load would be sand, gravel, and larger material. However, no uniform line of demarkation is possible since it depends on flow conditions and on sediment sources.

The bed material load is of great importance in determining the shape and stability of stream channels. For this reason considerable engineering research has been directed toward its prediction. Einstein (1950), using dyed particles, was able to demonstrate that a continuous exchange of particles between the bed and the water column takes place in a reach where the number of particles leaving the downstream end equals the number of particles entering the upstream end. Gessler (1971) notes that aggradation occurs when the upstream sediment supply exceeds the capacity of the flow to transport sediment out of the reach. Given sufficient time, the sediment depositing at the upstream end of the reach causes the bed slope to increase, which in turn increases the velocity or bottom shear stress, thereby increasing resuspension until a new equilibrium is attained. Degradation, on the other hand, occurs when the sediment carrying capacity of the flow exceeds the upstream supply rate.

The resulting net erosion reduces the slope, which in turn reduces the velocity or bottom shear stress, thereby reducing resuspension until a new equilibrium is attained. Thomas (1977) notes that degrading reaches may tend to become incised while aggrading reaches may tend to meander.

Despite the amount of study that has gone into sediment transport, accurate predictions remain difficult. As discussed briefly in the Guidance Manual Book VIII, Screening Procedure (Mills et al. 1982), many procedures require data on the suspended solids concentration at some reference depth. The Einstein (1950) procedure and its modifications do not require such data but are rather complex. The Einstein procedures, furthermore, involve only bed material load; wash load is determined by external sources and is thus not predictable from the stream's sediment carrying capacity (Nordin and McQuivey 1971). Nevertheless, it can be noted that many sediment transport formulas can be put in the form (Gessler 1971):

$$g_s = a(\tau - \tau_c)^p \qquad (B1)$$

where g_s is sediment load per unit width, τ is shear stress, τ_c is a critical shear stress at which sediments start to move, a is some coefficient, and p some power.

Shear stress, τ (Newton/m^2), is given by:

$$\tau = \gamma RS \qquad (B2)$$

where γ is the specific weight of water (approximately 9807 N/m^3), R is the hydraulic radius (m), and S is the slope of the energy grade line (m/m). To obtain τ in dynes/cm^2 multiply N/m^2 by 10. The importance of shear stress in controlling both settling and resuspension will be further discussed later.

Shen and Hung (Shen 1971) have suggested a simple empirical

regression formula for predicting the suspended bed material concentration. Using flume and river data they obtained:

$$\log C = a_0 + a_1 X + a_2 X^2 + A_3 X^3 \quad \text{(B3a)}$$

$$X = V^i S^j W^k \quad \text{(B3b)}$$

where C is bed material load concentration (mg/ℓ), V is the average flow velocity (ft/sec), S again the energy slope (ft/ft), and W the fall velocity (cm/sec). The regression values are:

a_0 = -107404.459	i = 0.007502
a_1 = 324214.747	j = 0.004288
a_2 = -326309.589	k = -0.002400
a_3 = 109503.872	

The standard error of log C was 0.217 (68% of the data was within 0.217 base 10 logarithmic cycles of the predicted value).

Equation B3 and all of the numerous other approaches for predicting bed load and bed material load may be of limited value for toxicant modeling. Much of the toxicant may be adsorbed to the finer particles (with higher surface-to-mass ratios) comprising the wash load. By definition of the wash load, these finer particles are not found in the stream bed in substantial quantities. By implication, toxicant bound to wash load particles would have limited interaction with the bed.

B3. DEPOSITION AND EROSION

The net particle flux (μg/cm^2/sec) across the bed-water interface can be expressed as the difference between the deposition (settling) flux, S_D, and the erosion (entrainment or resuspension) flux S_E (Fukuda and Lick 1980). The deposition flux is related to the settling velocity, w_s (cm/sec), and the water column solids concentration, m_1 (mg/ℓ), by:

$$S_D = w_s m_1 \quad \text{(B4)}$$

The erosion flux is related to the resuspension velocity, w_{rs}, and the bed solids concentration, m_2, by:

$$S_E = w_{rs}\, m_2 \tag{B5}$$

The assumption here is that deposition and resuspension are independent processes that can occur simultaneously.

B.3.1 Deposition

In evaluating the settling velocities of sediment particles, three physical processes can be considered (O'Melia 1980): (a) gravity, (b) Brownian motion or molecular diffusion, and (c) turbulent or laminar fluid shear (velocity gradients). The degree to which each of these processes governs particle behavior depends on the characteristics of both the fluid and the particles.

The effect of gravity on particle settling can be expresses in terms of Stokes Law:

$$v_s = (g/18u)\ (\rho_s - \rho)d^2 \tag{B6}$$

where v_s is the Stokes settling velocity (cm/sec), g is the acceleration of gravity (980 cm/sec^2), $\rho_s - \rho$ is the difference in the densities of the particle and of water, d is the spherical particle diameter, and u is the absolute viscosity of water (poise, g/cm - sec). (Note that $u = \nu\rho$, where ν is the kinematic viscosity (cm^2/sec) tabulated in Figure 3.2.8). The Stokes velocity, v_s, applies to a single particle in a quiescent medium. The effective settling velocity in the field, w_s, may differ from v_s.

The Stokes settling velocity is quite sensitive to the particle diameter; for example, a doubling of particle diameter would quadruple the fall velocity. For noncohesive particles, the size distribution is simply a property of the sediments. For cohesive particles, the size distribution depends on the properties of both the particles and the

fluid. Aggregation into flocs occurs when particles having sufficient physico-chemical attraction collide with each other. Such collisions may result primiarily from Brownian motion for small particles, and fluid shear and differential settling velocities for larger particles. Valloulis and List (1984) have modeled these processes in a sedimentation basin. Disaggregation of flocculant particles may also occur through fluid shear and through collisions (Lick 1982). Uchrin and Weber (1980) noted that laboratory measured settling velocities were substantially more rapid than expected from the Stokes velocity of the individual particles, apparently due to particle aggregation.

Vertical movement of particles may also be brought about by dispersion, consisting of Brownian motion and turbulent diffusion (resulting from eddies produced by fluid shear). Away from the bed-water boundary Brownian diffusion is expected to be negligible compared with turbulent diffusion. The importance of turbulent diffusion relative to settling can be directly compared (Lick 1982). A characteristic time for settling to occur is $t_s = H/v_s$, where H is depth of water. A characteristic time for turbulent diffusion is $t_d = H^2/2D_v$, where D_v is the vertical eddy diffusivity. The dominant mechanism is that with the shorter characteristic time. Increasing the particle size and the depth favors settling as the dominant mechanism; increasing the turbulence favors diffusion (Lick 1982). Thus, the HydroQual (1982) recommendation to reduce w_s to perhaps 10% of v_s in shallow streams seems consistent with this reasoning.

In this vein Hayter and Mehta (1983), constructing a general model of particle behavior in estuaries, applied the relationship:

$$w_s = (1 - \frac{\tau}{\tau_c})\, v_s \qquad (B7)$$

where τ_c is a critical shear stress above which little deposition of the sediment would occur (as measured in flume tests). They suggest a minimum value of w_s being 5% of v_s.

Lick (1982) applies a different line of reasoning to a thin film of water near the bed-water interface, where turbulent diffusion is assumed to decrease. The flux through this film can be written:

$$S_D - S_E = (D_B + D_v) \frac{dm_1}{dz} + v_s m_1 \tag{B8}$$

where $S_D - S_E$ (ug/cm^2 - sec) is the net downward flux (per Equations B4 and B5), D_v is vertical eddy diffusivity (cm^2/sec), m_1 (mg/l) is the particle concentration near the interace, z is vertical distance from the bottom, and D_B is the Brownian diffusivity for the particles, given by:

$$D_B = \frac{kT}{3\pi\mu d} \tag{B9}$$

where k is the Boltzmann constant (1.38×10^{-16} g - m^2/K - sec) and T is absolute temperature. D_B and v_s are thus functions of particle size; D_v is a function of shear stress and distance z from the bed-water interface. When resuspension is negligible, the concentration gradient is positive within the thin film, because particles are being lost to the bed surface. In this case the flux due to particle diffusion adds to the flux due to gravity settling, thereby increasing the rate of deposition.

Combining Equations B4 and B8, Lick (1982) determined the effective settling velocity w_s :

$$w_s = v_s / 1 - \exp(-v_s/v_d) \tag{B10}$$

where v_d is the minimum limiting value of w_s when only diffusion (both Brownian and turbulent) is considered. Lick (1982) determined v_d to be:

$$v_d = 0.06\ (\tau/\rho)^{1/2}\ \ (\rho/D_m\mu)^{2/3} \qquad (B11)$$

Figure B5 illustrates the solution of w_s, v_s, and v_d over a range of particle sizes for a shear stress, τ, of 10 dynes/cm^2. For large particles $w_s = v_s$ and the effect of diffusion through the boundary film is negligible. For small particles $w_s = v_d$ and the effect of gravity settling is negligible. The particle size at which control of deposition shifts from diffusion to settling depends on shear stress. This theoretical approach assumes that all particles that hit the bed surface adhere to it. This limitation might be related to why increasing τ increases w_s for small particles, a contrast to the previously described empirical approach (Equation B7), where increasing τ decreases w_s.

B.3.2 Bed Erosion

Erosion or entrainment is the scour of sediments from any part of the stream bed into suspension in the water column. To remove material from the bed the flow-generated forces must overcome the stabilizing forces, which consist of the immersed weight and (for silt or clay beds) the cohesive strength. Lee et al. (1981) and Lick (1982) list five factors controlling entrainment: (a) turbulent shear stress at the bed-water interface, (b) water content (porosity) of the bed, (c) sediment composition, including minerology, organic content, and size distribution, (d) activity of benthic organisms, (e) vertical distribution of sediment properties, related to the manner of deposition.

Lee et al. (1981) and Fukuda and Lick (1980) found entrainment rates to be directly proportional to shear stress and water content. Also, sediments with a fine-grained (clay size) fraction deposited at the surface were more easily erodable than vertically well-mixed sediments with the same composition. For example, after a brief net depositional period, the freshly deposited sediments will tend to have a smaller mean

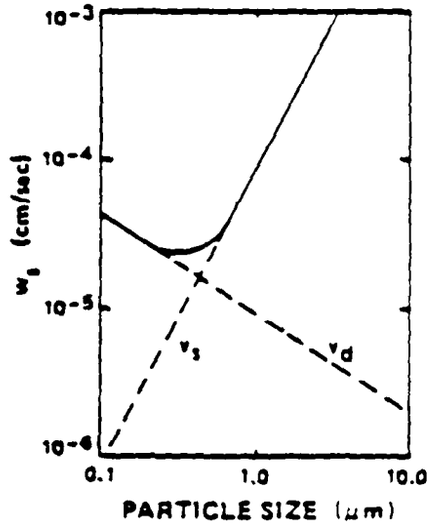


Figure B5. Deposition velocity w_s as a function of particle size for a shear stress of 10 dynes/cm^2 (from Lick 1982).

size and a higher water content; therefore, these surface sediments will be more easily entrained when shear stress increases.

The erosion rate may be formulated in terms of the shear stress on the bed, τ, and the erosion resistance of the bed. The erosion resistance of the bed is generally empirically estimated; it cannot be predicted solely from the basic properties of particle size distribution and porosity.

Figure B6 illustrates a typically measured relationship between erosion flux and shear stress. Once beyond critical shear stress, τ_c, the erosion flux, S_E, increases rapidly. In modeling consolidated estuarine beds, Hayter and Mehta (1983) estimate

$$S_E = a\left(\frac{\tau - \tau_c}{\tau_c}\right) \tag{B12}$$

where both a and τ_c are empirically derived constants.

B.3.3 Particle Exchange: Continuous Versus Discontinuous

The conservation of sediment load through a stream reach may occur under two conditions: (a) deposition and resuspension are occurring continuously, but at equal rates ($S_D = S_E$, or $w_s m_1 = w_{rs}\ m_2$), or (b) deposition and resuspension rates are both zero. The former situation can be considered an equilibrium state; the latter cannot. For the equilibrium condition, the suspended solids concentration would be given by $m_1 = m_2\ w_{rs}/w_s$. For the zero rate situation, whatever concentration exists at the head of the reach is carried downstream unchanged.

In flume experiments with noncohesive sediments, Einstein (1950) demonstrated (using dyed particles) that conservation of load was the result of an equilibrium balance between deposition and resuspension.

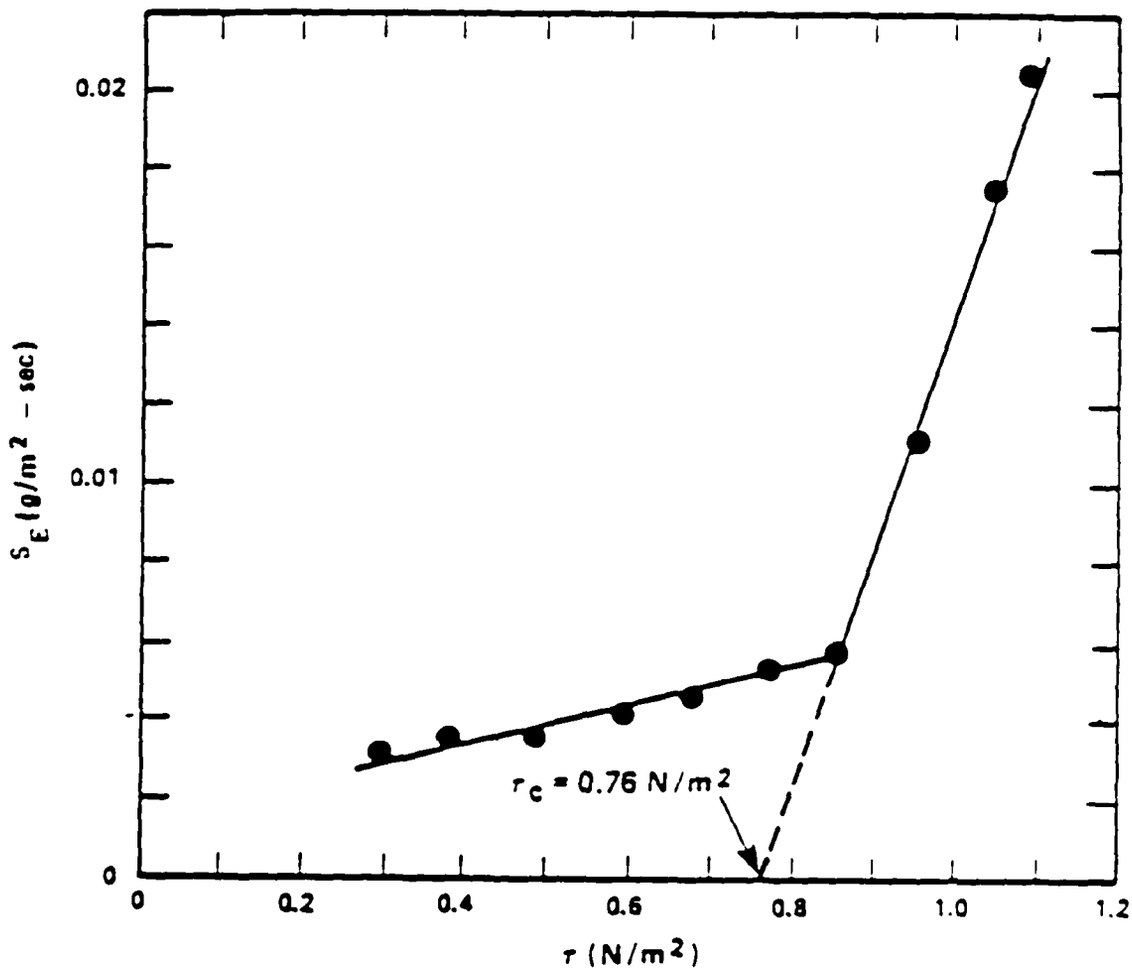


Figure B6. Example of Relationship between Erosion Rate S_E and Bed Shear Stress τ (after Hayter and Mehta 1983).

Although the concentration did not change, a continuous exchange of particles was occurring through the simultaneous processes of deposition and resuspension.

Whether cohesive sediments exhibit the same behavior is open to question. For clay particles Partheniades (1971) and Hayter and Menta (1983) note evidence that the critical shear stress below which no erosion can occur is greater than the critical shear stress above which no deposition can occur. That is, there appeared to be a shear stress range within which neither erosion nor deposition is significant. Within this range the velocity was sufficient to prevent the suspended particles from flocculating and adhering to the bed but insufficient to break the cohesion of the consolidated bed particles. Above this range only erosion occurs, while below this range only deposition occurs.

In the experiments with lake sediments, which are likely to be finer and more cohesive than river sediments, Lick (1982) observed a complex behavior seemingly intermediate between the continuous and simultaneous deposition and erosion observed for sand and the alternating deposition or erosion observed with clay. He found that to a partial degree a continuous exchange of particles was occurring through simultaneous deposition and erosion. Some types of particles, however, tended to remain only in the water column; others tended to remain only in the bed.

Lick (1982) thus notes that erosion and deposition are not completely reversible and that a hysteresis effect is often present. For a particular shear stress, the steady state concentration will be higher if the shear stress (and suspended concentration) had been decreasing over time than if it had been increasing over time.

8.4 SEDIMENT SOURCES

External sources of suspended sediments can originate from either point or nonpoint sources. Point sources of sediments are generally minimal, and in any event, are easily quantifiable. Nonpoint sources of

concern are governed by natural and culturally accelerated erosion processes. Although urban runoff can have significant localized impacts on streams (Porcella and Sorenson 1980; Tomlinson et al. 1980), the preponderance of sediments delivered to U.S. streams by accelerated erosion are derived by sheet erosion from agricultural lands (Omernik 1977). Sheet erosion is the wearing away of a thin layer of land surface.

Sheet erosion rates depend on rainfall and flow properties, soil geomorphology and topography, and land use (including vegetative cover and soil management practices). Although predicting soil loss is very complicated, the Universal Soil Loss Equation, developed by Wischmeier and Smith (1960), has been extensively used to estimate average annual soil loss in tons/acre. To predict sediment yield of a watershed, the USLE is coupled with a "sediment delivery ratio", the fraction of an area's soil loss that actually reaches the stream. Table B3 summarizes the range of sediment yields expected in various regions of the country.

Details on use of the USLE and sediment delivery ratio are contained in Volume VIII of the Guidance Manual (Mills et al. 1982) and in several other EPA publications, including McElroy et al. (1976), U.S. EPA (1976), and Zison et al. (1977). That material will not be repeated here. However, it can be noted that for many water quality modeling purposes, the utility of the USLE is constrained by being limited to annual average soil loss. It is not intended for event modeling (Wischmeier 1976). To predict sediment yield from single events, Mills et al. (1982) describes the Williams (1975) modification of the USLE.

Several other approaches are available for predicting the sediment and pollutant yield of events. For urban runoff these include U.S. EPA (1975), Mills et al. (1982), Geiger and Dorsch (1980), and Klemetson et al. (1980). For agricultural runoff they include Williams (1980), Novotny (1980), and Donigian and Crawford (1976). Given sufficient resources, the method of choice might be the Agricultural Runoff Management Model (ARM) (Donigian and Davis 1978).

TABLE B3. SEDIMENT YIELD FROM DRAINAGE AREAS OF 100 SQUARE MILES OR LESS OF THE UNITED STATES (Todd 1970)

Region	Estimated sediment yeild		
	High	Low	Average
	tons/sq mi/yr		
North Atlantic	1,210	30	250
South Atlantic Gulf	1,850	100	800
Great Lakes	800	10	100
Ohio	2,110	160	850
Tennessee	1,560	460	700
Upper Mississippi	3,900	10	800
Lower Mississippi	8,210	1,560	5,200
Souris-Red-Rainy	470	10	50
Missouri	6,700	10	1,500
Arkansas White-Red	8,210	260	2,200
Texas Gulf	3,180	90	1,800
Rio Grande	3,340	150	1,300
Upper Colorado	3,340	150	1,800
Lower Colorado	1,620	150	600
Great Basin	1,780	100	400
Columbia-North Pacific	1,100	30	400
California	5,570	80	1,300

APPENDIX C

FIELD AND LABORATORY METHODS FOR FLINT RIVER SURVEYS

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Metals in the ambient environment frequently occur at levels below the detection limit of many of the analytical methods commonly employed by State and Federal agencies. Consequently, in order to assure obtaining data useful for model calibration, the WLA analyst needs to be able to discuss the overall adequacy of the methods used by laboratory and field personnel. The key issues are (a) the sensitivity, and perhaps accuracy, of the analytical methods and (b) the freedom from detectable contamination during sample handling, a problem if very sensitive analytical methods are used. This appendix describes the sampling and analytical methods found to be useful during the Flint River surveys.

The sampling program began in August 1981 and ended in March 1982. During this time, four sampling surveys were conducted on the Flint River. Water was analyzed for the total and dissolved forms of cadmium, copper, and zinc. Chemical and physical parameters of the water, which are believed to influence metal speciation or to interact with solids, were also analyzed. The parameters included were suspended solids, pH, specific conductivity, hardness, dissolved oxygen, total alkalinity, and temperature. River flow and velocity were also estimated.

All aspects of sample collection, filtration, and preservation were evaluated so that the final analytical results reflected actual quality of the river water sampled. Care was taken to choose equipment made of materials that would minimize contamination.

River water was collected using a half-gallon linear polyethylene wide mouth Nalgene bottle fixed to a polypropylene rope with stainless steel clamps. The bottle was weighted from below with lead, and the bottle mouth was sheltered with a plastic awning or lid suspended from the rope just above it. The purpose of the lid was to keep out debris as the sample was pulled up.

Sampling was usually done from bridges at three marked positions that are at 1/4 the distance across the stream, at 1/2 the distance, and at 3/4 the distance. The sampling device was lowered quickly below the surface of the water, rinsed once, emptied, then filled again. Three such samples from the various bridge positions were combined in a ten-liter polyethylene carboy which was previously rinsed with some water from the first sample. It is from this composite sample that an aliquot for analysis was taken.

A sample processing scheme is presented in Figure C1. All filtering operations were conducted in the mobile laboratory as well as pH, conductivity, alkalinity, and metal preservations. Temperature and dissolved oxygen were measured in-situ. Total metal analysis, dissolved metal analysis, and hardness were analyzed at the EPA Large Lakes Research Station.

Trace Metals

Trace metal samples were collected in new linear polyethylene bottles washed with hot water in a dishwater, rinsed with deionized water, with 30% v/v nitric acid, and with deionized water; then they were soaked in 2% v/v nitric acid for two weeks, rinsed six times with deionized water, and dried in an oven with the caps ajar. Bottle blanks were analyzed to insure that contamination was kept to a minimum, and to provide a value used to correct for low level background contamination. Ten of every 100 bottles were randomly selected and analyzed for background levels. A blank test was performed by filling the bottles with a pre-analyzed acidified batch of water (3m nitric acid/liter). This batch was generally below the detection limit for each metal. The solutions in the bottles were then analyzed, and the resulting mean concentration is the bottle blank. The stored bottle blank samples were analyzed with the river samples.

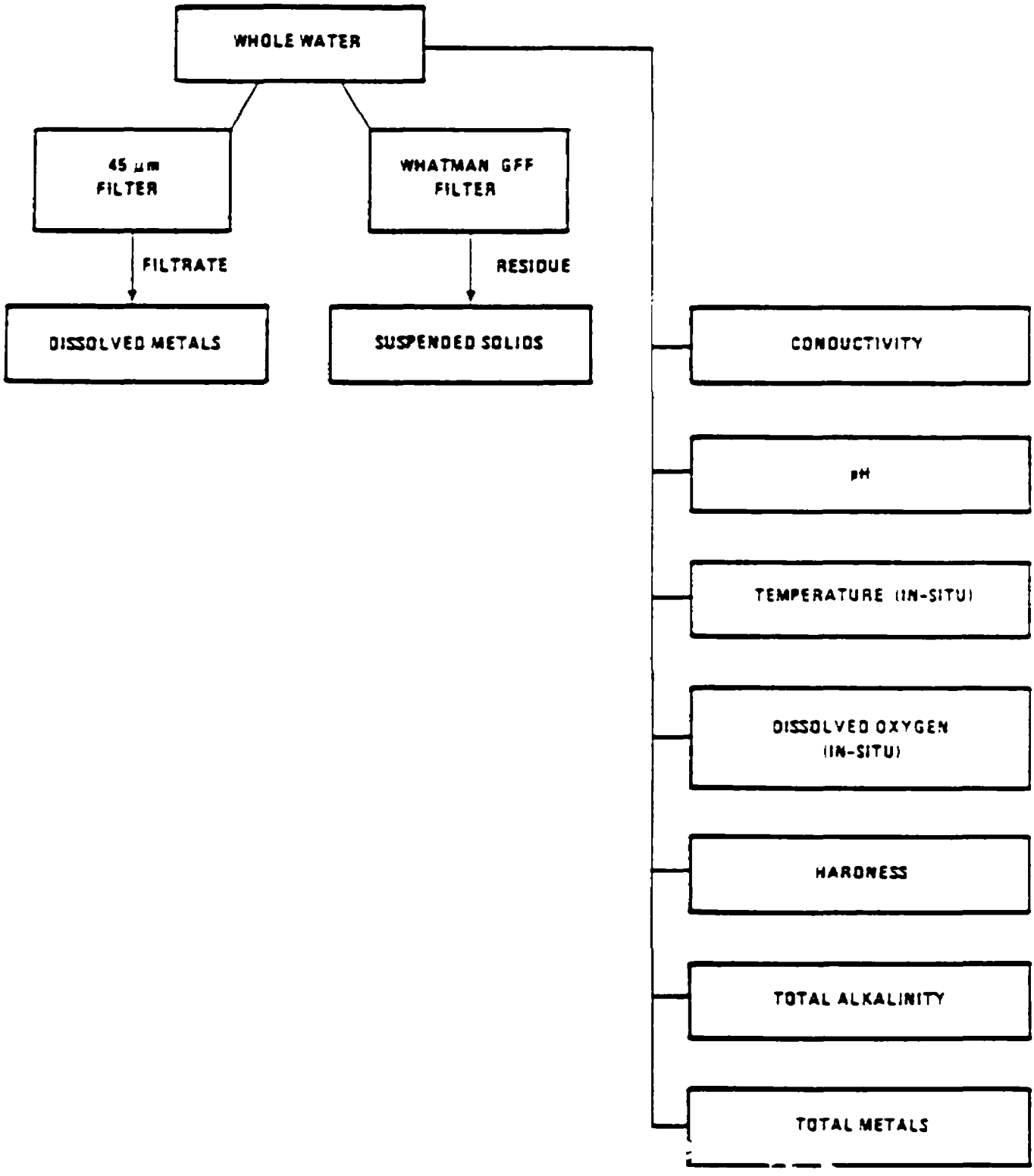

FIGURE C1 SAMPLE PROCESSING SCHEME FOR FLINT RIVER WATER

Every tenth sample included a duplicate aliquot or split of the composite water which was processed the same way as any other sample collected. The standard deviation calculated for samples and their duplicates gives an estimate of the overall precision, including both field and instrumental variations.

The following equation was used to calculate the standard deviation.

$$\text{Standard deviation} = \sqrt{\frac{\sum d^2}{2k}}$$

where d = difference between the sample and its duplicate

k = number of duplicates

Since the matrix of the sample can affect the precision, river water from each survey was handled separately. See Table C1 for results. Detection limits for the metals analyzed are reported in Table C2.

Certain samples were analyzed once a day for a number of days as "between run" replicates (Table C3). The variability of these replicates is assumed to be due to laboratory and instrumental procedures only. The field duplicates mentioned earlier have potentially higher standard deviations since there is additional variability from field techniques, i.e., bottle blanks, filtering and possible non-homogenity of the water in the 10 composite sample. Comparing the results of Tables B1 and B3 suggests that the variability of the results for all the metals was mainly due to laboratory and instrumental procedures.

Total river water (unfiltered) was collected in a 500 mℓ linear polyethylene bottle pre-cleaned as above. A 100 mℓ portion of that water was filtered through a .45 μm Sartorius cellulose acetate filter. The filtering apparatus was a Millipore polycarbonate Sterifil filtration system. Before use, the system was soaked in 4% v/v HNO_3, then rinsed well with deionized water. The filter was set in place, and 50 mℓ of deionized water was filtered, then discarded. Fifty mℓ of sample was then filtered and discarded. Sample water was then filtered until the filter began to clog. Before filling the 175 mℓ bottle with filtrate, the first 50 mℓ of filtrate was used to rinse it out.

TABLE C1. RESULTS OF FIELD DUPLICATES (SPLITS)

Metal	August 1981 Survey - Flint River Samples		December 1981 Survey - Flint River Samples		March 1982 Survey Flint River Sample	
	Number of Pairs	Standard Deviation (μg/ℓ)	Number of Pairs	Standard Deviation (μg/ℓ)	Number of Pairs	Standar Deviati (μg/ℓ)
Dissolved Cd	19	.05	6	T.02	14	.03
Total Cd	18	.07	7	.04	14	.04
Dissolved Cu	19	1.1	7	.4	13	.5
Total Cu	18	.9	7	.3	14	.7
Dissolved Zn	20	4	7	5	14	2
Total Zn	18	4	7	W2	13	2

NOTE: If $\frac{1}{2}$ [Detection Limit] $\leq$ [Measured Metal Concentration] < [Detection Limit], then the result is recorded as "T" preceding the detection limit.

If [Measured Metal Concentration] < $\frac{1}{2}$ [Detection Limit], then the result is recorded as "W" preceding a value $\frac{1}{2}$ the detection limit.

TABLE C2. DETECTION LIMITS

Metal	Detection Limit (μg/ℓ)
Cadmium	.02
Copper	.08
Zinc	4

TABLE C3 RESULTS OF BETWEEN-RUN REPLICATES

Metal	Number of Samples	Standard Deviation (µg/ℓ)
Dissolved Cd	6	.03
Total Cd	15	.07
Dissolved Cu	4	.6
Total Cu	18	1.2
Dissolved Zn	5	W2
Total Zn	18	2

The models 603 and 460 (Perkin Elmer) atomic absorption instruments equipped with graphite furnaces were used to analyze the samples. The drying, charring, and atomization program were optimized for river and effluents using optimization as described in "Analytical Methods for Atomic Absorption Spectrophotometry Using the HGA Graphite Furnace," Perkin Elmer (1977). See Table C4 for information on analytical conditions. All flameless analyses were done in duplicate while the flame analysis (zinc) was done in triplicate.

If chemical interferences were present which enhanced or suppressed the analytical atomization signal, then the standard method was used to calculate the sample concentration. If no interferences were present, then samples were calculated directly from a linear regression of the synthetically prepared metal standards. The latter case still involved a standard addition determination on every fifth sample in order to monitor recovery. Recovery here is defined as the slope of the standard addition calculation on a sample, times 100, divided by the mean slope of the standard addition on standards.

No chemical interferences were found when analyzing copper and zinc. However, since interferences were present which suppressed the analytical signal for cadmium, standard additions were used to determine the concentration of this metal.

Standards were prepared fresh daily and acidified (3 mℓ HNO_3/ℓ). Typically, 5 standards were digested along with every 20 samples and 3 blanks. The digestion procedure was a modified nitric acid digestion for total metal determination from "Methods for Chemical Analysis of Water and Wastes" (U.S. E.P.A., 1974). Hydrochloric acid was eliminated from the EPA procedure due to the interference of chloride ion with the analysis of zinc and cadmium (Analytical Methods for Furnace

TABLE C4 ANALYTICAL CONDITIONS

Metal	Method	Instrument	Wave Length (nm)	Lamp	Background[a] Correction?	Typical Working Range in ug/l
Cadmium	Graphite Furnace A.A.	Perkin Elmer 460	228.8	Cd Electrodeless Discharge Lamp	Yes	.02 - .5
Copper	Graphite Furnce A.A.	Perkin Elmer 460	324.7	Cu Hollow Cathode Lamp	Yes	.08 - 20
Zinc	Flame Atomic Absorption	Perkin Elmer 603	213.9	Zn Hollow Cathode Lamp	Yes	4 - 150

[a]Background correction was especially important to take care of non-specific atomic absorption for Cd and Zinc analysis.

Atomic Absorption Spectroscopy, Perkin Elmer, 1980). The digested blanks consisted of deionized water plus the same amount of HNO_3 added to the samples and standards. The median absorbence of the blanks was used to correct the samples. Digested standards were corrected by a standard blank. Calculations of concentrations were then based on these corrected absorbences. The filtered samples (dissolved) received no sample pretreatment.

In order to determine contamination introduced in the filtering process, two filter blanks were taken in each eight-hour shift in the field. This involved filtering an aliquot of deionized water. An unfiltered sample of this deionized water was also taken at the same time. This unfiltered sample is the batch blank in Table C5. The analytical results of the two types of samples were compared; if they were equal, then no filtering contamination was believed to occur. Equality here is confirmed by a T test. The results in Table C5 show that no correction was required for the filtering process in the August, December, and March surveys.

Since the filter blank results from both a bottle blank and a blank for the filtering process, it is assumed that if the filter blank were negligible, then the bottle blank would also be negligible. This was the case for all the metals during the surveys except for copper in August 1981. Bottle blanks were therefore checked for copper in the August 1981 set. The levels found in these bottles were below the detection limit for all three metals. We therefore concluded that the .447 μg/ℓ Cu in the sample of batch water was due to the copper in the batch water only.

Trace metal water samples were preserved by adding 3 mℓ of HNO_3 per liter of sample. Samples were refrigerated at 7°C.

TABLE C5. FILTRATION BLANKS

(Note: B.B. - Batch Blank and F.B. = Filter Blank)

Metal	Survey	Number (B.B., F.B.)	Standard Mean (µg/ℓ) (B.B., F.B.)	Deviation (µg/ℓ) (B.B., F.B.)	T-Test Result
Cadmium	Aug. 81	47, 47	0.011, 0.022	0.022, 0.027	*Same
Cadmium	Dec. 81	15, 13	0.001, -0.001	0.008 0.009	Same
Cadmium	Mar. 82	18, 18	0.018, 0.038	0.009, 0.108	Same
Copper	Aug. 81	47, 47	0.447, 0.562	0.440, 0.563	Same
Copper	Dec. 81	15, 13	-0.067, 0.092	0.209, 0.263	Same
Copper	Mar. 82	17, 17	-0.026, -0.104	0.494, 0.239	Same
Zinc	Aug. 81	47, 47	0.681, 0.745	1.476, 2.027	Same
Zinc	Dec. 81	16, 14	2.938, 3.143	1.769, 2.107	Same
Zinc	Mar. 82	18, 18	-0.487, -0.394	1.889, 1.83	Same

*At the 95% confidence level the mean batch blanks and filter blanks were equal; therefore, no blank correction was needed for the filtering process.

Results of several intercomparison studies are presented in Table C6. In both of these series, performance was considered "good." The true values of the unknowns fell within our 95% confidence interval. This interval is defined as our reported result plus or minus two standard deviations.

For both digested and dissolved samples, five standards were run at the beginning and end of each day's run. Half of the standards at the beginning of the day were spiked with known standards (standard additions). The remaining standards were spiked at the end of the day. The average slope of these standard additions to standards was used in the denominator of the recovery formula.

Conventional Parameters

Methods used for non-metal parameters are described in Table C7. Dissolved oxygen and temperature were in-situ measurements. Specific conductivity, pH, total alkalinity, and total non-filterable residue (suspended solids) were analyzed in the mobile laboratory. Hardness was analyzed at the Grosse Ile. Lab.

TABLE C5 INTERCOMPARISON WITH U.S. EPA ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY, CINCINNATI

(Concentrations in µg/ℓ)

Sample	Cd (Result, True Value)	Cu (Result, True Value)	Zn (Result, True Value)
Q.C. Series 475			
Sample 1	-	-	(65, 60)
Sample 2	(1.3, 1.5)	(7.8, 8.0)	(16.7, 12)
Q.C. Series 575			
Sample 1	(.31, .46)	(1.4, 1.4)	(29, 30)

TABLE C7. ANALYTICAL METHODS - CONVENTIONAL PARAMETERS

Parameter	Method	Equipment/ Instrumentation	Source of Method
Temperature	Thermometry	Thermometer	Standard Methods (1975)
Dissolved Oxygen	Dissolved Oxygen Probe	Yellow Springs Instruments Co., Inc.	Yellow Springs Instruments Co., Inc.
Specific Conductivity	Electrical Conductance	Beckman Conductivity Bridge (Model RC-19)	Beckman Manual (1973)
pH	pH Electrode	Fisher Accumet (Model 520 pH/ION meter)	Fisher Instrument Manual No. 26285
Alkalinity, Total	Titration to pH 4.5 with .02N H SO	Fisher Automatic Titration Model 471	EPA, Methods for Chemical Analysis of Water and Wastes (1979)
Residue, Total Non-Filterable	Gravimetric Measurement	GFF Filters (Whatman) Sartorious 2003 MPl Balance	EPA, Methods for Chemical Analysis of Water and Wastes (1974)
Hardness	Titrimetric	Fisher Automatic Titration Model 471 Used in the Manual Mode	Standard Methods for the Examination of Water and Wastewater, 14th Ed. (1975)

APPENDIX D

BEHAVIOR OF HALOGEN DISINFECTION RESIDUALS

APPENDIX D

BEHAVIOR OF HALOGEN DISINFECTION RESIDUALS

This appendix presents information on the aquatic fate of wastewater disinfection residuals. This discussion has been added at the request of the Office of Water Programs Operations (Construction Grants), recognizing that (a) chlorine residuals are commonly discharged in quantities toxic to aquatic life, and (b) chlorine is not discussed in the portion of the Guidance Manual covering BOD, DO, and ammonia (Driscoll et al. 1983), and since it is not a "priority pollutant", it is not covered by Mabey et al. (1982) and Callahan et al. (1979).

As chlorination is by far the most common disinfection practice in this country, the emphasis is on chlorine residuals; nevertheless, some information on bromine chloride is also included. The discussion is intended to apply to fresh water; halogen chemistry in saltwater, described by Haag and Lietzke (1981), is not identical to that in fresh water.

The discussion is limited to the fate of halogen oxidants. It does not deal with the formation of halogenated organic by-products; such formation is of minor importance in determining the half-life of the disinfectant itself. Although some of these by-products may be carcinogenic, their production is of greater public health significance during potable water treatment than during wastewater disinfection (Metcalf & Eddy 1982). Information on production of halogenated organics is provided by the National Research Council (1979) and Jolley (1975). It is worth noting here, however, that the formation of trihalomethanes (the by-products of greatest concern) appears to be depressed by the presence of ammonia, a usual constituent of municipal wastewaters that have not undergone complete nitrification (Metcalf & Eddy 1982).

The following discussion has been edited from the Metcalf & Eddy (1982) report, Impacts of Wastewater Disinfection Practices on Coldwater

Fisheries. Additional details on disinfectant chemistry can be found in Weber (1972).

D.1 AQUATIC FATE

Most wastewater treatment plants discharge effluent through an outfall pipe or through a small ditch which then combines with the receiving water. In such cases, initial mixing of the effluent depends upon the outfall or ditch characteristics, the river characteristics, and the magnitude of flows of each. For a few large treatment plants, waste is discharged through submerged multi-port diffusers.

A common method of estimating the dilution of wastewater effluent is to calcuate the ratio of river flow to effluent discharge flow. This number may range several orders of magnitude. Typical ratios may be 100 for small plants discharging to average sized rivers, and 1 or 2 for plants discharging to small tributaries.

The pitfall of using the ratio of flows to estimate dilution is that complete mixing (lateral and vertical) is implicitly assumed. In cases of small tributaries with low dilutions (e.g., 1 or 2) this may be a reasonable assumption. However, for higher dilutions (e.g., 100 or more), a long distance is often necessary to complete the lateral mixing process. In most cases, complete vertical mixing may be a reaonable assumption.

Chlorine

The initial chemical reactions of chlorine in aqueous solution depend on the application form. Chlorine gas hydrolyzes in solution as shown below:

$$Cl_2 + H_2O \longrightarrow HOCl + H^+ + Cl^-$$

This reaction is rapid and essentially complete if the pH is greater than 6. Application of sodium or calcium hypochlorite will yield hypochlorite

ion (OCl^-) initially, which will rapidly establish equilibrium with hypochlorous acid (HOCl):

$$NaOCl + H_2O \rightleftharpoons HOCl + Na^+ + OH^-$$

Chlorine present in wastewater or receiving waters is usually measured as total residual chlorine (TRC). TRC is the sum of free residual chlorine and combined residual chlorine. Free residual chlorine (FRC) is the free available oxidant in solution consisting of hypochlorous acid (HOCl) and hypochlorite ion (OCl^-). Combined residual chlorine (CRC) generally refers to the chloramines formed when hypochlorous acid reacts with ammonia. Free chlorine can also react with other organic compounds containing amino groups to form organic chloramines. Bactericidal strength is in the order: hypochlorous acid > hypochlorite ion > chloramines.

Chlorine demand occurs both in wastewater and the receiving waters. Chlorine demand is the difference between the appplied chlorine dose and the free residual chlorine. It is due to a variety of reactions includng oxidation and decomposition. Some important reactions of chlorine in the freshwater environment are presented in Table D1 and a schematic summary of the important reaction pathways is presented in Figure D1.

The principal determinants of the likely reaction products in municipal wastewaters and fresh surface waters are concentrations of chlorine and ammonia and pH. Chlorine enters the receiving water mainly in the form of combined chlorine (mono- and di-chloramine) due to the typical ammonia concentrations found in wastewater. For highly nitrified effluents, free chlorine would be the main constituent. This residual chlorine is lost rapidly from the receiving water due to several reactions including: demand from oxidation reactions; combination with organic material; photochemical decay; and decompositon. Although measurements of chlorine decay rates are not common, some results are presented in Table D2. Several generalizations can be made from results presented in the table, including (1) rates are widely varying, (2) decay

TABLE D1. PRINCIPAL REACTIONS OF CHLORINE IN SOLUTION

Reaction type	Example
Hydrolysis	$Cl_2 + H_2O \longrightarrow HOCl + HCL$
Ammonia	
Substitution	$HN_3 + HOCl \longrightarrow NH_2Cl + H_2O$
Oxidation	$2\ HNCl_2 + H_2O \longrightarrow N_2 + HOCl + 3\ H^+ + 3Cl^-$
Inorganic oxidation	$Mn^{+2} + HOCl + 2\ H_2O \longrightarrow MnO(OH)_2 + 3\ H^+ + Cl^-$
Decomposition (with sunlight)	$2\ HOCl \longrightarrow 2\ H^+ + 2\ Cl^- + O_2$
Organic reactions	
Oxidation	$RCHO + HOCl \longrightarrow RCOOH + H^+ + Cl^-$
Substitution	$RNH_2 + HOCl \longrightarrow RNHCl + H_2O$

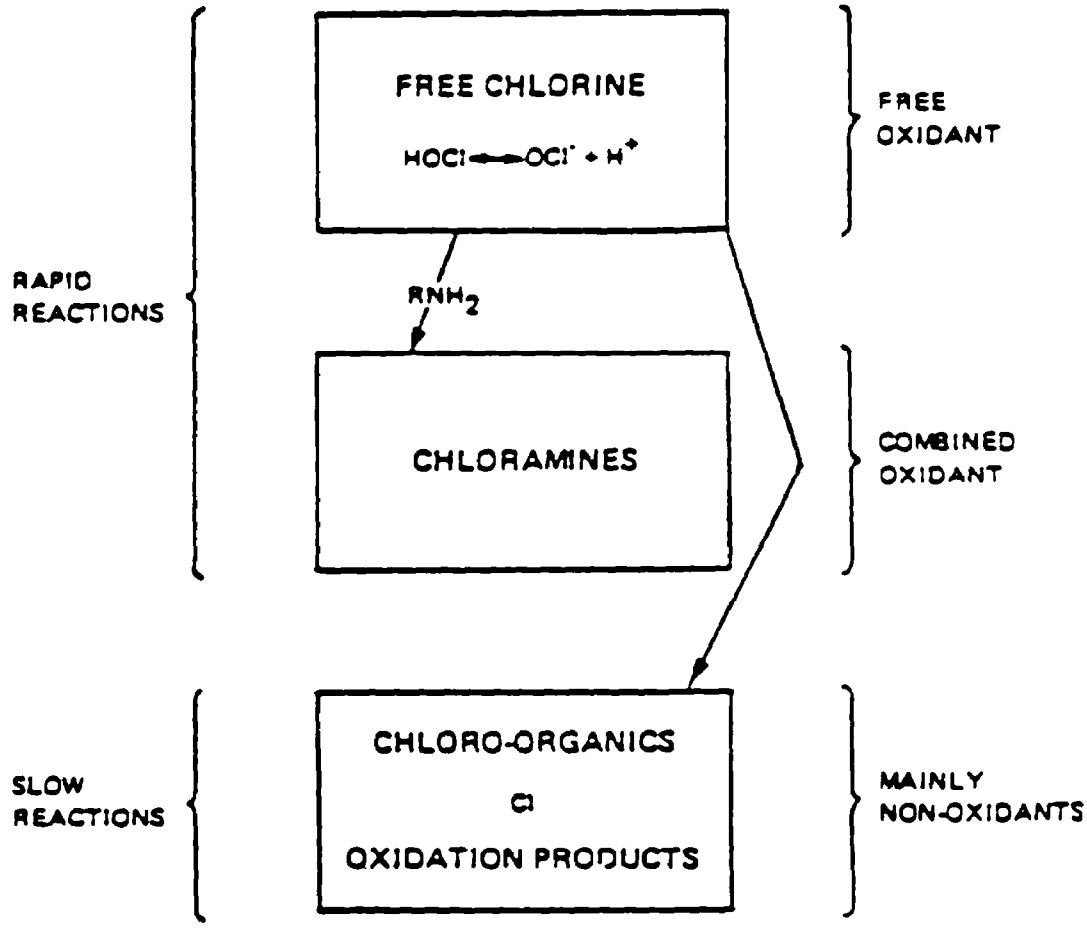

FIGURE D1. DIAGRAM OF CHLORINE REACTION PATHS IN FRESHWATER

TABLE D2. CHLORINE DECAY RATES

Chlorine Form	Decay rate, day^{-1}	Conditions	Reference
Free Chlorine (80% OCl^-)	50-178	Samples exposed to wind and sunlight.	Johnson (1978)
	4.6-18	Indoor samples exposed to UV light no stirring.	Johnson (1978)
	50-178	Initial rate for indoor samples due to easily oxidized compounds.	Johnson (1978)
Monochloramine	0.7-1.8	Indoors.	Johnson (1978)
	6.7-7.4	Outdoors samples exposed to sunlight and turbulence.	Johnson (1978)
Free chlorine in York River estuary (monochloramine formation suspected)	1.2-1.3		Johnson (1978) from Bender et al. (1975)
Monochloramine	1.3		Johnson (1978) from Bender et al. (1975)
Monochloramine in six Colorado Rivers	1.8-53	Light bottle field tests.	Heinemann et al. (1981)
	5.0-104	Based on field data without dilution.	Heinemann et al. (1981)
Total residual chlorine	20		Haas (1981)

of free chlorine is an order of magnitude faster than of monochloramine and (3) field decay rates are normally an order of magnitude faster than laboratory rates.

Bromine Chloride

Reactions of bromine chloride in freshwater are more complicated since two halogens are involved. Reactions in freshwater include the production of both hypobromous acid and hypochlorous acid:

$$BrCl + H_2O \rightleftharpoons HOBr + HCL$$

$$Br_2 + H_2O \rightleftharpoons HOBr + H^+ + Br$$

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl$$

As with chlorine, hypobromous acid will react with ammonia to form bromamines. Roberts and Gleason (1978) presented data on the decay of bromine residual in seawater with ammonia concentrations of 0.2 mg/l. Decay was extremely rapid since bromine residuals were not detected after only two hours. No other data on bromine residual decay were available.

D.2 CASE STUDY

The concepts discussed above are applied here for demonstration purposes. The Connecticut Department of Environmental Protection conducted physical, chemical, and biological measurements to assess the impact of the Fairfield Hills Sewage Treatment Plant on Deep Brook in Newtown (CT DEP 1981). The plant provides advanced treatment with the main treatment units being primary and secondary settling tanks, trickling filters, and intermittent gravity and sand filters. Current plant flow averages about 0.3 mgd. Plant effluent concentrations of TRC typically range from 0.8 to 3.0 mg/l.

Deep Brook is a fast flowing, well oxygenated tributary of the Pootatuck River with an average flow of 0.27 m^3/s and a 7-day 10-year low flow of 0.014m^3/s. The plant effluent discharges into Deep Brook about 610 meters above the Pootatuck River. Pootatuck River average flow

is 1.1 m^3/s and 7-day 10-year low flow is 0.12 m^3/s. Measurements of in-stream and effluent TRC were conducted on August 29, 1980.

Mean values of TRC concentrations measured using the amperometric titration method are presented in Figure D2. On the date of these measurements, river flow was 0.025 m^3/s and plant flow was 0.014 m^3/s. Total mixing is said to occur 15 meters downstream of the discharge point, although the basis for this statement (i.e., visual, dye study, etc.) is not stated. It seems reasonable to expect that mixing would be rapid with the plant flow nearly as large as the river flow (dilution ratio of 1.8). As shown in Figure D2, at a point 15 meters downstream the effluent concentration of TRC had been reduced from 3.8 to 2.0 mg/l, or diluted 1.9 times. This tends to support the 15-meter complete mixing assumption.

The TRC concentrations decreased to 0.2 mg/l (a factor of 10) at a point just before the confluence with the Pootatuck River. Since no dilution water enters the brook in this reach, the loss of chlorine was due to chemical reaction and decay. When in-stream chlorine concentrations are plotted on semi-log paper, a straight line gives a reasonable fit with the data, indicating that the die-off of chlorine for this case is approximately first order. Using the formula for first-order decay (Equation 2.3 in Section 2.4 of the text), a rate coefficient of about 100 per day is calculated. (To obtain this value, a stream velocity of 0.3 m/s has been assumed, as the actual value was not given.) This indicates that the in-stream loss of chlorine is extremely rapid. However, the value of 0.2 mg/l is still more than an order of magnitude higher than published maximum in-stream criteria. In Pootatuck River, TRC could not be detected after the Deep Brook confluence. Biological measurements indicated a highly stressed condition in Deep Brook downstream of the discharge.

In summary, a simple dilution calculation followed by a first order reaction coefficient was adequate in this case to estimate the chlorine

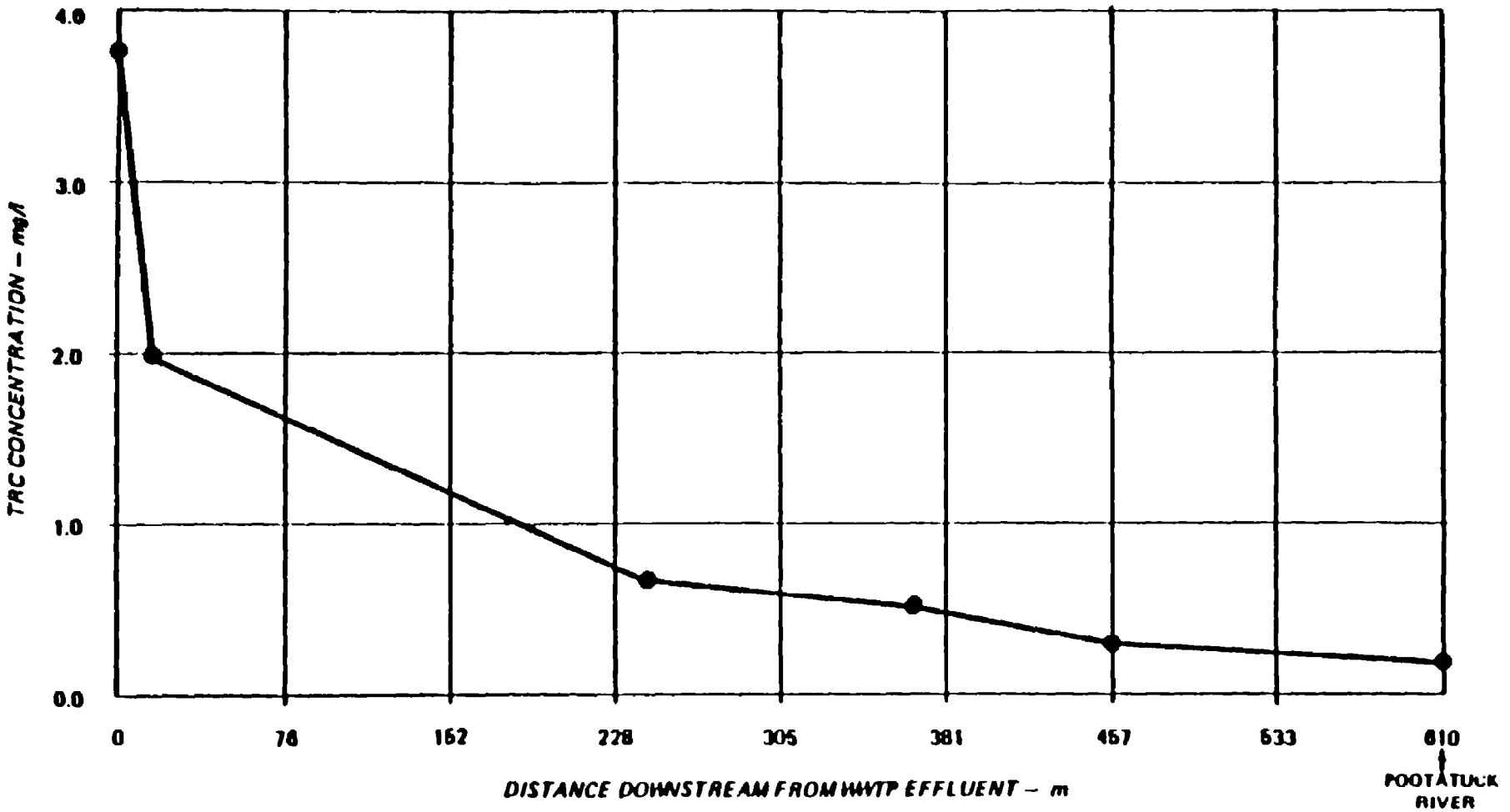

FIGURE D2. TRC CONCENTRATIONS IN DEEP BROOK

concentrations in Deep Brook. However, this method must be used with caution for several reasons. If stream-flows are higher, complete mixing would not occur as quickly, and this method does not apply in the zone of incomplete mixing. Also, as discussed earlier, in-stream reactions are extremely variable depending on environmental factors such as light, temperature, and streamflow.

ATTACHMENT I

WATER-SEDIMENT PARTITION COEFFICIENTS FOR PRIORITY METALS

by

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November 1982

ACKNOWLEDGEMENTS

The technical analysis reported in the study was performed by Michael T. Kontaxis, Project Scientist. Dominic M. DiToro and Donald J. O'Connor served as Project Consultants and provided technical guidance. John P. St. John served as Principal-in-Charge and drafted the report.

William L. Richardson of the U.S. Environmental Protection Agency, ERD-L at Grosse Ile, served as Project Officer for the Government.

ABSTRACT

The Office of Water of the U.S. Environmental Protection Agency is responsible for managing waste load allocation (WLA) activities throughout the nation. These procedures generally involve the application of mathematical modeling activities which require specialized information for proper implementation. One area which will receive increasing attention in this regard is the fate and transport of toxic pollutants, particularly certain priority heavy metals. An important characteristic of these materials is an affinity to complex and/or be adsorbed (partition) to particulate materials in the natural environment. As realistic modeling frameworks must properly track both dissolved and particulate forms of substance in the receiving water environment, it is important to determine partition coefficients for the priority metals for use in these analyses.

It was the purpose of the investigation reported herein to retrieve information and data by which to document and/or calculate water-sediment partition coefficients for various priority heavy metals. In addition, the available data was to be examined to determine possible functional relationships among partition coefficients and various environmental water quality variables.

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SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

1. The available technical literature contains very limited useable data for determination of partition coefficients for priority metals.

2. Of the various computerized data bases investigated in this study, the water quality file of STORET contains the largest amount of pertinent information by a large margin, approximately 20,000 useable records from various water body types. The most applicable data were derived from water column samples; bed sediment data, while available, did not provide sufficient information for calculation of partition coefficients.

3. Retrieved data were in the following order of abundance by priority metal: zinc, copper, lead, arsenic, nickel, chromium, cadmium, mercury, and silver. Analysis was confined to data collected in streams and lakes. Insufficient data were available for analysis of arsenic in lakes and silver in both types of water bodies.

4. Sufficient data are available for calculation of representative values of partition coefficients for the various priority metals, with the exceptions noted above. Much less information is available by which to assess relationships among partition coefficients and various environmental variables other than suspended solids.

5. Analysis of data indicated a pronounced apparent relationship between partition coefficients for the various priority

metals and suspended solids concentration. However, for any given solids concentration, calculated partition coefficients varied over a wide range of values, perhaps multiple orders of magnitude. No consistent correlation was found among partitioning and other environmental measures such as pH, alkalinity, temperature or BOD. Partition coefficient values for lakes were determined to be consistently greater than for streams for all priority metals except mercury.

6. The partition coefficient values determined for the various priority metals are satisfactory for application analyses. However, the values resulting from the regression analyses developed in this study are order of magnitude estimates only and the wide range of calculated partition coefficients should be considered in practical use.

It is recommended that a refined data base be accumulated for the various priority heavy metals. Such a data base should consist of controlled sampling of a variety of natural waterways and include simultaneous measurement of all physical, chemical and biochemical factors which may have a bearing on heavy metal partitioning. Laboratory studies may be appropriate to supplement the field investigations. These data should be evaluated to reassess the results of the present investigation.

SECTION 1

INTRODUCTION

1.1 BACKGROUND

The Office of Water of the U.S. Environmental Protection Agency is technically responsible for managing waste load allocation (WLA) activities within the organization and for providing technical assistance to the states. In addition, this office also has technical responsibility to review various advanced treatment (AT) projects proposed under the construction grants program by regional offices and the states. The AT projects often result from water quality studies and mathematical modeling analyses which are used to establish WLAs indicating that technology based effluent limitations are not sufficient to achieve or maintain water quality standards. It is important that WLAs be established in a proficient and technically correct manner so that recommended facilities are properly developed and cost-effectively designed.

In the performance of its mandate, the Office of Water has determined certain specific areas whereby assistance to the states is advisable to help maintain and/or improve the technical bases for WLAs and recommended AT facilities. One such area which will receive increasing attention is the fate and transport of toxic materials, particularly certain priority pollutant metals, as discharged from POTW's and other sources. Treatment requirements for these substances will depend upon properly determined WLAs, which in turn must be based on mechanistically realistic assessments of the transport and fate of these materials in the aqueous environment. An important characteristic of metals in this regard is the affinity to complex and/or

be adsorbed (partition) to natural particulate materials. Realistic modeling frameworks must have the capacity to track both the dissolved and particulate forms of metal in the receiving water as each phase may be transported by different mechanisms. Fundamental information which is required for this purpose is appropriate partition coefficients for metals, which define the fraction of metal in dissolved and particulate phases for specific environmental conditions.

1.2 OBJECTIVES OF THE STUDY

Specific objectives of the study are summarized as follows:

1) identify and retrieve appropriate reference material which contains information on partition coefficients for certain priority heavy metals.

2) identify and retrieve appropriate laboratory and field data which are satisfactory for calculation of partition coefficients for the priority metals.

3) calculate partition coefficients for priority metals from available data, display the results, and wherever possible, relate coefficients to appropriate environmental variables.

4) assess the quality of the data collected, the representativeness of reported or calculated partition coefficients and recommend methods for improvement.

5) provide a report summarizing the results of all work and including an appendix containing basic information resulting from the evaluations.

The specific priority metals of concern which are considered in the study are:

- Arsenic
- Cadmium
- Chromium
- Copper
- Lead
- Mercury
- Nickel
- Silver
- Zinc

1.3 SCOPE OF THE REPORT

The report summarizes various technical procedures which were implemented to obtain, categorize and evaluate data for priority heavy metal partition coefficients. Theoretical considerations are presented to provide a background for the analysis and to indicate data requirements. Required data are summarized by source and availability and classification procedures are described. Methods of analysis are described for the categorization of data, calculation of partition coefficients, and statistical evaluation of relationships between these values and various ambient environmental variables. Finally, the results of the analysis are presented and discussed.

SECTION 2

CHEMICAL PARTITIONING

One of the major characteristics which differentiates many chemicals and heavy metals from classical water quality variables is an affinity for adsorption to particulate material. Figure 2-1 schematically illustrates the principle. If a mass of soluble chemical is placed in a laboratory beaker of water, an initial concentration of dissolved chemical, c_d, will result. If particulate material is then added to the beaker and stirred, a portion of dissolved chemical will be sorbed onto the particulates and some of the chemical concentration will then be in particulate form, c_p. If this process is monitored with time as shown on the diagram, dissolved chemical will be reduced and particulate chemical will increase in a reversible reaction until an equilibrium is achieved at some point. The total chemical concentration at any time is equal to the sum of the dissolved and particulate concentrations:

$$c_T = c_d + c_p \qquad (2\text{-}1)$$

in which c_T is total chemical concentration and all concentrations are expressed on a bulk volume (liquid plus solid) basis.

The rate with which this reacion takes place and the relative relationship between the dissolved and particulate chemical, that is, the water-sediment partitioning, are both chemical specific. In most cases, reaction between the dissolved chemical and particulates occurs very rapidly, minutes to hours, and equilibrium is achieved quickly relative to the time characteristics of the environmental setting. The tendency to sorb is highly chemical specific and will range from very weak to strong, in the case of materials with low solubility.

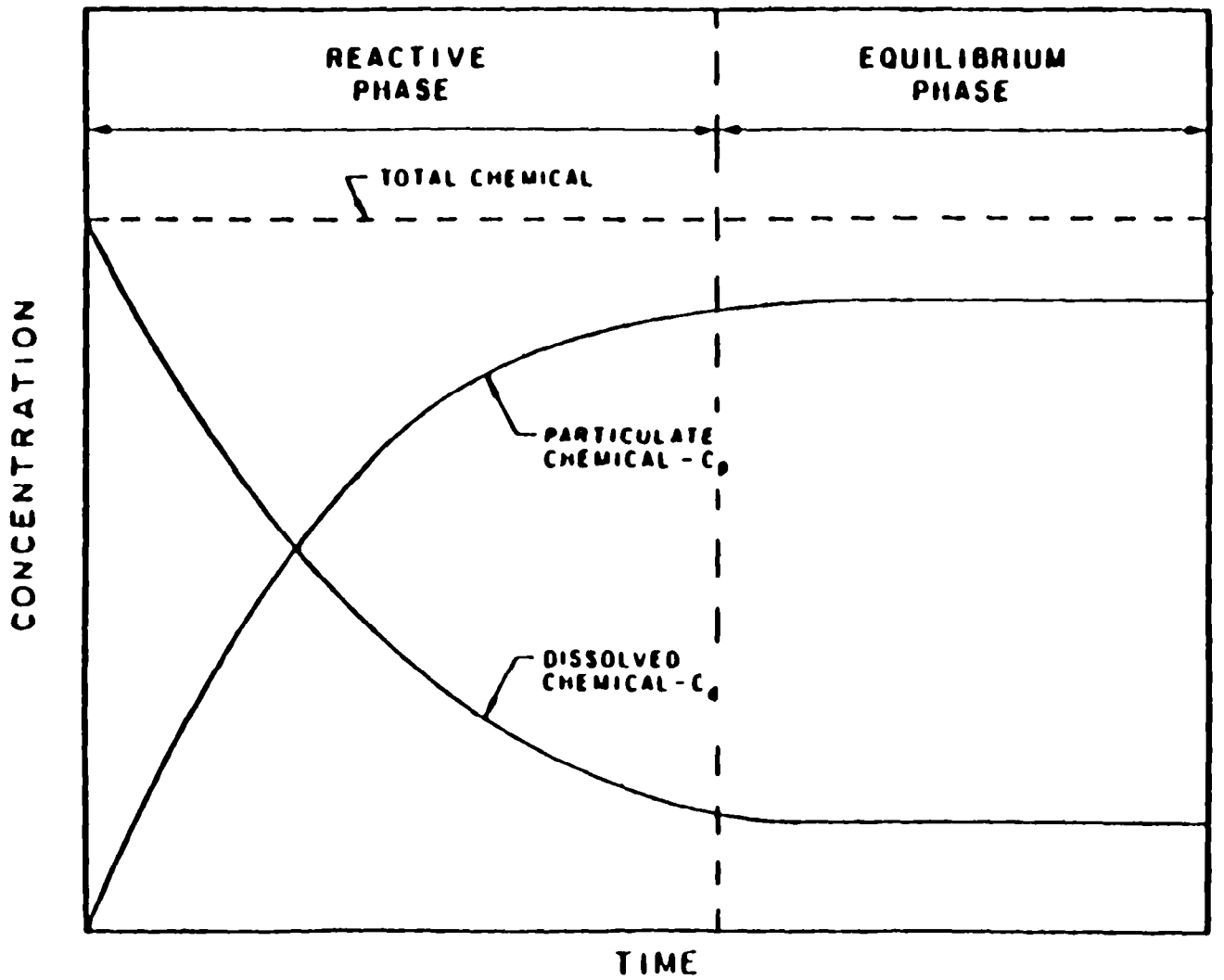


FIGURE 2-1

SCHEMATIC DIAGRAM OF CHEMICAL SORPTION

The affinity of a particular chemical or heavy metal to sorb can be quantitatively expressed by a sediment-water partition coefficient, K_p. A series of experiments of the type schematically indicated on Figure 2-1 may be conducted with differing initial dissolved concentrations of a specific chemical. After equilibrium is achieved, the particulate chemical concentration to suspended solids ratio, c_p/s_s, expressed as micrograms of chemical per gram of particulate material (µg/g), may be plotted as a function of the dissolved chemical remaining, c_d, expressed on a volumetric basis as microgram per liter of water (µg/l).

Figure 2-2 schematically illustrates the results of this laboratory experiment. A specific chemical will produce one of the lines shown on the logarithmic diagram, the relative position of which determines the partition coefficient. For a particular dissolved concentration, greater particulate concentrations result from larger partition coefficients as shown schematically by the various distributions. Data from chemicals which can be plotted and correlated as shown on Figure 2-2 behave according to the Freundlich isotherm defined as:

$$c_p/s_s = K_p(c_d)^{1/n} \qquad (2\text{-}2)$$

in which n is a constant characterizing the slope of the relationship. If the slope is near 1 indicating a linear relationship, the partition coefficient is defined as:

$$K_p = \frac{c_p/s_s}{c_d} \qquad (2\text{-}3)$$

As indicated, a specific chemical or heavy metal will yield one of the relationships indicated schematically on Figure 2-2 for a specific type of sorbing particulate material. However,

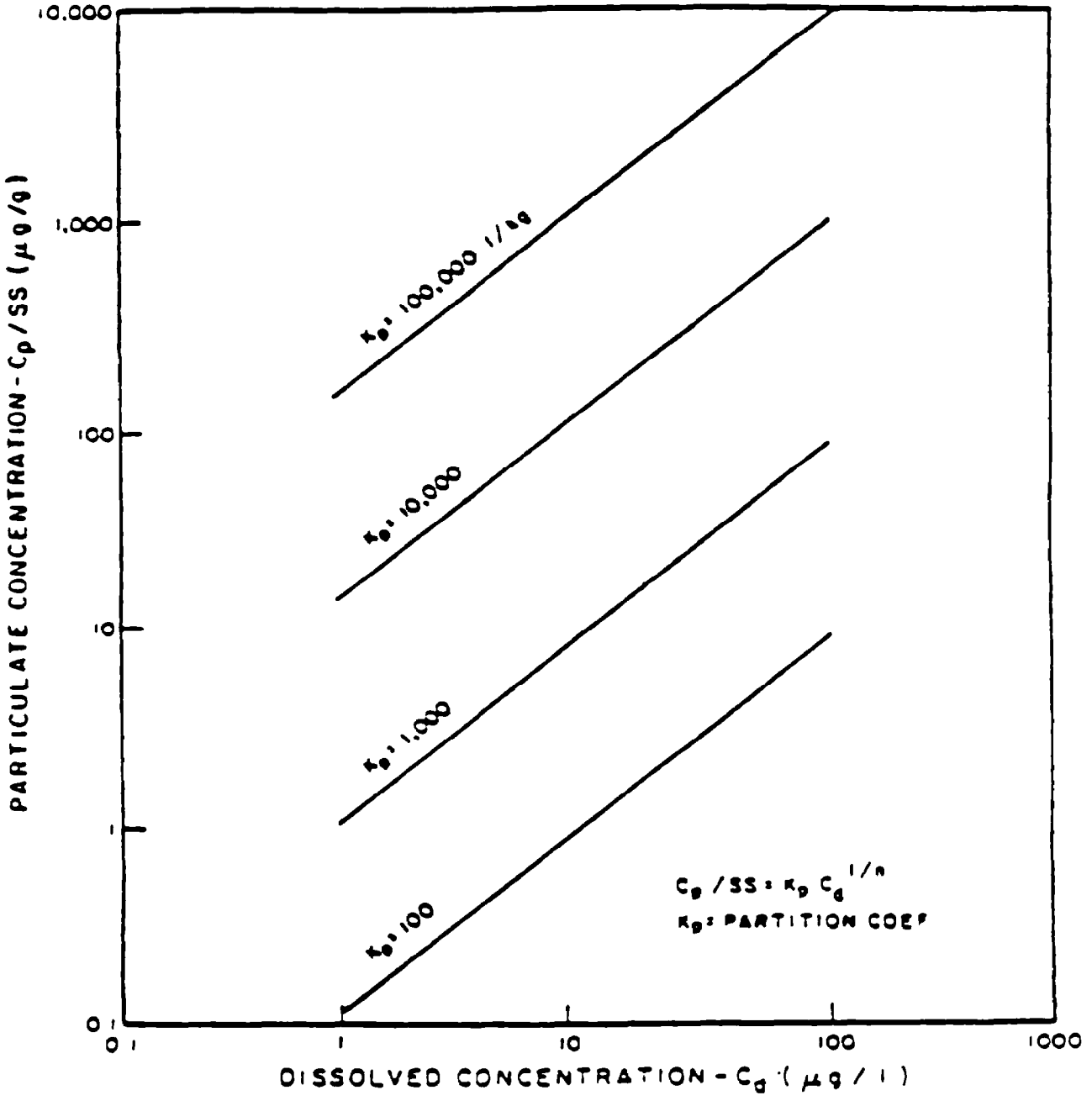


FIGURE 2-2

EXAMPLE ISOTHERMS AND PARTITION COEFFICIENTS

different relationships, and therefore, different partition coefficients, may be observed for the same chemical with various types of sorbants. For example, organic particulates or silty materials may attract a certain chemical more strongly than sandy materials. Further, different size classes of particulate material, as they may reflect different classes of particulates as sands, silts, clays, etc., may exhibit differing affinities, and partitioning, for a specific chemical. In principle, it is most advantageous, therefore, to perform experiments and determine a chemical's partitioning characteristics with the type of particulate material (suspended and bed sediment) to which it will come in contact in the natural environment.

As described, the nature of the sorbant may have a bearing on the magnitude of the partition coefficient for a particular substance. It has also been observed (O'Connor and Connolly) that partition coefficients may vary in accordance with the concentration of the sorbant as well as its nature. Figure 2-3 presents some empirical relationships between partition coefficients and sediment concentration for a variety of substances. For certain chemicals, it is observed that partition coefficients may be expected to vary by an order of magnitude or more depending upon the solids concentration. In the case of heavy metals, other factors such as pH, alkalinity or hardness, temperature, and conductivity may have an effect on the partition coefficient due to the complex chemical reactions which occur with these substances in the natural environment.

Much valuable information with which to define partition coefficients and relationships with various environmental variables can be determined from carefully developed and controlled laboratory experiments. It is noted, however, that such values are to be used subsequently in calculations to

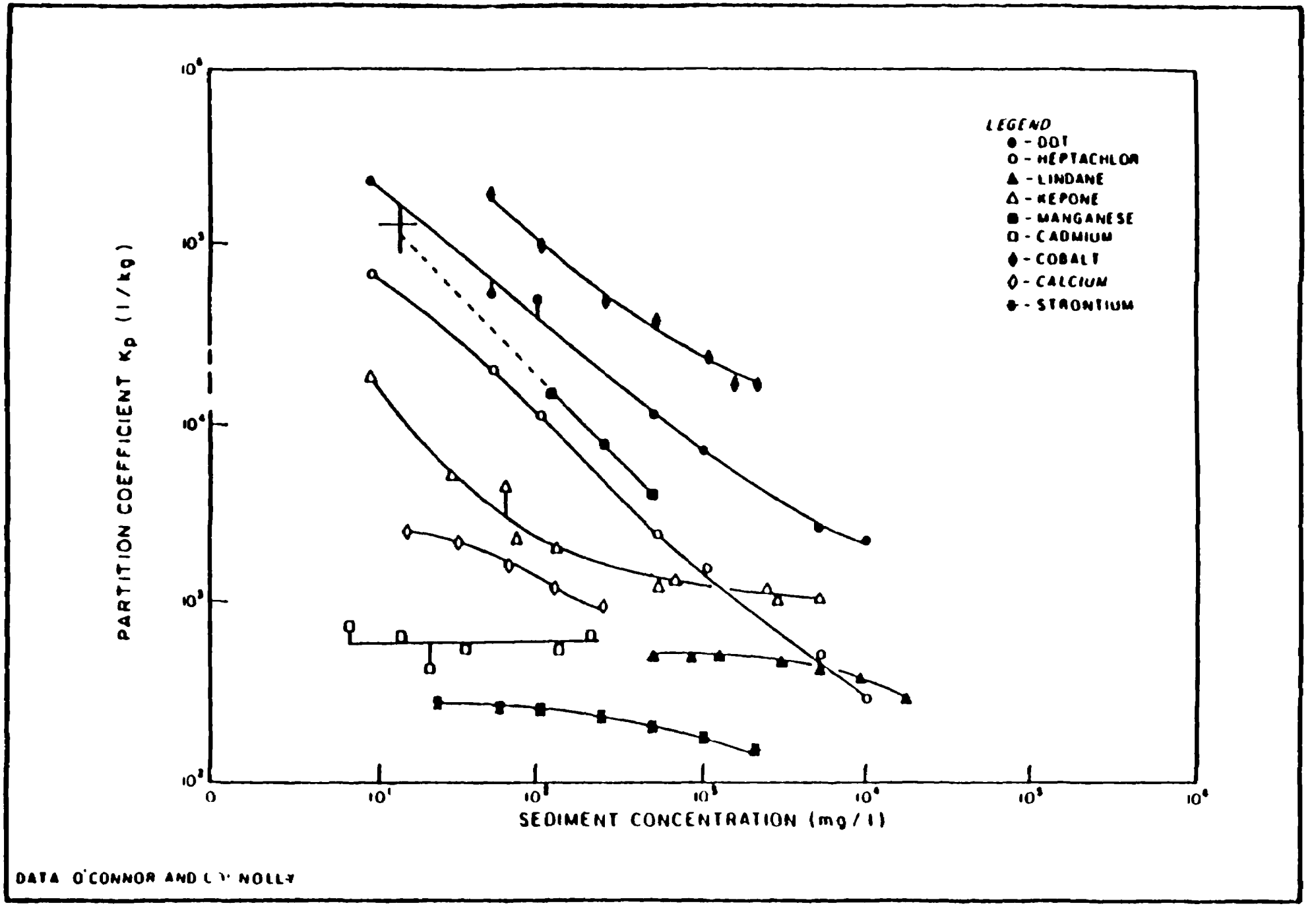


FIGURE 2-3

VARIATION OF PARTITION COEFFICIENT WITH SOLIDS CONCENTRATION

estimate what occurs in the field, this is, in the natural environment. Although the laboratory data are quite useful, it is appropriate to utilize field data wherever available in order to calculate partition coeffient values from those settings to which they will be subsequently applied. These natural conditions are likely to be far more physically, chemically, and biologically complex than the laboratory setting, but the information derived, therefore, is realistic in the natural sense and can serve to indicate how well or poorly partition coefficients can be defined for the natural setting.

SECTION 3

SUMMARY OF AVAILABLE DATA

3.1 DATA REQUIREMENTS

The minimum basic data requirements for calculation of partition coefficients for the various priority metals are dissolved and particulate concentrations and a measure of the associated particulates, suspended solids. This information allows determination of partition coefficients in accordance with Equation (2-3) and also provides for an examination of any solids dependent partitioning relationships such as illustrated on Figure 2-3. Additional information is required to assess other potential correlations between partitioning and ambient environmental variables.

In the case of heavy metals, other pertinent related data include pH, alkalinity, hardness and temperature, variables which may influence the chemical reactions which metallic substances undergo in the natural environment. Further, some information on the nature of the sorbing solids in terms of organic and inorganic fractions and size distribution is appropriate. Measures which may provide some information on the organic nature of the sorbing material are volatile suspended solids, biochemical oxygen demand (BOD), chemical oxygen demand (COD), and chlorophyll-a. Flow data, whether low, average, or high in a particular stream, may provide some indication of the type of particulate material (sand, silt, clay) likely to comprise suspended sediment in the water column in the absence of other information.

The foregoing type of information was sought from both laboratory and field investigations. In the case of field data, data were sought for both water column and bed sediment and for different types of water body, particularly streams and lakes. A distinction between partition coefficients calculated for each of these types of water bodies is appropriate as the nature of corresponding suspended sediment may be different, that is, more organic in the case of lakes.

3.2 SOURCES OF DATA

A large amount of field data resulting from various types of surveys resides on computerized data bases. The following data bases were examined for data availability: STORET (USEPA), NASQAN (USGS), the data base maintained by NOAA, and STAR (Canadian Centre for Inland Waters). In addition, the computerized reference service DIALOG was utilized to identify and secure additional reference material including both field and laboratory investigations. These data bases were reviewed to avoid potential multiple counting of samples. The following is a brief description of these data bases in relation to this project:

1) STORET

The water quality file of this data base contains water quality information obtained at numerous stations located in all states and operated by various agencies. It is the largest data base for water quality information by far.

2) NASQAN

Water quality data of this file are contained in STORET. NASQAN data updates are transferred to STORET on a biweekly basis. Data can be retrieved in the USGS format.

3) NOAA

This data base contains data for ocean, near-shore ar estuarine samples. The estuarine samples cover the areas of Puget Sound and New York Bight. A search of these areas was requested. The search for Puget Sound revealed no metals data. The search request for New York Bight did not result in information in time for processing.

4) STAR

This data base contains two subsystems. One subsystem contains data exclusively for the Great Lakes. The other subsystem, NAQUADAT, contains river water quality data for Canada. The NAQUADAT data are not included in STORET and it has not been updated in the last four years. The cost per retrieval request was prohibitively expensive and beyond the scope of this investigation.

5) DIALOG

This reference service contains numerous citations of publications in a great variety of technical fields. The citations are arranged in subject-related files. A strategy was devised to search relevant files in order to identify sources containing data consistent with the requirements of the study. The files searched were:

National Technical Information Service
Water Resources Abstracts
Environmental Bibliography
Pollution Abstracts
Instructional Resources Information Systems

Enviroline
Compendex
Ocean Abstracts
Comprehensive Index (Dissertation Abstracts)

A small number of usable publications were identified and obtained.

6) Miscellaneous

A search of all pertinent in-house publications was conducted.

3.3 AVAILABILITY OF DATA

The small number of references obtained from DIALOG contained no significant amount of useful information. Only a modest amount of pertinent data was obtained from in-house sources of reference material. On this basis, and in accordance with the evaluation of the various computerized data bases as described above, it was concluded that the water quality file of STORET would provide the vast majority of usable samples, and almost all effort should be directed to this source. A retrieval strategy was then devised to search the data records of all stations in all states, and identify ambient, remark-code-free samples which contain, at minimum, the concentration of total and dissolved species of metal and suspended solids. For such samples, data retrieval also included temperature, pH, alkalinity, hardness, flow, COD, BOD, volatile non-filterable residue (volatile suspended solids), chlorophyll-a corrected, and uncorrected chlorophyll. No data were available on the size distribution of suspended solids in the water column. Although data are available on bed sediment samples, the information is not

sufficiently complete (dissolved chemical missing) for calculation of partition coefficients. Data retrieval was therefore restricted to water column data. The results of these retrievals were obtained on magnetic tapes for subsequent analysis.

3.4 CLASSIFICATION AND DISTRIBUTION OF DATA

It was determined from initial STORET retrievals that the useful data base for some of the priority metals was quite large with samples of interest numbering in the thousands. Data handling and subsequent analysis was therefore performed by computer. All of the basic minimum data which were retrieved for each priority metal permitted calculation of a partition coefficient in accordance with Equation (2-3). However, a purpose of the study was to assess any relationships between partitioning and various environmental variables as discussed. In order for these determinations to be valid, the basic data must be measured simultaneously on the same sample or at the same time. Hence, the data base for each priority metal was sorted into various types of records, each of which was characterized by the simultaneous determination of various parameters. In this manner, a large data base could be examined for sampling information most useful for cross-correlation purposes, and the appropriate data records accessed for analysis.

The definitions established for the various data records are as follows:

Type	Data Content of Record
0	Total and dissolved metal and suspended solids concentrations
1	data of type 0 and pH
2	data of type 1 and alkalinity
3	data of type 2 and temperature
4	data of type 3 and (COD or BOD)
5	data of type 4 and (volatile suspended solids, or chl-a corrected or chl-a uncorrected)
6	data of type 4 and 5

Hardness was judged to be redundant with alkalinity for correlation purposes and thus not included in the data records. Flow information was judged to be too meager for meaningful correlation and also excluded from evaluation.

For each priority metal, the total number of records and the distribution of these records per type was determined for each station in each state. At the end of the first stage of data processing, a summary table was developed for each metal which contains an aggregation of records and stations per state, a distribution of records per type for each state and the total number of all records.

Table 3-1 is an example data summary for the priority metal, zinc. The table shows the total number of records and stations and the distribution of record types within each state reporting data. The total record count for zinc is 5397. These records include data from streams, lakes, estuaries, coastal zones, manholes, and other miscellaneous origins. Figure 3-1 is a

TABLE 3-1

ZINC DATA SUMMARY

STATE		TOTAL RECORDS	BY RECORD TYPE 0	1	2	3	4	5	6	STATIONS
AK	2	2	0	0	1	1	0	0	0	1
AZ	4	27	2	21	0	0	4	0	0	7
AR	5	5	0	0	0	0	5	0	0	2
CA	6	48	14	8	0	1	0	12	13	23
CO	8	79	25	46	0	4	4	0	0	19
CT	9	7	7	0	0	0	0	0	0	1
DC	11	74	74	0	0	0	0	0	0	1
FL	12	3	0	1	0	0	2	0	0	2
GA	13	26	8	15	0	3	0	0	0	9
ID	16	283	26	29	8	210	10	0	0	43
IL	17	126	7	8	7	9	4	71	20	37
IN	18	41	15	19	0	5	1	1	0	24
IA	19	12	2	2	1	7	0	0	0	8
KS	20	8	1	1	0	6	0	0	0	4
KY	21	100	9	6	1	12	71	1	0	31
LA	22	1056	78	1	622	1	321	0	33	186
ME	24	12	0	11	0	1	0	0	0	3
MD	25	18	7	2	0	5	2	2	0	7
MA	26	393	251	0	2	20	10	109	1	46
MI	27	15	2	1	2	8	2	0	0	8
MN	28	10	0	1	5	0	4	0	0	6
MS	29	435	97	14	9	315	0	0	0	69
MO	30	220	30	3	1	27	25	125	0	48
MT	31	1	0	1	0	0	0	0	0	1
NE	32	16	0	1	1	0	14	0	0	3
NV	34	120	0	2	1	6	108	0	3	18
NJ	35	46	12	3	0	8	22	0	1	20
NM	36	27	9	9	0	4	1	4	0	13
NY	37	10	1	0	0	9	0	0	0	4
NC	38	9	0	2	1	2	4	0	0	4
ND	39	433	17	14	4	75	1	322	0	120
OH	40	17	7	4	0	5	0	1	0	10
OK	41	10	1	0	0	8	1	0	0	6
OR	42	14	2	1	0	1	0	7	3	13
PA	44	1	0	1	0	0	0	0	0	1
RI	45	5	3	0	0	2	0	0	0	3
SC	46	13	1	5	0	7	0	0	0	5
SD	47	46	3	1	0	21	3	13	0	29
TN	48	85	2	0	0	1	10	0	72	18
TX	49	159	12	110	18	2	17	0	0	14
UT	51	1244	1243	0	0	1	0	0	0	28
VA	53	101	7	32	1	57	4	0	0	23
WA	54	11	3	1	0	4	2	0	0	4
WV	55	1	0	0	0	1	0	0	0	1
WI	56	21	2	3	0	9	[illegible]	0	[illegible]	14
WY	57	1	0	0	1	0	[illegible]	0	[illegible]	1
*	58	5	0	0	0	2	[illegible]	0	[illegible]	4

TOTAL RECORD COUNT = 9397

*U.S. Territories & Possessions

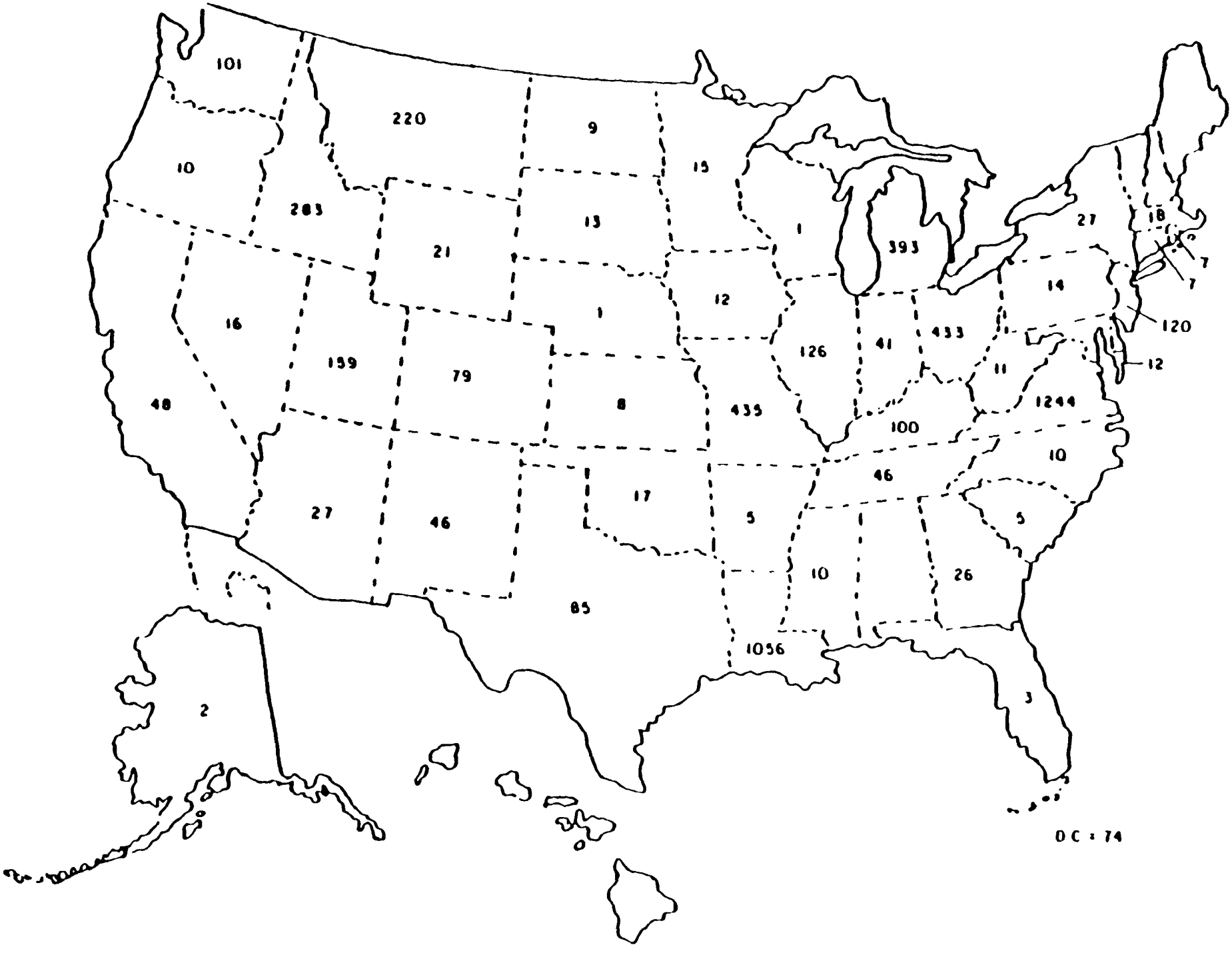

101
220
9
15
10
283
13
1
393
27
18
21
7
7
14
12
1
120
16
126
41
433
159
79
11
12
48
8
435
1244
100
10
46
17
27
46
5
5
10
26
85
1056
2
3
DC = 74

FIGURE 3-1

summary of the geographical distribution of the available records by state. Similar information is presented for each of th priority metals on Figures A-1 through A-9 in the Appendix.

In the basis of this analysis, the total number of records available for each metal is as follows:

Metal	Total Number of Records
zinc	5397
copper	4557
lead	3166
arsenic	2035
nickel	1998
chromium	820
cadmium	799
mercury	631
silver	50

These records formed the basis of the subsequent technical analysis.

SECTION 4

METHODS OF ANALYSIS

4.1 TECHNICAL OVERVIEW

A substantial amount of data for the priority metals is available for analysis. Approximately 20,000 data records were developed for the priority metals in accordance with the data classifications described previously. This amount of information required the application of computer processing and the development of a technical strategy for data handling and analysis. As a result, specialized software was developed to process STORET information for each priority metal which was contained on a series of magnetic tapes. This software was used to select appropriate data, compartmentalize it as appropriate into a series of "bins" and calculate partition coefficients. The values were then subsequently processed by various statistical techniques to search for relationships among partitioning and various environmental variables.

4.2 BIN ANALYSIS

An objective of the study is to determine correlations, if any, which exist among calculated partition coefficients and ambient environmental conditions as represented by various physical, chemical and biochemical measurements simultaneously performed or observed. The data records for each priority metal reflect a wide range of conditions for analysis. In order to search for correlations, the procedure selected consisted of segmenting the data progressively into a series of compartments, or bins, each of which would be specifically defined by a particular range of environmental variables. For example, a bin

may be defined as that portion of the data base which has limits of suspended solids of 10 to 30 mg/l, a pH range of 6.0 to 7.0, and alkalinity from 20 to 50 mg/l, etc. All data records falling within various bins defined in a similar manner could then be used to calculate partition coefficients for those ranges of the environmental variables. The resulting information could then be evaluated by direct observation as well as statistically to assess any relationships which may exist.

The computer program developed to implement the bin analysis selects data for each priority metal on the basis of station type, so that the data base can be segregated for streams, lakes, etc. A series of bins are then established with the dimensions of the bins specified as appropriate values for the environmental variables under consideration. The dimensionality of the bin is related to the type of data record; that is, number of variables, under consideration. As a general rule, the greater the number of variables under consideration, the greater is the number of bins and therefore the less amount of partition coefficient information within each bin. The data base for increasing numbers of concurrently measured environmental variables also becomes more restricted. This is of concern from a statistical standpoint. The total number of bins is the product of the number of intervals established for each of the variables. The analysis proceeds with the calculation of partition coefficients from the data records falling within each bin, the bin mean partition coefficient and the coefficient of variation. The bin statistical parameters are calculated under the assumption that the individual partition coefficients are log normally distributed within the bin. The assumption of log normality was tested with zinc and was found to be true.

4.3 STATISTICAL ANALYSIS

At the conclusion of the bin analysis, a statistical analysis was performed to assess any empirical functional relationships between the calculated partition coefficients and the environmental variables selected to define the bins. A multiple correlation routine was used for this purpose. The following generalized regression equation was applied.

$$K_p = K_{po} (x_1)^{\alpha} (x_2)^{\gamma} 10^{\beta T} [H]^{-Z} \qquad (4\text{-}1)$$

in which:

K_p	=	partition coefficient (l/kg)
x_1, x_2	=	environmental variables (mg/l)
T	=	temperature (^{o}C)
H	=	hydrogen ion concentration (as a measure of pH
$K_{po}, \alpha, \beta, \gamma, Z$	=	coefficient and exponential constants determined from regression

Equation (4-1) as stated, provides for an analysis of the relationship between partition coefficients, temperature, pH, and two environmental variables. Any number of environmental variables could be specified as appropriate. In the regression analysis, all bins with population five or less are rejected as statistically not significant. For each of the remaining bins, the means of the intervals defining the bins were correlated with the mean of the partition coefficient of the bin. These quantities were used in the linearized form of the above relation:

$$\log K_p = \log K_{po} + \alpha \log x_1 + \gamma \log x_2 + \beta T + Z pH \qquad (4\text{-}2)$$

The regression analysis includes appropriate statistical measures such as correlation coefficient, r, and standard deviation σ, of the exponential constants.

SECTION 5

RESULTS OF ANALYSIS

5.1 PARTITION COEFFICIENTS

The bin analysis was used to calculate partition coefficients for each priority metal as described. The data base was segregated by origin of sample and separate analyses were performed on data reported from streams and lakes. In order to facilitate the identification of possible interrelationships by direct observation as well as by statistical means, the bin analyses were restricted to three dimensional arrays. The initial analysis was focused on variables which could exert a pronounced affect on partitioning for heavy metals, suspended solids, pH, and alkalinity. Thus, all records identified as Type 2 and higher order in Section 3 were selected from the data base for initial analysis. The bin intervals for stream data were specified as follows:

Suspended solids (mg/l)

10 to 30; 30 to 50; 50 to 100; 100 to 200; 200 to 500

pH

5.0 to 6.0; 6.0 to 7.0; 7.0 to 8.0; 8.0 to 9.0

Alkalinity

0 to 20; 20 to 50; 50 to 100; 100 to 200; 200 to 500

Thus, the initial analysis of stream data consisted of 100 compartments in each of which a series of partition coefficients were calculated depending upon data availability. The bin intervals were selected to represent reasonable ranges of the indicated variables while also maintaining a sufficient population of data in a large number of bins for statistical reliability. Analysis of lake data also included a suspended solids interval of 0 to 10 mg/l.

Table 5-1 illustrates the results of this analysis for zinc data reported for streams. The table presents the bin mean of the partition coefficients calculated within each bin in liters/kilogram, the coefficient of variation, and the number of bin records. For zinc, a total of 1782 records were used in the calculations.

Similar analyses were performed for all priority metals except silver (streams and lakes) and arsenic (lakes) for which sufficient data do not exist. The analysis was also repeated with other environmental variables as subsequently discussed.

5.2 CORRELATION WITH ENVIRONMENTAL VARIABLES

Observation of the calculated partition coefficients in Table 5-1 indicates an apparent inverse variation with suspended solids, but a less clear relationshio, if any, with pH and alkalinity. Similar results were obtained for the other priority metals. Simple and multiple regression analyses were then performed to better define any functional relationships.

Table 5-2 presents a summary of the statistical parameters obtained for zinc in streams. The table indicates an overall geometric mean partition coefficient of approximately 55,000 l/kg

TABLE 5-1

BIN ANALYSIS

ZINC IN STREAMS

PARTITION COEFFICIENT ANALYSIS FOR SUSPENDED SOLIDS IN THE [illegible] TO [illegible] MG/L RANGE

PH RANGE: FROM 5.00 TO 6.00

ALKALINITY RANGES >>>	0.TO 20.	20.TO 50.	50.TO 100.	100.TO 200.	200.TO 500.
TEMP RANGES VVV					
ALL	0.1999E 06	0.0000E 00	0.0000E 00	0.1399E 06	0.0000E 00
	0.795 5	0.000 0	0.000 0	0.000 1	0.000 0

PH RANGE: FROM 6.00 TO 7.00

ALKALINITY RANGES >>>	0.TO 20.	20.TO 50.	50.TO 100.	100.TO 200.	200.TO 500.
TEMP RANGES VVV					
ALL	0.1231E 06	0.1083E 06	0.7932E 05	0.1159E 06	0.0000E 00
	2.287 31	1.933 27	0.674 9	0.609 5	0.000 0

PH RANGE: FROM 7.00 TO 8.00

ALKALINITY RANGES >>>	0.TO 20.	20.TO 50.	50.TO 100.	100.TO 200.	200.TO 500.
TEMP RANGES VVV					
ALL	0.9798E 05	0.2178E 06	0.1976E 05	0.2491E 06	0.3729E 05
	1.548 15	2.267 60	2.044 114	2.939 141	1.269 39

PH RANGE: FROM 8.00 TO 9.00

ALKALINITY RANGES >>>	0.TO 20.	20.TO 50.	50.TO 100.	100.TO 200.	200.TO 500.
TEMP RANGES VVV					
ALL	0.0000E 00	0.3767E 05	0.1688E 06	0.2157E 06	0.2698E 06
	0.000 0	0.670 9	1.220 22	2.475 109	2.420 10

PARTITION COEFFICIENT ANALYSIS FOR SUSPENDED SOLIDS IN THE [illegible] TO [illegible] MG/L RANGE

PH RANGE: FROM 5.00 TO 6.00

ALKALINITY RANGES >>>	0.TO 20.	20.TO 50.	50.TO 100.	100.TO 200.	200.TO 500.
TEMP RANGES VVV					
ALL	0.0000E 00	0.0000E 00	0.0000E 00	0.0000E 00	0.0000E 00
	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0

PH RANGE: FROM 6.00 TO 7.00

ALKALINITY RANGES >>>	0.TO 20.	20.TO 50.	50.TO 100.	100.TO 200.	200.TO 500.
TEMP RANGES VVV					
ALL	0.6399E 05	0.8377E 05	0.9997E 05	0.7742E 05	0.0000E 00
	1.382 19	3.306 9	1.444 9	0.467 3	0.000 0

PH RANGE: FROM 7.00 TO 8.00

ALKALINITY RANGES >>>	0.TO 20.	20.TO 50.	50.TO 100.	100.TO 200.	200.TO 500.
TEMP RANGES VVV					
ALL	0.3911E 05	0.9904E 05	0.7509E 05	0.1917E 06	0.4968E 05
	0.824 2	1.579 25	1.607 51	1.699 60	0.919 19

PH RANGE: FROM 8.00 TO 9.00

ALKALINITY RANGES >>>	0.TO 20.	20.TO 50.	50.TO 100.	100.TO 200.	200.TO 500.
TEMP RANGES VVV					
ALL	0.0000E 00	0.5079E 05	0.4767E 05	0.4852E 05	0.9653E 05
	0.000 0	1.679 9	1.505 12	1.469 51	1.950 17

PH RANGE: FROM 5.00 TO 6.00

ALKALINITY RANGES >>>	0.00	20.	20.00	50.	50.00	100.	100.00	200.	200.00	500.
TOOD RANGES											
ALL	0.16210E 03	0.33905E 03	0.30306E 03	0.33330E 03	0.0000E 00
	1.000 3	.050 2	0.000 2	0.000 2	0.000 0

PH RANGE: FROM 6.00 TO 7.00

ALKALINITY RANGES >>>	0.00	20.	20.00	50.	50.00	100.	100.00	200.	200.00	500.
TOOD RANGES											
ALL	0.37950E 03	0.37800E 03	0.[illegible]E 03	0.10220E 06	0.0000E 00
	1.627 21	2.116 26	2.142 11	6.669 4	0.000 0

PH RANGE: FROM 7.00 TO 8.00

ALKALINITY RANGES >>>	0.00	20.	20.00	50.	50.00	100.	100.00	200.	200.00	500.
TOOD RANGES											
ALL	0.83570E 03	0.33300E 03	0.97910E 03	0.91100E 03	0.0633E 03
	1.042 6	1.320 33	1.303 12	2.038 64	1.019 28

PH RANGE: FROM 8.00 TO 9.00

ALKALINITY RANGES >>>	0.00	20.	20.00	50.	50.00	100.	100.00	200.	200.00	500.
TOOD RANGES											
ALL	0.00000E 00	0.26195E 03	0.37930E 03	0.11290E 06	0.0000E 00
	0.000 0	0.287 2	1.663 13	3.559 50	2.964 10

PARTITION COEFFICIENT ANALYSIS FOR SUSPENDED SOLIDS IN THE 100. TO 200. MG/L RANGE

PH RANGE: FROM 5.00 TO 6.00

ALKALINITY RANGES >>>	0.00	20.	20.00	50.	50.00	100.	100.00	200.	200.00	500.
TOOD RANGES											
ALL	0.19490E 03	0.00000E 00	0.39920E 03	0.00000E 00	0.0000E 00
	0.533 2	0.000 0	0.303 1	0.000 0	0.000 0

PH RANGE: FROM 6.00 TO 7.00

ALKALINITY RANGES >>>	0.00	20.	20.00	50.	50.00	100.	100.00	200.	200.00	500.
TOOD RANGES											
ALL	0.77990E 03	0.26125E 03	0.93630E 03	0.32970E 06	0.0000E 00
	0.760 7	1.206 18	1.192 21	0.000 1	0.000 0

PH RANGE: FROM 7.00 TO 8.00

ALKALINITY RANGES >>>	0.00	20.	20.00	50.	50.00	100.	100.00	200.	200.00	500.
TOOD RANGES											
ALL	0.29120E 03	0.32030E 03	0.11960E 03	0.25370E 03	0.2[illegible]E 03
	0.604 2	1.269 24	1.745 132	1.716 93	2.[illegible] 0

PH RANGE: FROM 8.00 TO 9.00

ALKALINITY RANGES >>>	0.00	20.	20.00	50.	50.00	100.	100.00	200.	200.00	500.
TOOD RANGES											
ALL	0.00000E 00	0.16296E 03	0.19170E 03	0.20770E 03	0.1[illegible]E 03
	0.000 0	0.153 2	1.002	1.639 24	0.[illegible] 0

PARTITION COEFFICIENT ANALYSIS FOR SUSPENDED SOLIDS IN THE 200. TO 400. MG/L RANGE

PH RANGE: FROM 5.00 TO 6.00

ALKALINITY RANGES >>>	0.00	20.	20.00	50.	50.00	100.	100.00	200.	200.00	500.
TOOD RANGES											
ALL	0.00000E 03	0.30000E 00	0.10300E 03	0.00000E 03	0.0000E 00
	0.377 0	0.000 0	0.000 0	0.000 0	0.000 0

PH RANGE: FROM 6.00 TO 7.00

ALKALINITY RANGES >>>	0.00	20.	20.00	50.	50.00	100.	100.00	200.	200.00	500.
TOOD RANGES											
ALL	0.20[illegible]E 03	0.16[illegible]E 03	0.19[illegible]E 03	0.00000E 00	0.0000E 00
	2.997 9	0.897 10	1.193 12	0.000 0	0.000 0

PH RANGE: FROM 7.00 TO 8.00

ALKALINITY RANGES >>>	0.00	20.	20.00	50.	50.00	100.	100.00	200.	200.00	500.
TOOD RANGES											
ALL	0.19930E 03	0.17126E 03	0.20740E 03	0.[illegible]E 03	0.0000E 00
	0.611 2	1.627 19	1.444 0	1.511 0	0.000 0

PH RANGE: FROM 8.00 TO 9.00

ALKALINITY RANGES >>>	0.00	20.	20.00	50.	50.00	100.	100.00	200.	200.00	500.
TOOD RANGES											
ALL	0.00000E 00	0.26294E 03	0.44290E 03	0.0000E 00	0.[illegible]E 03
	0.000 0	0.251 2	1.111 5	0.000 0	1.13[illegible] 3

TABLE 5-2

SUMMARY OF STATISTICAL PARAMETERS FOR ZINC
REGRESSION WITH SOLIDS, PH, ALKALINITY

	0	1	2	3	4	5	6	Total Records
Records by Type	1988	379	686	861	653	674	146	5397

Sort by Type ≥ 2 & by Water Body Stream: Records Analyzed 1732

FIRST BIN ANALYSIS

No. of Acceptable Bins (> 5 Records) 50: Bin Avg K_p (l/kg) = 54,916

CORRELATION COEFFICIENTS (partial)

$r(K_p, SS) = -0.833$; $r(K_p, pH) = 0.163$; $r(K_p, Al) = 0.091$

REGRESSIONS

1: K_p vs ss;

$K_p = 1.05 \times 10^6 \times (ss)^{-0.685}$; $r_{mult} = 0.833$, $\sigma_{exp} = 0.065$

2: K_p vs ss & [H];

$K_p = 0.32 \times 10^6 \times (ss)^{-0.683} \times [H]^{-0.0687}$; $r_{mult} = 0.846$, $\sigma_{exp1} = 0.004$

$\sigma_{exp2} = 0.0360$

3: K_p vs ss & [H] & Al;

$K_p = 0.32 \times 10^6 \times (ss)^{-0.683} \times [H]^{-0.0687} \times [Al]^{-0.003}$; $r_{mult} = 0.846$, $\sigma_{exp1} = 0.065$

$\sigma_{exp2} = 0.044$

$\sigma_{exp3} = 0.072$

TABLE 5-2 (continued)

SECOND BIN ANALYSIS (For $K_p^* = K_p SS^{-1}$)

No. of Acceptable Bins (> 5 Records) 14; Bin Avg $K_p^* = 1.0$

CORRELATION COEFFICIENT (partial): $r(K_p^*, pH) = 0.049$, $r(K_p^*, Al) = 0.486$

REGRESSIONS

1: K_p^* vs Al:

$K_p^* = 0.614 \times (Al)^{0.119}$; $r_{mult} = 0.486$, $\sigma_{exp} = 0.062$

2: K_p^* vs Al & [H]:

$K_p^* = 0.944 \times (Al)^{0.146} \times [H]^{0.032}$; $r_{mult} = 0.527$, $\sigma_{exp1} = 0.074$

$\sigma_{exp2} = 0.040$

from all data. Simple correlation coefficients are presented for partition coefficient variation with suspended solids, pH, and alkalinity, respectively. These values indicate a very strong dependency of partitioning with suspended solids and weak relationships with the other variables on a simple basis. Statistical parameters are also shown for the multiple step-wise regression. Exponential constants, multiple correlation coefficients, and the standard deviation of the exponential constants are presented for the sequential regression of partition coefficients with suspended solids, suspended solids and pH, and finally suspended solids, pH and alkalinity.

It is observed from Table 5-2 that the exponential constants for pH, as represented by the hydrogen ion concentration, and alkalinity are relatively small. Further, the multiple correlation coefficient is not markedly improved by the inclusion of these variables in the regression. It is possible that the strong dependency of partitioning with solids is masking a correlation with these variables. Hence, a second bin analysis was performed where the solids dependency of partitioning was removed by rearranging the regression equation:

$$K_p^{\,1} = K_p \cdot (s_s)^{-a} = K_{po}^{\,1}\,(ALK)^{Y}\,[H]^{-Z} \qquad (5\text{-}1)$$

in which s_s suspended solids, ALK is alkalinity with other terms as previously defined. The exponential constant, a, taken as that determined in the first bin analysis. The product of the partition coefficient and suspended solids, the partition parameter, as shown above was then regressed with alkalinity and pH. Simple and multiple regressions were performed.

Table 5-2 indicates relatively weak correlation coefficients and exponential constants resulting from this analysis.

Graphical presentation of the results supports the observation. Figure 5-1 shows the partitioning parameter $K_p \cdot s_s^{-a}$ for zin- plotted as a function of alkalinity for various pH levels in bot.. streams and lakes. Similarly, Figure 5-2 presents the same data with the partitioning parameter plotted as a function of pH for various ranges of alkalinity. No consistent trends are observed from these diagrams. The multiple regression analysis was performed on stream and some lake data for all priority metals with similar results.

A similar type of regression analysis was performed to determine any relationship between the partitioning parameter and other environmental variables: temperature, and BOD as a surrogate parameter possibly representative of organic material. As with alkalinity and pH, no consistent relationships could be determined among the variables. Table 5-3, for zinc data in streams, is an illustration of the results of these analyses.

Sufficient opportunity was not available within the tim constraints of the investigation to assess other potential interrelationships.

From the foregoing analyses, it was concluded that the only clear and consistent relationship observed between partition coefficients and the environmental variables tested was with suspended solids. For almost all priority metals, a strong correlation was indicated between the mean partition coefficient value within the various bins and the average bin suspended solids value. In view of this consistent dependency, the final functional relationships developed for these variables was based on analysis of all available data records which contained the basic information necessary for calculation of the partitio- coefficient. The only data needed to determine these relatior.

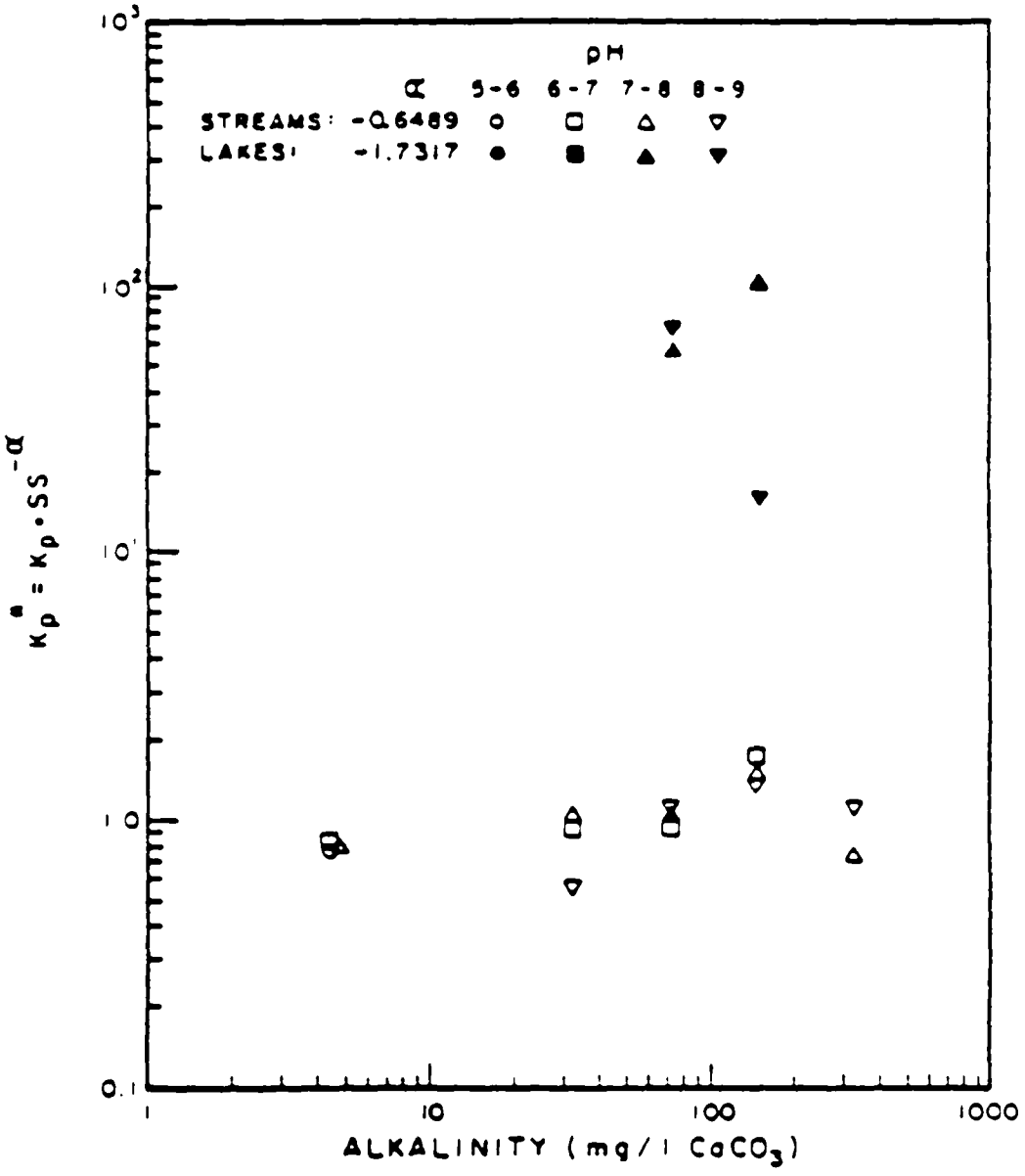


FIGURE 5-1

K_p^* AS FUNCTION OF ALKALINITY

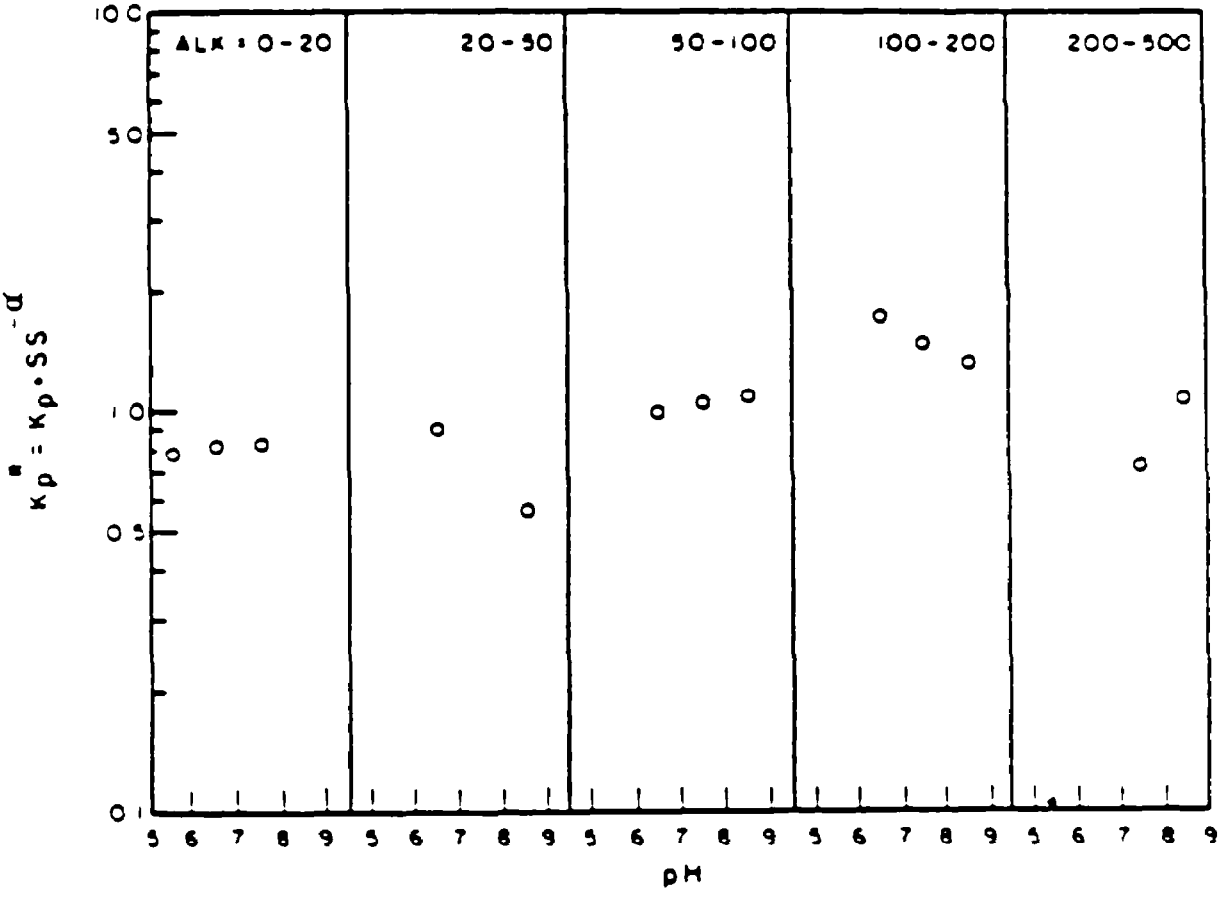


FIGURE 5-2

K_p^* AS FUNCTION OF pH

TABLE 5-3

SUMMARY OF STATISTICAL PARAMETERS FOR ZINC

	0	1	2	3	4	5	6	Total Records
Records by Type	1988	379	686	861	663	674	146	5397

Sort by Type 0 & by Water Body streams: Records Analyzed 2253

FIRST BIN ANALYSIS

No. of Acceptable Bins (> 5 Records) 7: Bin Avg K_p (l/kg) = 45,000

CORRELATION COEFFICIENTS (partial)

$r(K_p, SS) = -0.995$;

REGRESSION

K_p vs SS:

$K_p = 1.25 \times 10^6 \times (ss)^{-0.7039}$; $\sigma_{exp} = 0.0317$

SECOND BIN ANALYSIS (For $K_p^* = K_p SS^{-3}$)

No. of Acceptable Bins (> 5 Records) 15; Bin Avg $K_p^* = 9.7$

CORRELATION COEFFICIENT (partial): $r(K_p^*, BOD) = -0.450$, $r(K_p^*, T) = -0.224$

REGRESSIONS

1: K_p^* vs BOD:

$K_p^* = 30.2 \times (BOD)^{-0.443}$; $r_{mult} = 0.450$, $\sigma_{exp} = 0.293$

2: K_p^* vs BOD & T:

$K_p^* = 32.2 \times (BOD)^{-0.414} \times 10^{-0.001T}$; $r_{mult} = 0.465$, $\sigma_{exp1} = 0.316$

$\sigma_{exp2} = 0.003$

ships are dissolved and particulate chemical, and suspended solids. The lowest order of data records, Type 0, and above could be used, thus substantially expanding the data base for final analysis. Hence, the final correlations between partitioning and suspended solids concentration in streams and lakes were based on all available data records in STORET for these types of water bodies from which a partition coefficient value could be determined. This represents a relatively large fraction of the total available data base with only data from estuarine, ocean, miscellaneous sources, etc., not included in the analysis.

An illustration of the results of this analysis is presented on Figures 5-3A and 5-3B, for the priority metal zinc in streams and lakes, respectively. As before, the data records were sorted into a number of bins, each of which was characterized by a specified range of suspended solids. Partition coefficients were calculated from the data records falling within each compartment, and the bin means and other statistical parameters were determined. The bin means were then regressed with bin mean suspended solids concentrations. The logarithmic diagrams present the bin mean partition coefficients plotted with bin average suspended solids concentration and the regression line which correlates the data. Also shown on the diagrams are the standard deviations of the bin values for the log normally distributed partition coefficients. The strong correlation between the calculated partition coefficients and suspended solids is evident from the diagrams. The analysis also indicates a wide variation in the partition coefficients calculated within the various solids intervals as indicated by the large standard deviations. Values can vary by four orders of magnitude.

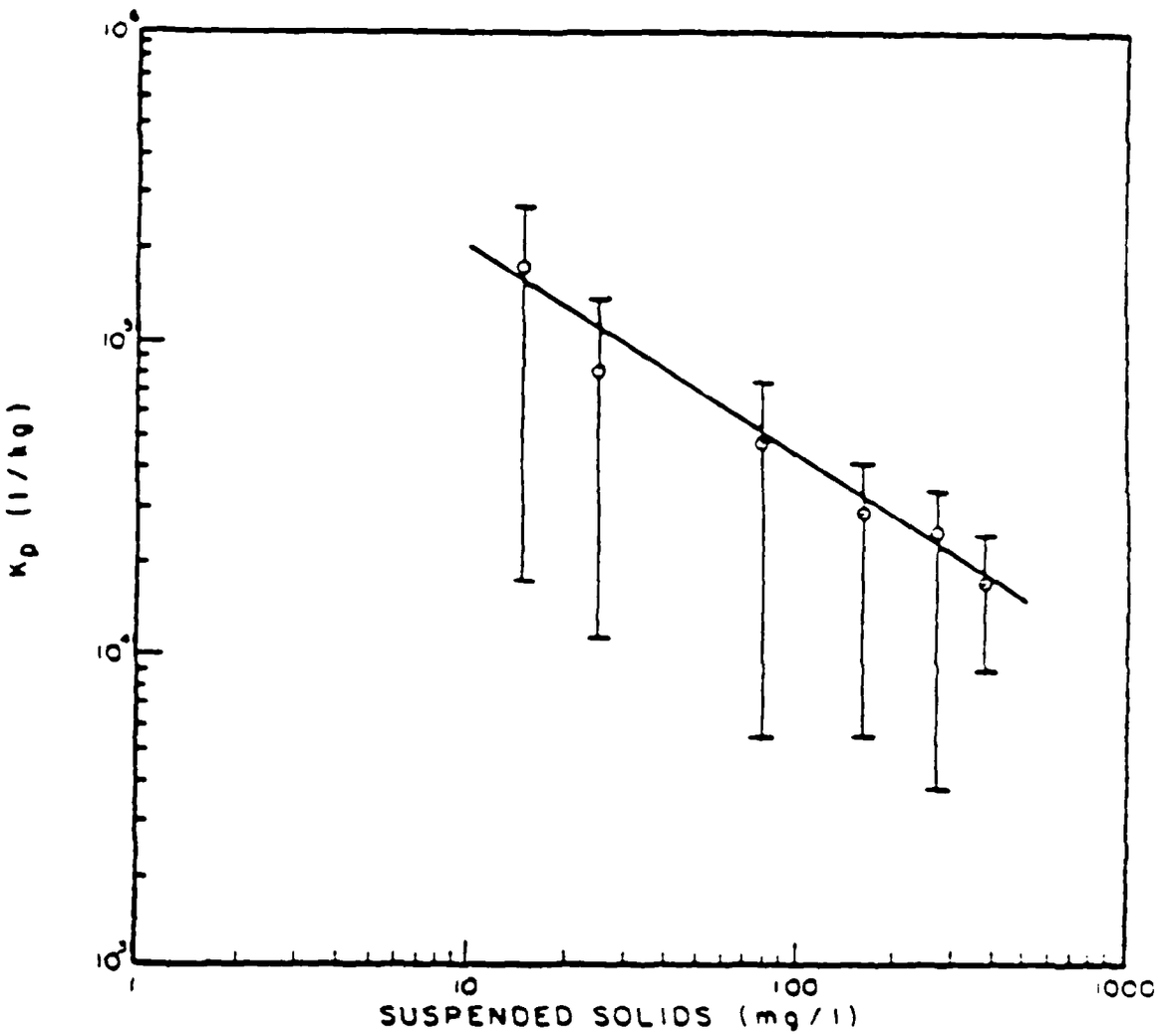


FIGURE 5-3A

PARTITION COEFFICIENT AS FUNCTION OF SUSPENDED SOLIDS
ZINC IN STREAMS

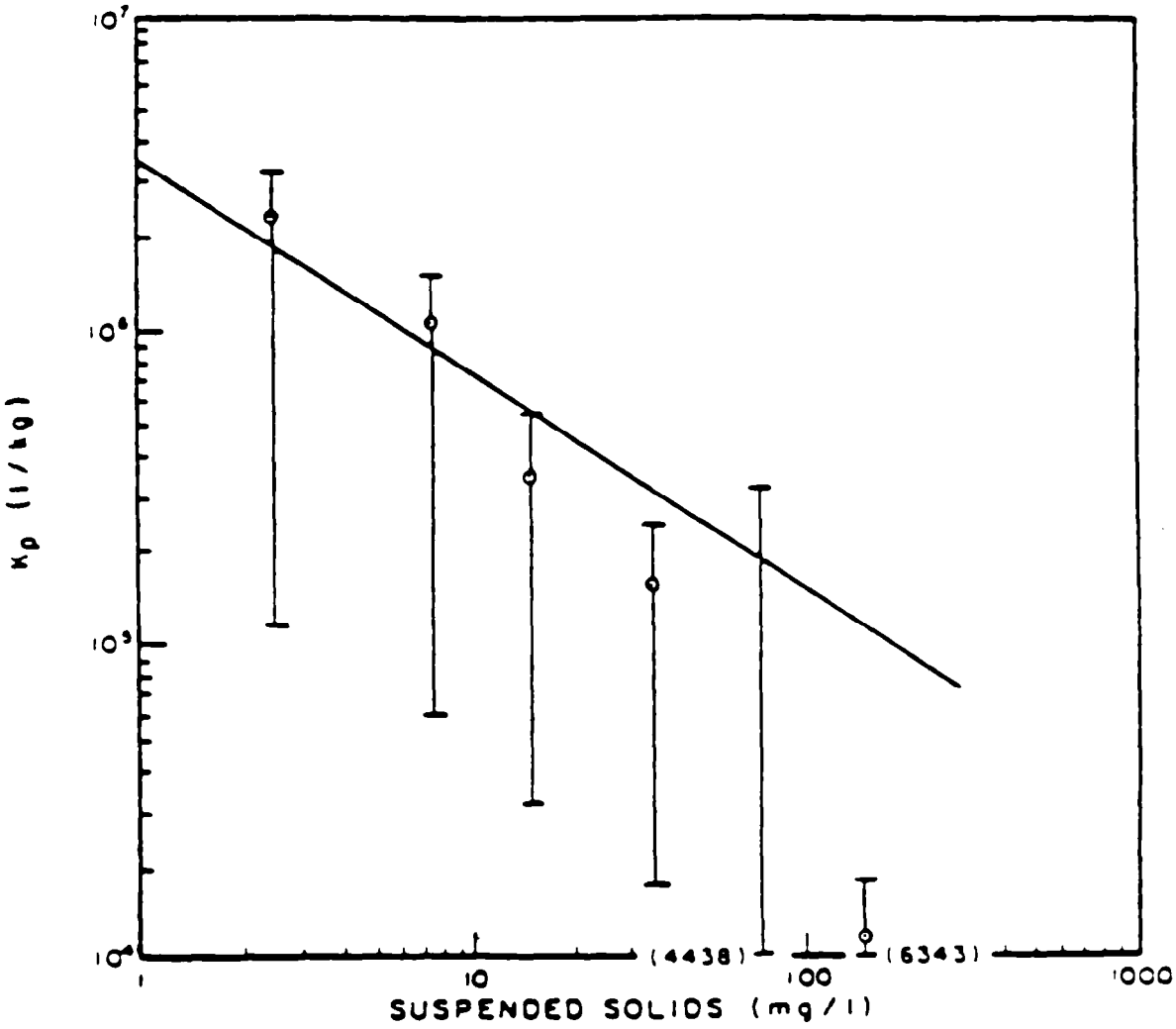


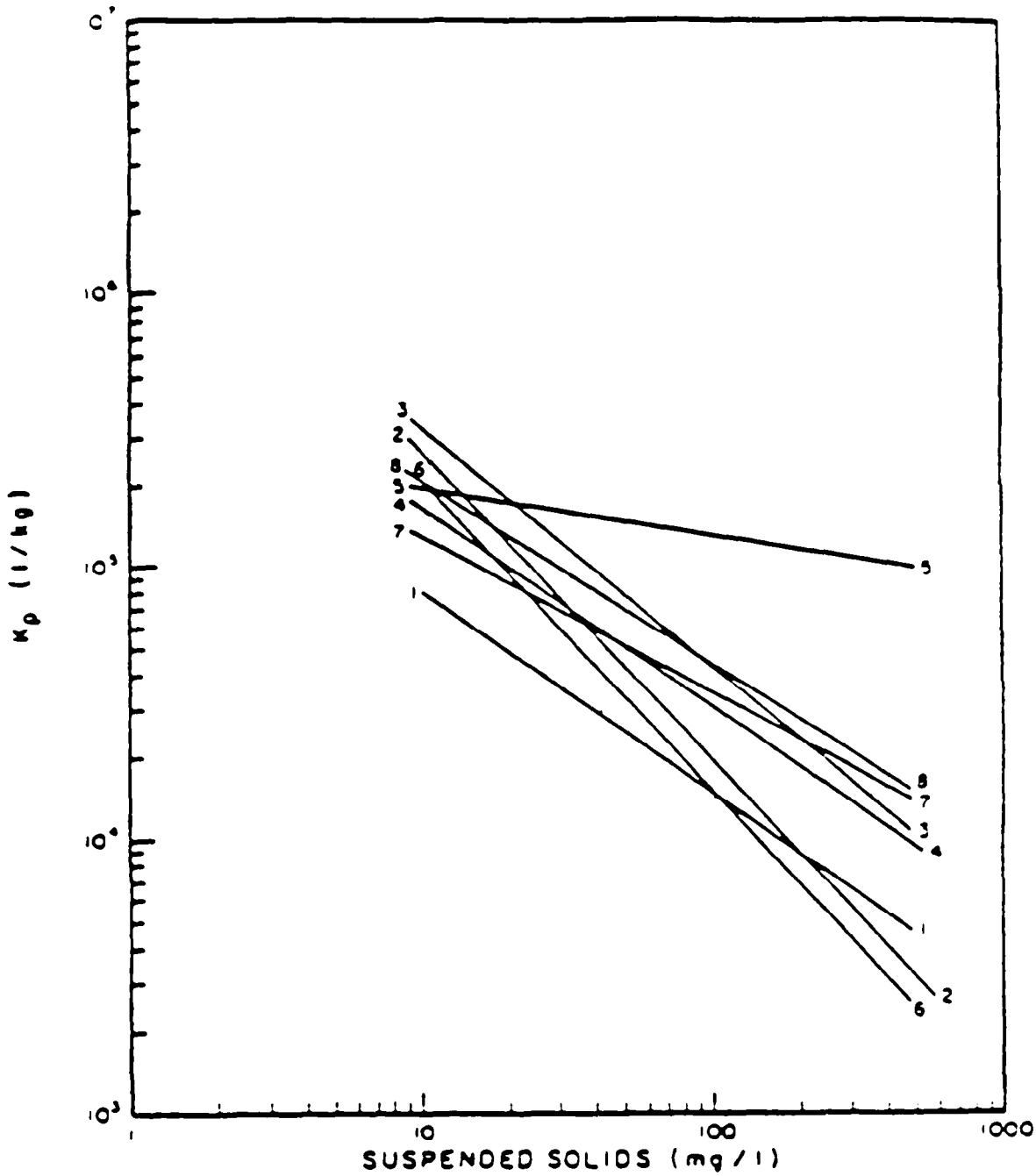
FIGURE 5-3B

PARTITION COEFFICIENT AS FUNCTION OF SUSPENDED SOLIDS
ZINC IN LAKES

The analysis indicated above was performed for each priority metal for both streams and lakes. The exceptions were silver (streams and lakes) and arsenic (lakes for which sufficient information was not available. Figures 5-4A and 5-4B present a summary of the regression lines for partition coefficients and suspended solids for the various priority metals for streams and lakes, respectively. These diagrams can be used for the best estimate of a partition coefficient value for a particular priority metal based on suspended solids concentration. Figures A-10 through A-17 in the Appendix present the data and the regression lines for each priority metal in streams and lakes. These diagrams should be consulted in the selection of a partition coefficient value in order to indicate the degree of variability which may exist around a particular value on the basis of the analysis of available data.

Table 5-4 is a summary of the statistical properties of the regression equations for partition coefficients and suspended solids as developed for the priority metals. The number of data records in each evaluation is indicated along with the exponential constant, correlation coefficient, and standard deviation of the slope. It is evident from the table that the bin mean partition coefficients are very highly correlated with suspended solids in all cases but lead.

It is noted that the calculated partition coefficients from lakes are consistently greater than values in streams for the same priority metal, in all cases except for mercury. This may be due, in general, to a more organic nature of suspended materials in lakes than in streams.

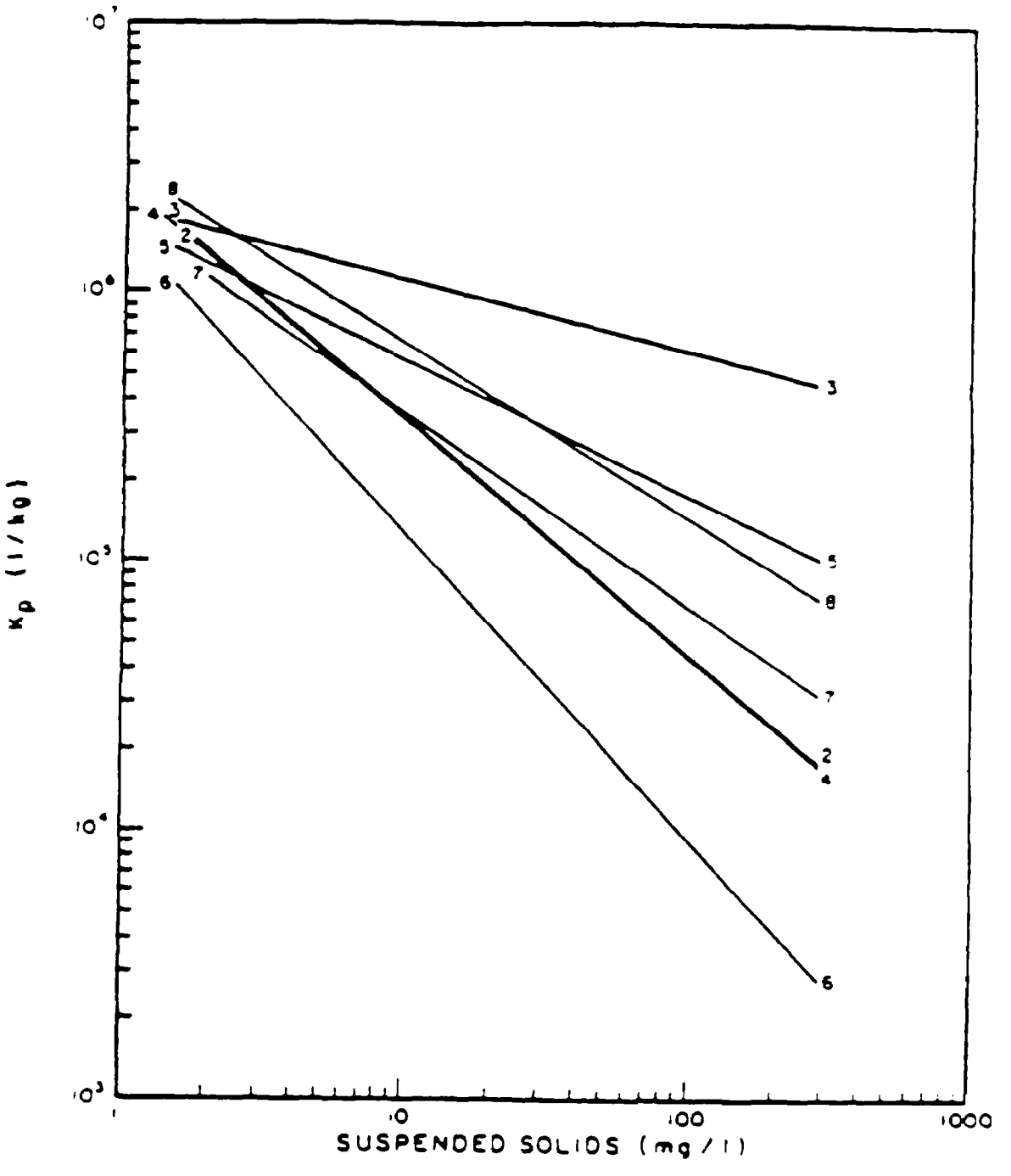


METALS:

1 - ARSENIC
2 - CADMIUM
3 - CHROMIUM
4 - COPPER
5 - LEAD
6 - MERCURY
7 - NICKEL
8 - ZINC

FIGURE 5-4A

PARTITION COEFFICIENT AS FUNCTION OF SUSPENDED SOLIDS
ALL METALS IN STREAMS



METALS:

1 - ARSENIC (NO DATA FOR LAKES)
2 - CADMIUM
3 - CHROMIUM
4 - COPPER
5 - LEAD
6 - MERCURY
7 - NICKEL
8 - ZINC

FIGURE 5-4B

PARTITION COEFFICIENT AS FUNCTION OF SUSPENDED SOLIDS
ALL METALS IN LAKES

TABLE 5-4

STATISTICAL PARAMETERS FOR VARIOUS METALS
REGRESSION WITH SUSPENDED SOLIDS

$$K_p = K_{po}\ SS^{+a}$$

METAL	STREAMS					LAKES				
	Records	K_{po}		r	σ_a	Records	K_{po}		r	σ_a
Arsenic	1635	0.48×10^6	-0.7286	-0.993	0.0372	1	-	-	-	-
Cadmium	254	4.00×10^6	-1.1307	-0.998	0.0990	296	3.52×10^6	-0.9246	-0.993	-.0593
Chromium	345	3.36×10^6	-0.9304	-0.914	-0.2061	211	2.17×10^6	-0.2662	-0.818	0.1321
Copper	2722	1.04×10^6	-0.7436	-0.994	0.0354	577	2.85×10^6	-0.9000	-0.955	0.1600
Lead	1545	0.31×10^6	-0.1856	-0.350	0.2219	411	2.04×10^6	-0.5337	-0.965	0.0836
Mercury	369	2.91×10^6	-1.1356	-0.990	0.0894	169	1.97×10^6	-1.1718	-0.962	0.2359
Nickel	1394	0.49×10^6	-0.5719	-0.974	0.0591	285	2.21×10^6	-0.7578	-0.970	0.1083
Silver[a]	-	-	-	-	-	-	-	-	-	-
Zinc	2253	1.25×10^6	-0.7038	-0.995	0.0317	914	3.34×10^6	-0.6788	-0.849	0.2441

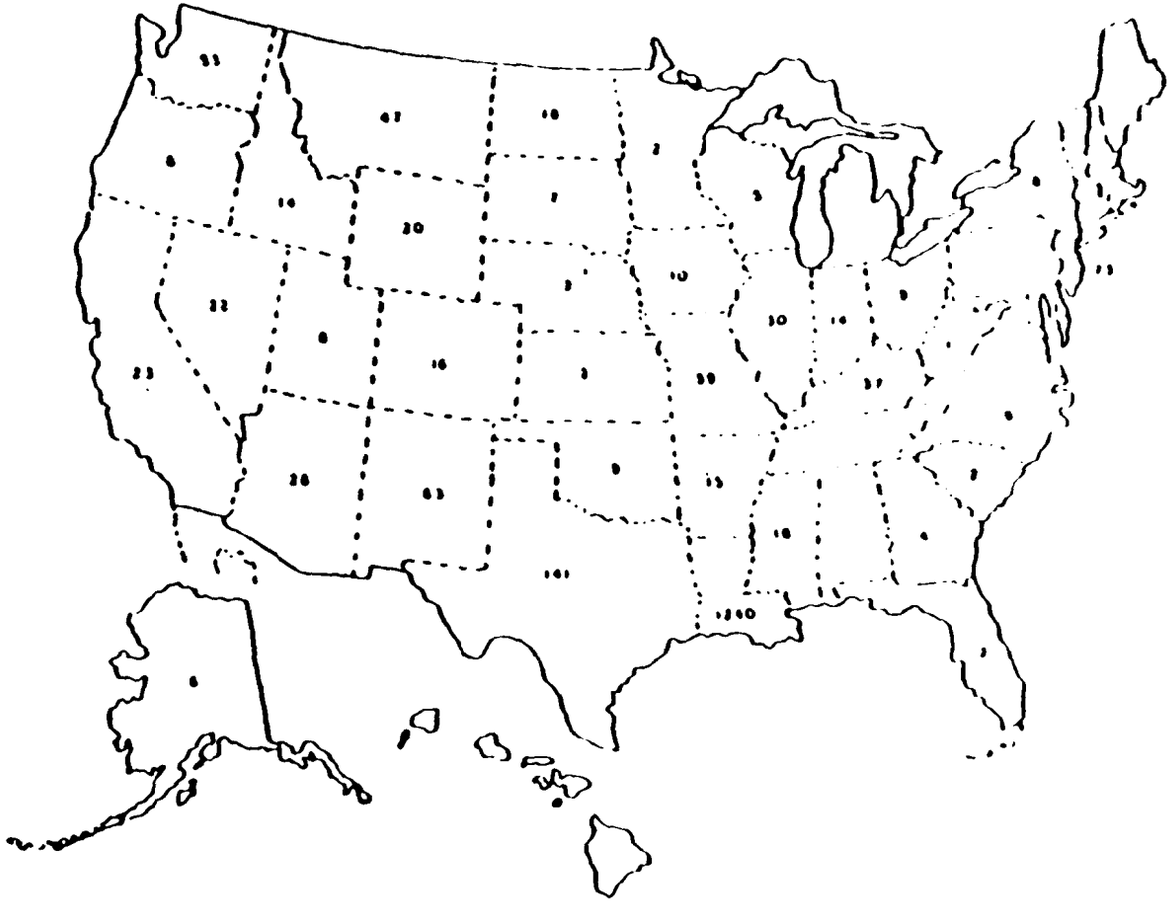
[a] Insufficient bins to perform regression

APPENDIX

TABLE A-1

STATE CODES

Alabama	01	Missouri	29
Alaska	02	Montana	30
Arizona	04	Nebraska	31
Arkansas	05	Nevada	32
California	06	New Hampshire	33
Colorado	08	New Jersey	34
Connecticut	09	New Mexico	35
Delaware	10	New York	36
District of Columbia	11	North Carolina	37
Florida	12	North Dakota	38
Georgia	13	Ohio	39
Hawaii	15	Oklahoma	40
Idaho	16	Oregon	41
Illinois	17	Pennsylvania	42
Indiana	18	Rhode Island	44
Iowa	19	South Carolina	45
Kansas	20	South Dakota	46
Kentucky	21	Tennessee	47
Louisiana	22	Texas	48
Maine	23	Utah	49
Maryland	23	Vermont	50
Massachusetts	25	Virginia	51
Michigan	26	Washington	53
Minnesota	27	West Virginia	54
Mississippi	28	Wisconsin	55
		Wyoming	56



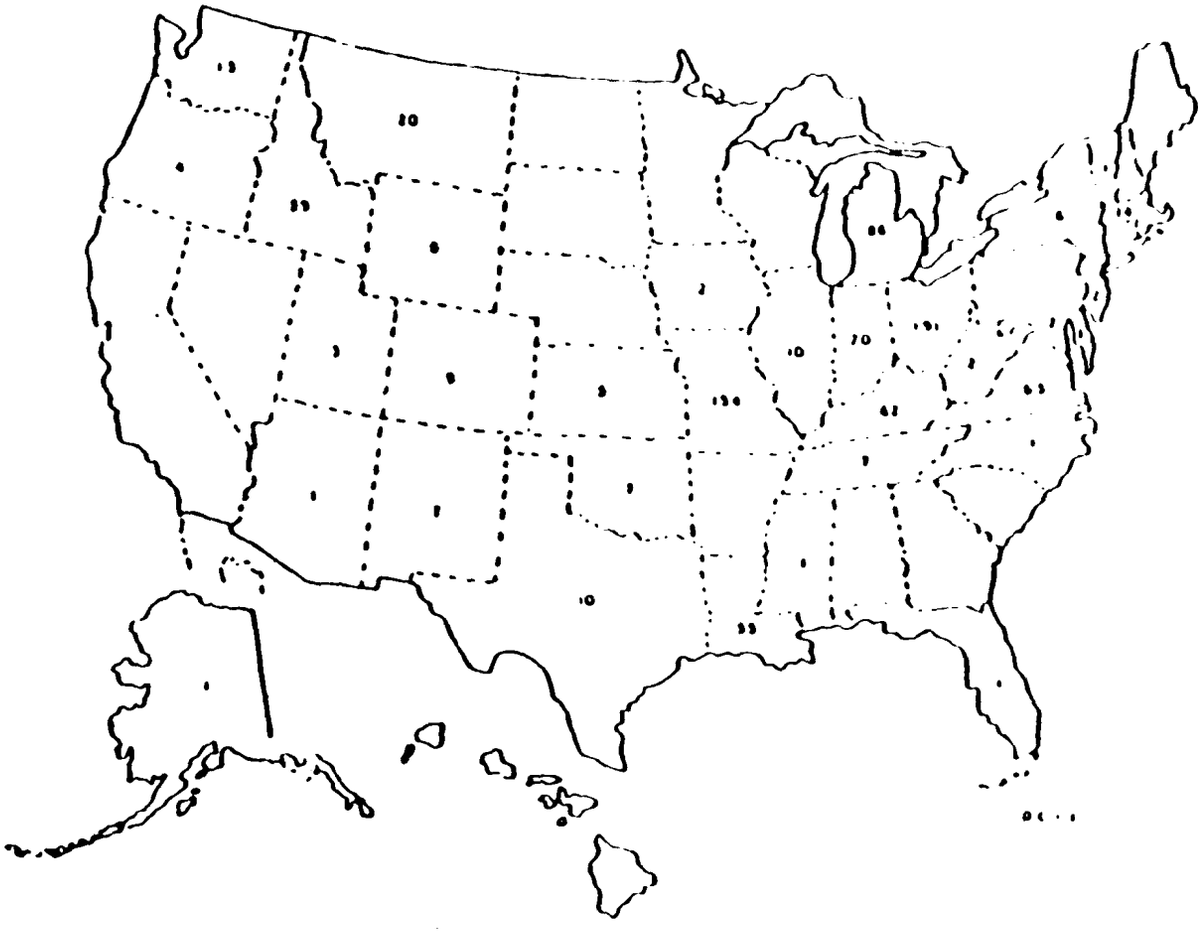
SUMMARY BY STATE

STATE NO.	TOTAL RECORDS	BY RECORD TYPE 0	1	2	3	4	NUMBER 5	6	SEASONS
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

TOTAL RECORD COUNT = [illegible]

FIGURE A-1

ARSENIC DATA RECORDS AVAILABLE BY STATE



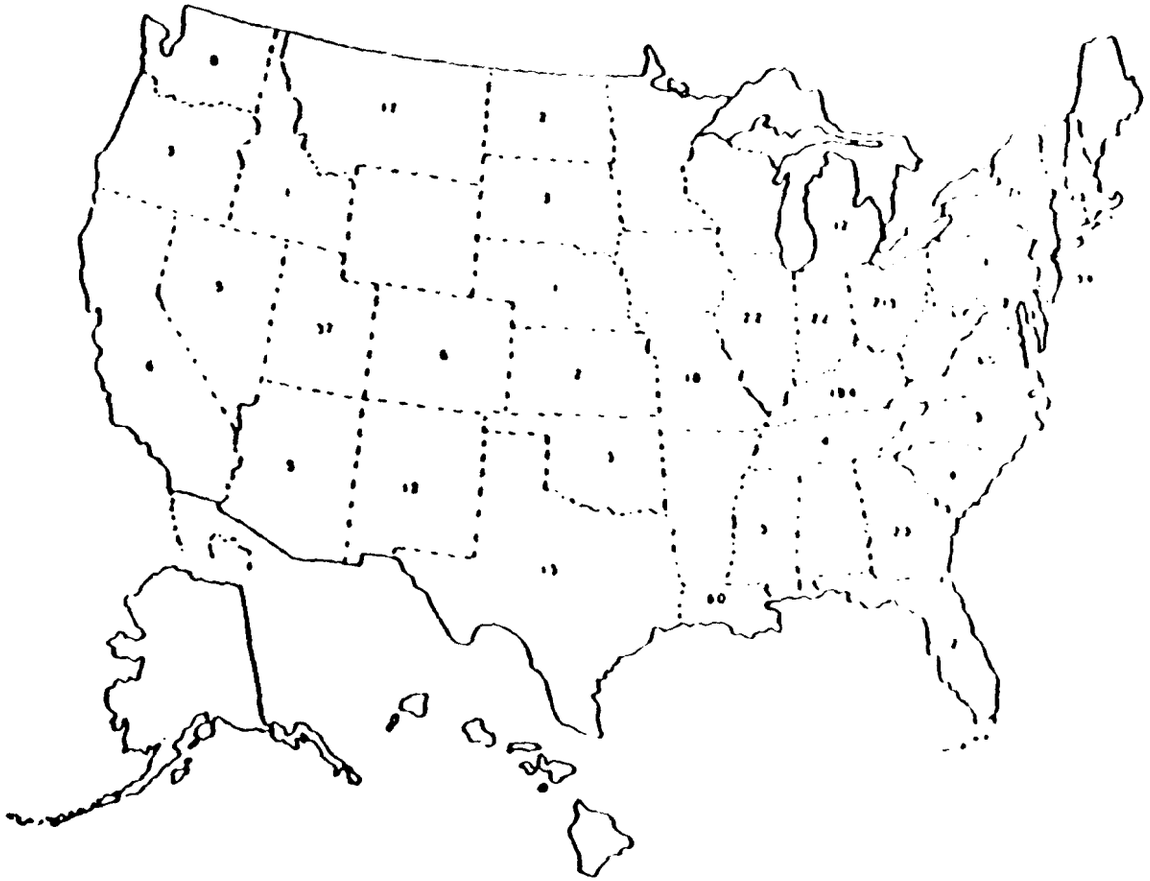
SUMMARY BY STATE

STATE NO.	TOTAL RECORDS	BY RECORD TYPE 0	1	2	3	4	5	6	NUMBER STATIONS
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

TOTAL RECORDS COUNTED : [illegible]

FIGURE A-2

CADMIUM DATA RECORDS AVAILABLE BY STATE



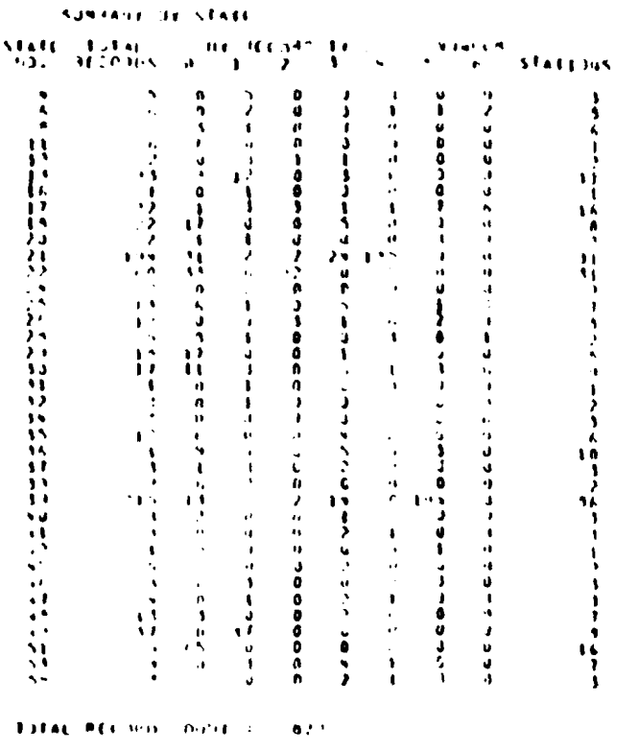
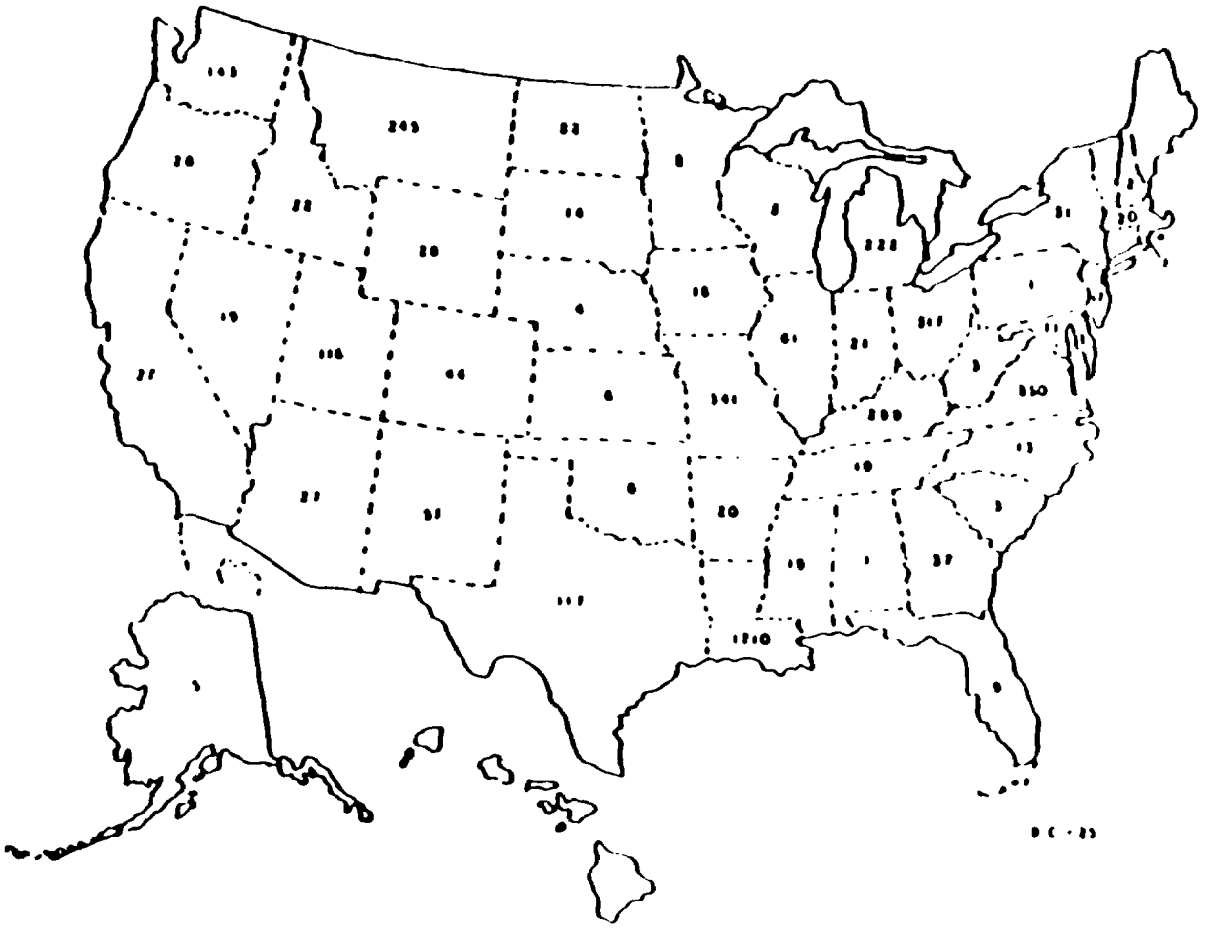


FIGURE A-3

CHROMIUM DATA RECORDS AVAILABLE BY STATE



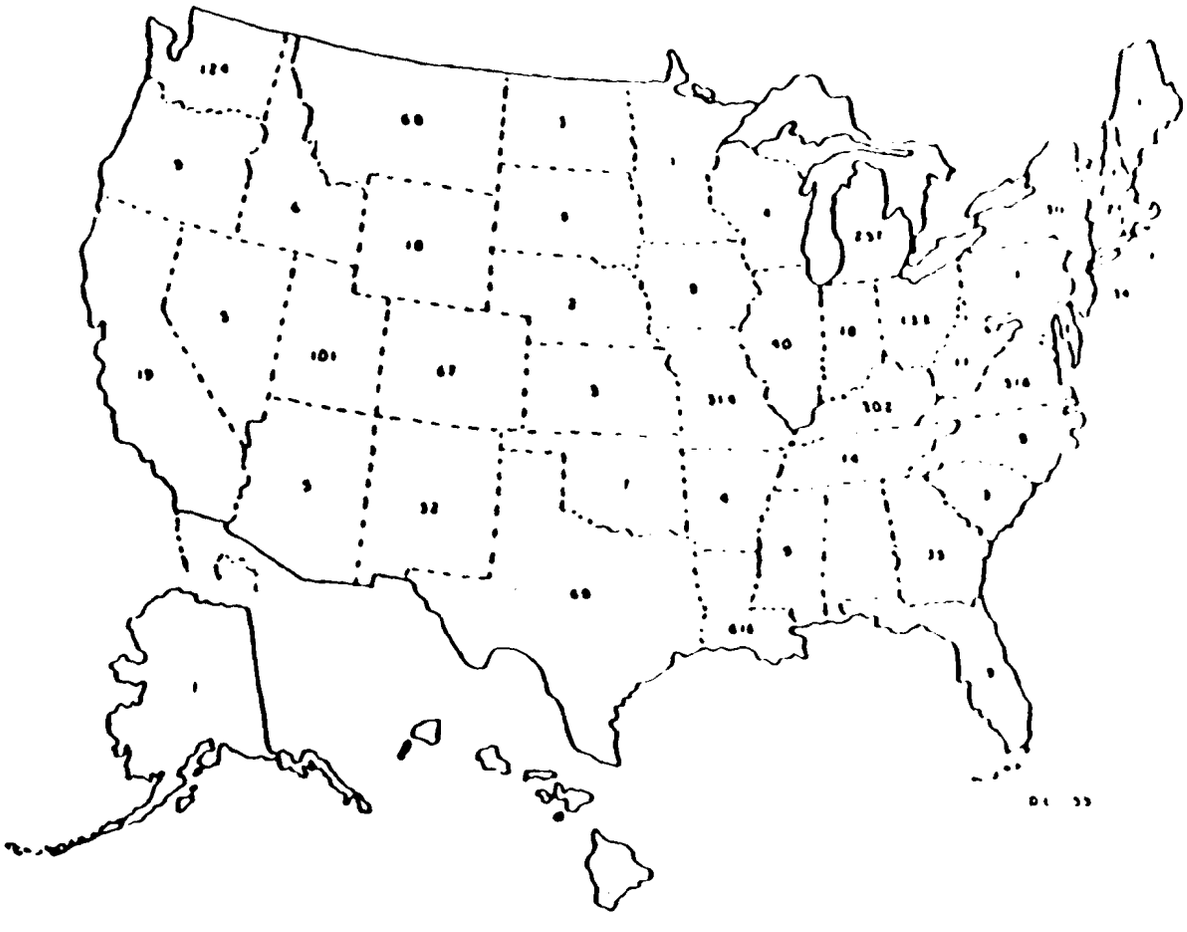
SUMMARY BY STATE.....COPPER

State No.	Total Records	0	1	2	3	4	5	6	Stations
1	[illegible]	0	0	3	1	0	1	0	1
2	5	0	0	2	3	0	0	0	2
4	27	0	21	0	1	1	2	0	6
5	20	0	0	1	2	17	0	0	6
6	27	2	3	0	6	2	5	11	11
8	69	15	24	0	1	6	2	0	14
11	25	25	0	0	0	0	1	0	1
12	9	5	0	1	0	2	1	1	6
13	37	8	28	1	1	0	0	0	12
16	22	1	13	2	6	0	0	0	11
17	81	0	1	4	8	1	17	21	24
18	21	13	1	0	7	0	0	0	9
19	16	8	0	0	8	0	0	0	9
20	6	1	1	0	4	0	0	0	4
21	299	60	6	2	37	219	0	0	18
22	1310	79	2	1212	1	176	1	35	240
23	11	0	10	0	1	0	0	0	1
25	20	7	1	0	7	2	1	0	7
26	222	207	0	1	1	12	0	1	35
27	22	4	2	1	11	2	0	0	8
28	19	1	2	2	4	8	0	1	10
29	391	92	11	6	212	0	0	0	60
30	245	61	3	4	29	19	139	0	48
31	4	0	3	0	1	0	0	0	2
32	19	0	2	1	0	16	0	0	3
33	2	0	0	0	2	0	0	0	1
34	17	0	0	2	0	14	0	1	5
35	57	11	3	2	6	35	0	0	18
36	31	12	10	1	5	2	1	0	17
37	13	0	0	0	12	1	0	0	3
38	22	0	4	1	3	14	0	0	7
39	317	4	3	6	38	0	266	0	34
40	8	1	0	0	5	0	0	0	4
41	28	1	0	0	23	4	0	0	9
42	1	0	0	0	0	0	1	0	1
44	1	0	1	0	0	0	0	0	1
45	3	2	0	0	1	0	0	0	1
46	14	1	5	0	8	0	0	0	7
47	19	0	1	0	10	7	0	0	10
48	117	1	0	0	1	12	1	102	19
49	116	2	104	1	4	5	0	0	14
51	350	148	0	2	0	0	0	0	19
53	141	5	47	4	78	9	0	0	24
54	3	0	0	0	3	0	0	0	1
55	2	0	0	0	2	0	0	0	1
56	28	7	4	1	10	6	0	0	18
57	2	0	0	1	1	0	0	0	1
58	10	0	0	0	4	6	0	0	1

Total Records Count = 8557

FIGURE A-4

COPPER DATA RECORDS AVAILABLE BY STATE



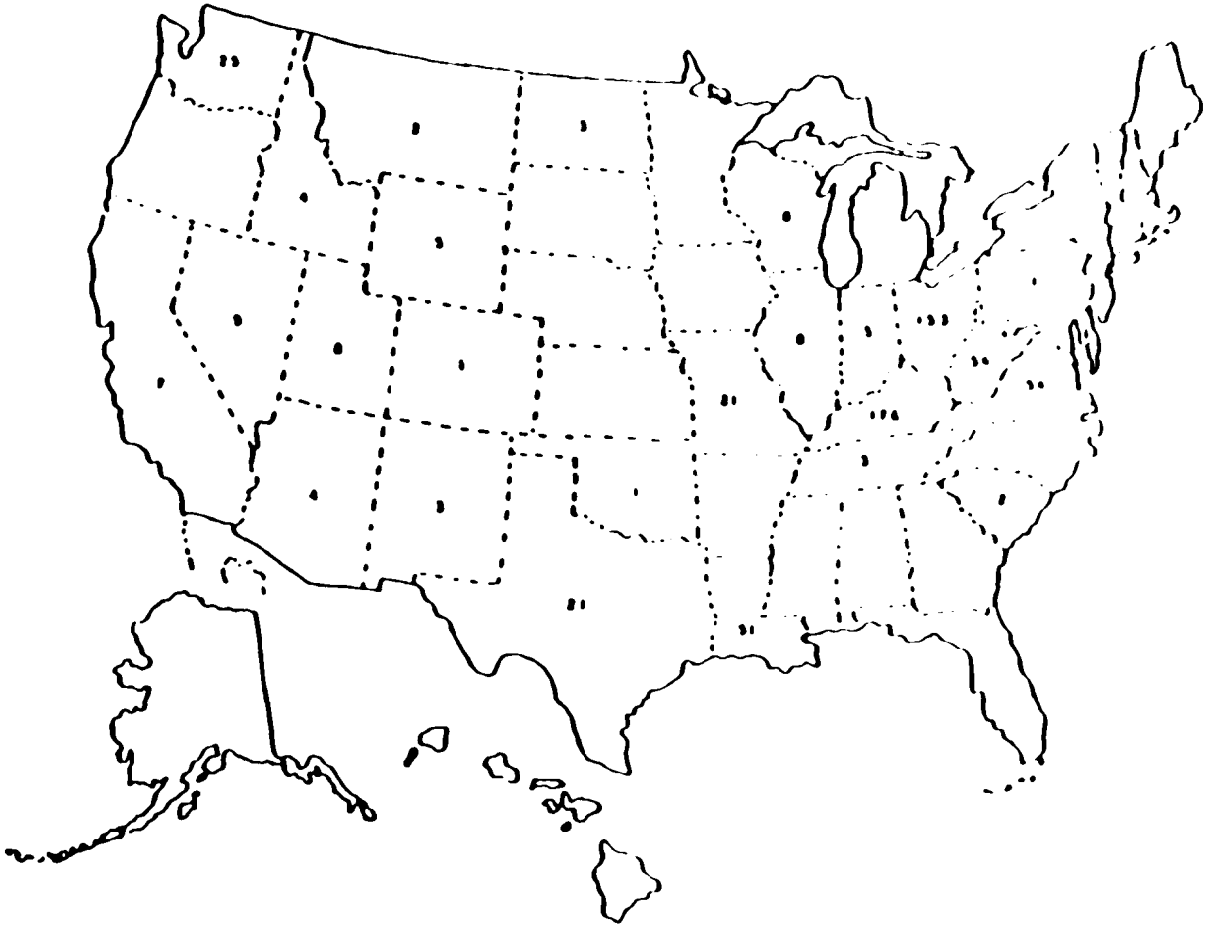
SUMMARY BY STATE....

State No.	Total Records	0	1	2	3	4	5	6	Stations
2	[illegible]	0	0	1	0	0	0	0	1
4	[illegible]	0	0	0	[illegible]	1	0	0	1
5	[illegible]	0	1	0	[illegible]	1	0	0	[illegible]
6	19	4	4	0	2	[illegible]	[illegible]	5	6
9	67	15	45	0	[illegible]	[illegible]		0	16
11	55	[illegible]	0	0	0	0	0	0	1
12	9	1	1	0	2	[illegible]	0	0	4
13	15	12	20	0	3	0	[illegible]	0	11
16	4	2	1	0	[illegible]	1	0	0	1
17	40	0	[illegible]	[illegible]	1	1	[illegible]	18	11
18	10	9	7	0	1		0	0	8
19	9	8	0	0	5	0	0	0	7
20	5	1	0	0	0	4	0	0	1
21	302	85	12	7	30	209	[illegible]	0	40
22	616	10	0	115	0	[illegible]	[illegible]	0	112
23	1	0	0	0	1	0	0	0	1
25	[illegible]	3	[illegible]	1	[illegible]	[illegible]	1	0	[illegible]
26	[illegible]	[illegible]	0	0	1	[illegible]	[illegible]	1	18
27	1	1	0	0	0	0	0	0	1
28	8	0	1	3	0	5	0	0	4
29	119	21	8	5	[illegible]	0	0	0	[illegible]
30	68	16	0	0	13	14	25	0	10
31	2	0	2	0	0	0	0	0	1
32	5	0	0	0	0	5	0	0	2
33	1	0	0	0	1	0	0	0	1
34	[illegible]	0	1	4	10	[illegible]	0	1	13
35	[illegible]	4	3	1	3	[illegible]	0	0	16
36	30	10	5	2	9	4	0	0	15
37	9	1	0	0	8	0	0	0	4
38	3	0	1	0	0	2	0	0	2
39	111	3	20	1	5	0	104	0	[illegible]
40	7	1	1	0	5	0	0	0	6
41	9	1	0	0	8	0	0	0	4
42	1	0	0	0	1	0	0	0	1
44	1	1	0	0	0	0	0	0	2
45	3	0	0	0	3	0	0	0	2
46	8	1	0	0	1	0	0	[illegible]	1
47	14	0	0	0	10	4	0	0	11
48	69	2	0	0	1	12	0	[illegible]	22
49	101	8	86	0	4	1	0	0	19
50	2	0	0	0	2	0	0	0	1
51	516	514	0	0	2	0	0	0	19
53	129	1	90	4	66	7	0	0	26
54	11	0	8	0	5	0	0	0	5
55	4	0	0	0	4	0	[illegible]	0	1
56	15	[illegible]	1	0	4	4	0	0	11
58	[illegible]	0	0	0	1	4	0	0	1

Total Records Counted = [illegible]

FIGURE A-5

LEAD DATA RECORDS AVAILABLE BY STATE



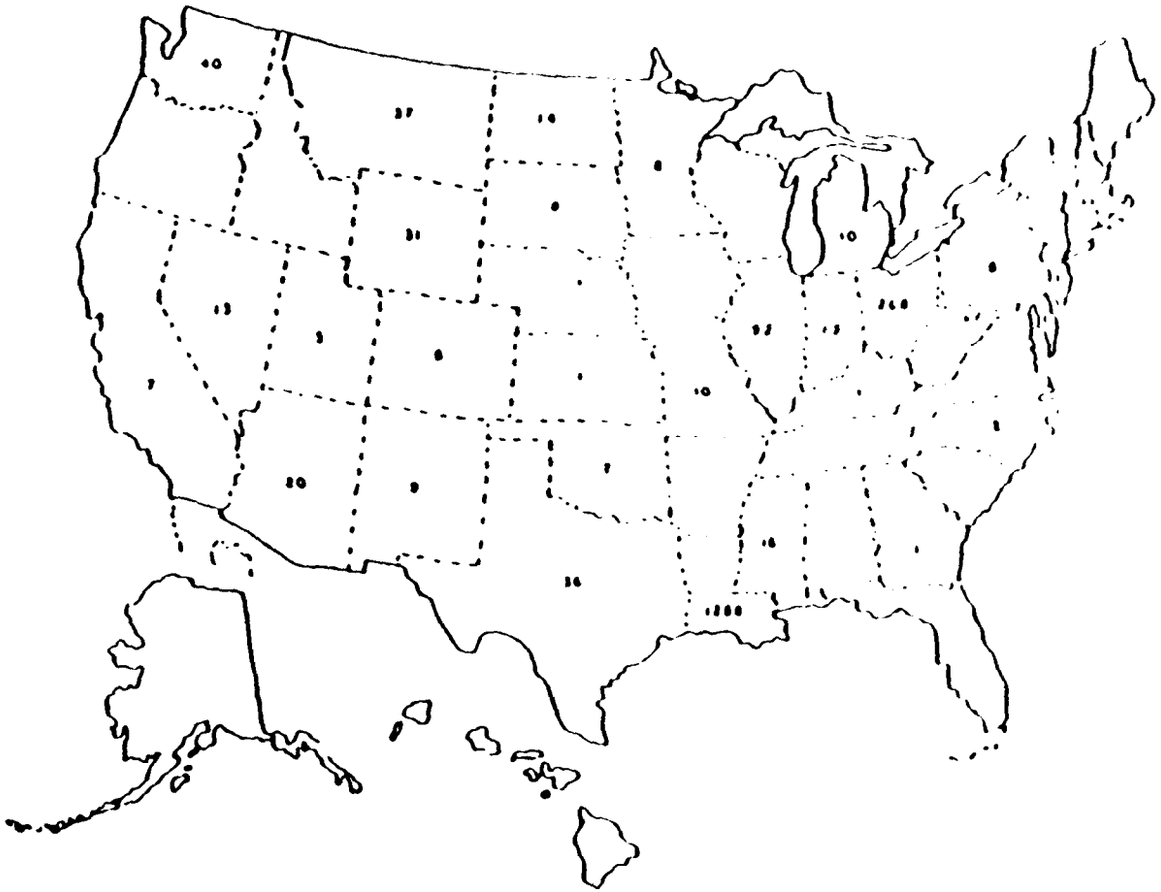
SUMMARY BY STATE

STATE NO.	TOTAL RECORDS	NO. RECORD TYPE 0	1	2	3	4	5	6	NUMBER STATIONS
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

TOTAL RECORDS FOUND = [illegible]

FIGURE A-6

MERCURY DATA RECORDS AVAILABLE BY STATE



SUMMARY OF STATE

STATE & TOTAL NO.	RECORDS	BY RECORD TYPE 0	1	2	3	4	5	6	STATIONS
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

TOTAL RECORDS [illegible]

FIGURE A-7

NICKEL DATA RECORDS AVAILABLE BY STATE

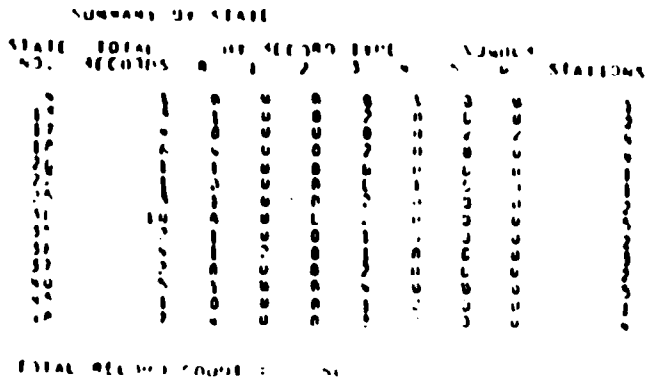
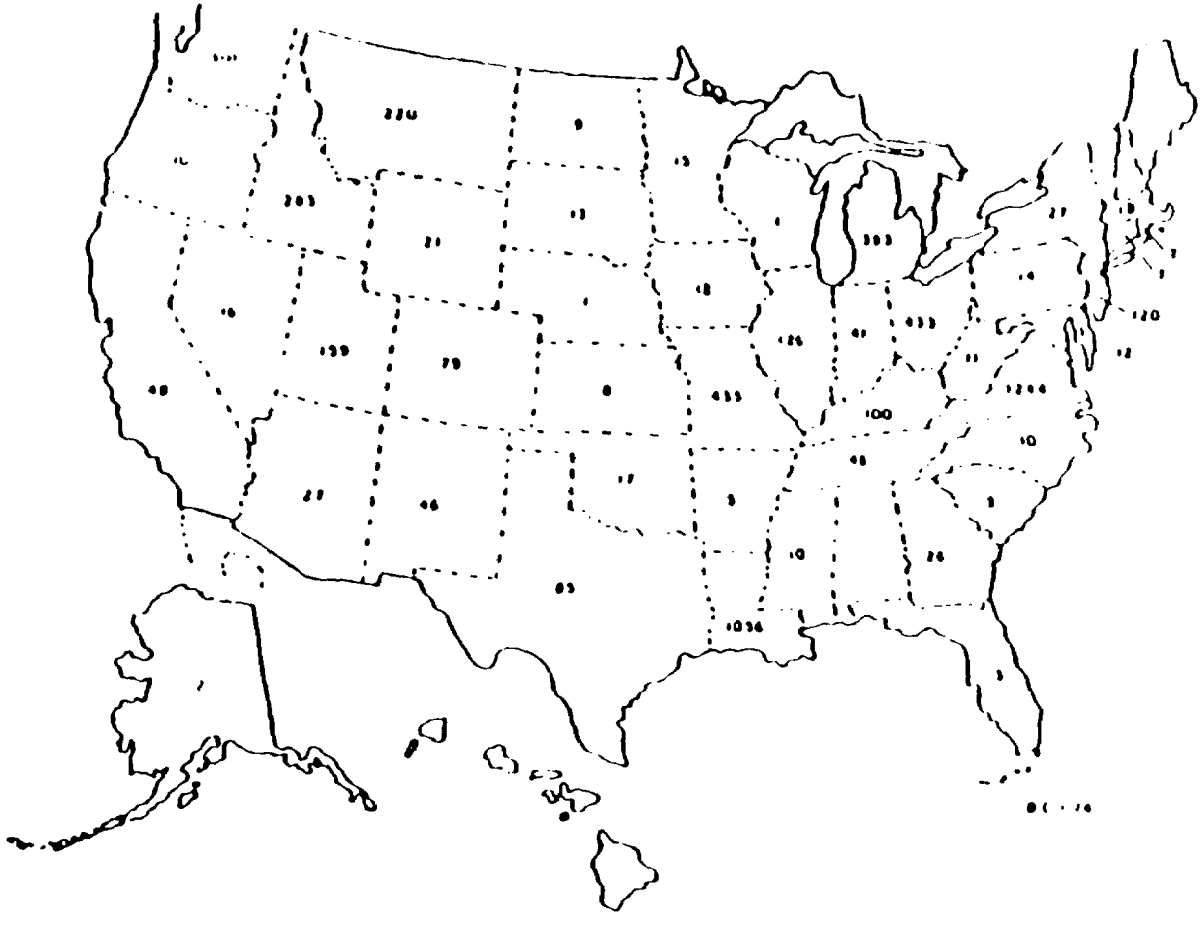


FIGURE A-8

SILVER DATA RECORDS AVAILABLE BY STATE



SUMMARY BY STATE

STATE NO.	TOTAL RECORDS	BY RECORD TYPE 0	1	2	3	4	YUGOLK 5	6	STATIONS
2	2	0	0	1	1	0	0	0	1
4	27	2	21	0	0	4	0	0	7
5	5	0	0	0	0	5	0	0	2
6	48	19	0	0	1	0	12	13	23
8	79	25	46	0	4	4	0	0	19
9	7	7	0	0	0	0	0	0	1
11	19	74	0	0	0	0	0	0	1
12	3	0	1	0	0	2	0	0	2
13	26	8	15	0	3	0	0	0	5
16	283	26	29	0	210	10	0	0	43
17	120	1	0	7	9	4	71	23	37
18	41	15	19	0	5	1	0	0	24
19	12	2	2	1	7	0	0	0	4
20	8	1	1	0	6	0	0	0	4
21	100	9	6	1	12	71	1	0	51
22	1056	78	1	622	1	321	0	33	184
24	12	0	11	0	1	0	0	0	9
25	18	7	2	0	5	2	2	0	7
26	193	251	0	2	20	18	109	1	46
27	15	2	1	2	0	2	0	0	8
28	10	0	1	5	0	4	0	0	6
29	435	97	19	9	315	0	0	3	69
30	220	38	3	1	37	25	126	0	48
31	1	0	1	0	0	0	0	0	1
32	16	0	1	1	0	14	0	0	3
34	120	0	2	1	6	100	0	3	18
35	46	12	3	0	0	22	0	1	20
36	27	9	9	0	4	1	4	0	13
37	10	1	0	0	9	0	0	0	4
38	9	0	2	1	2	4	0	0	4
39	413	17	19	4	35	1	122	0	120
40	17	7	4	0	5	0	1	0	10
41	10	1	0	0	0	1	0	0	6
42	14	2	1	0	1	0	2	3	13
44	1	0	1	0	0	0	0	0	1
45	5	1	0	0	2	0	0	0	3
46	13	1	4	0	7	0	0	0	6
47	46	3	1	0	21	3	13	0	29
48	85	2	0	0	1	18	0	72	18
49	1[illegible]	12	110	18	2	17	0	0	14
51	1244	1243	0	0	1	0	0	0	28
53	101	7	32	1	57	4	0	0	23
54	11	3	1	0	5	2	0	0	6
55	1	0	0	0	1	0	0	0	1
56	21	2	3	0	9	7	0	0	15
57	1	0	0	1	0	0	0	0	1
58	6	0	0	0	2	4	0	0	4

TOTAL RECORD COUNT = 5397

FIGURE A-9

ZINC DATA RECORDS AVAILABLE BY STATE

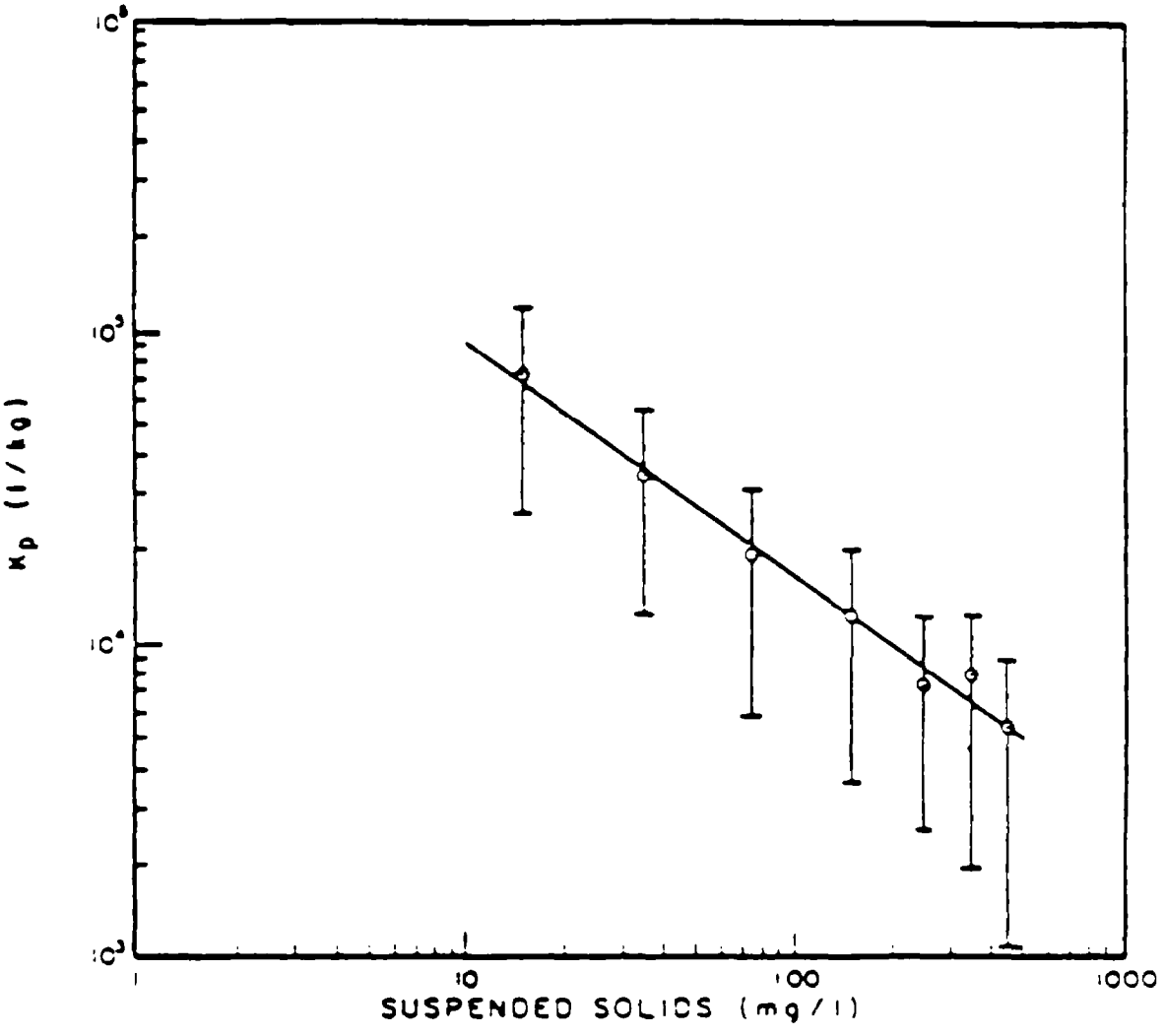


FIGURE A-10A

PARTITION COEFFICIENT AS FUNCTION OF SUSPENDED SOLIDS
ARSENIC IN STREAMS

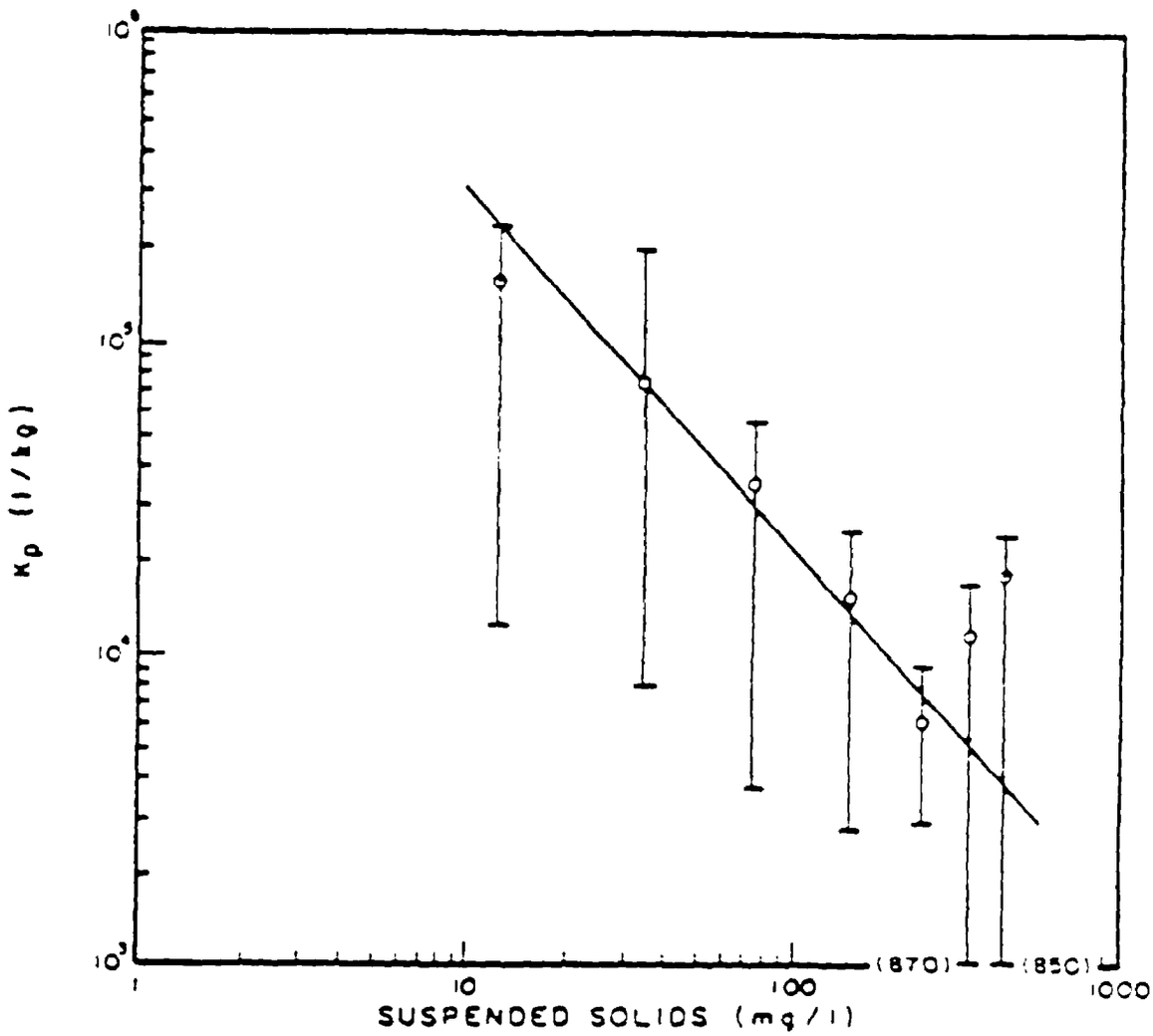


FIGURE A-11A

PARTITION COEFFICIENT AS FUNCTION OF SUSPENDED SOLIDS
CADMIUM IN STREAMS

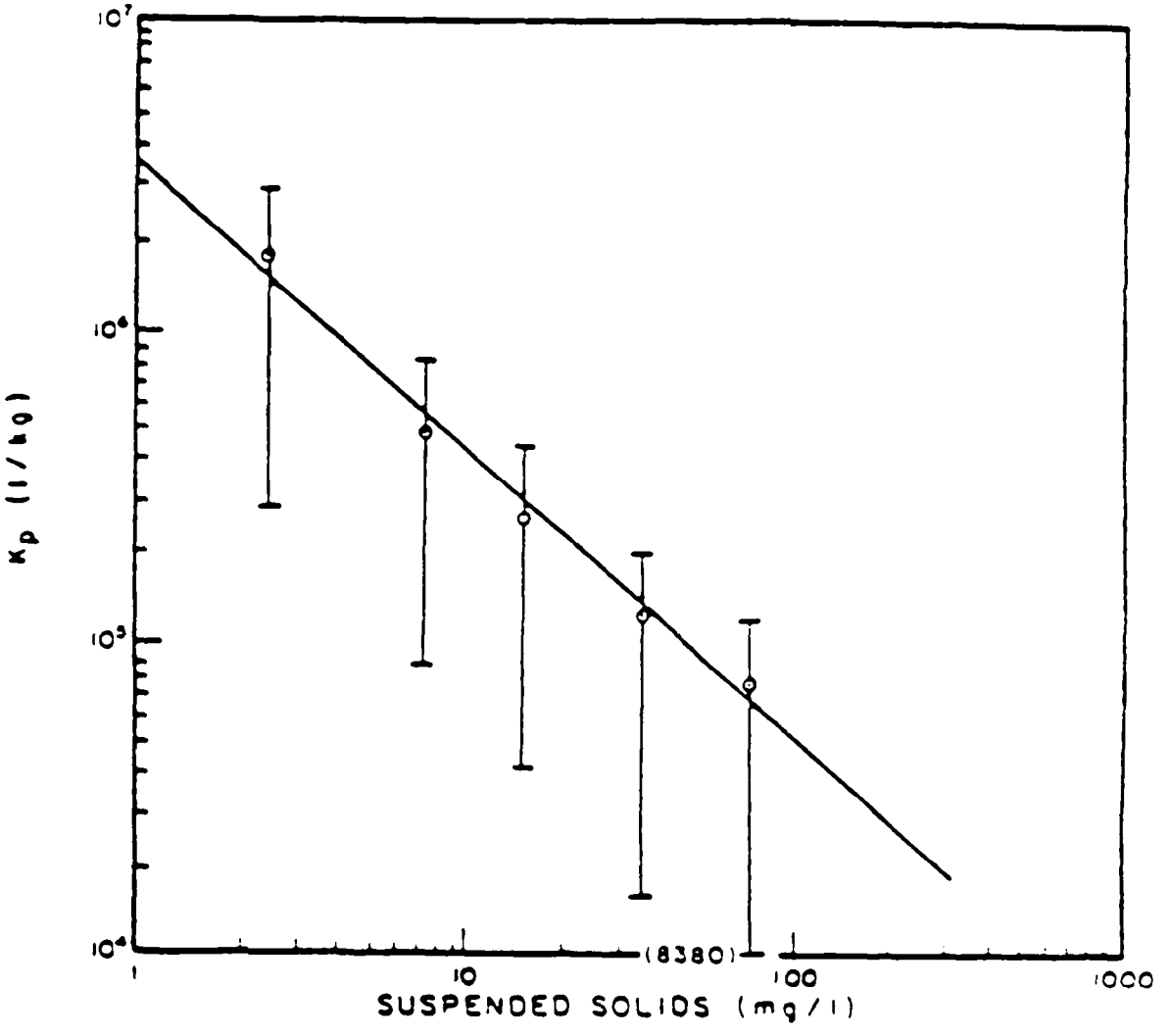


FIGURE A-11B

PARTITION COEFFICIENT AS FUNCTION OF SUSPENDED SOLIDS
CADMIUM IN LAKES

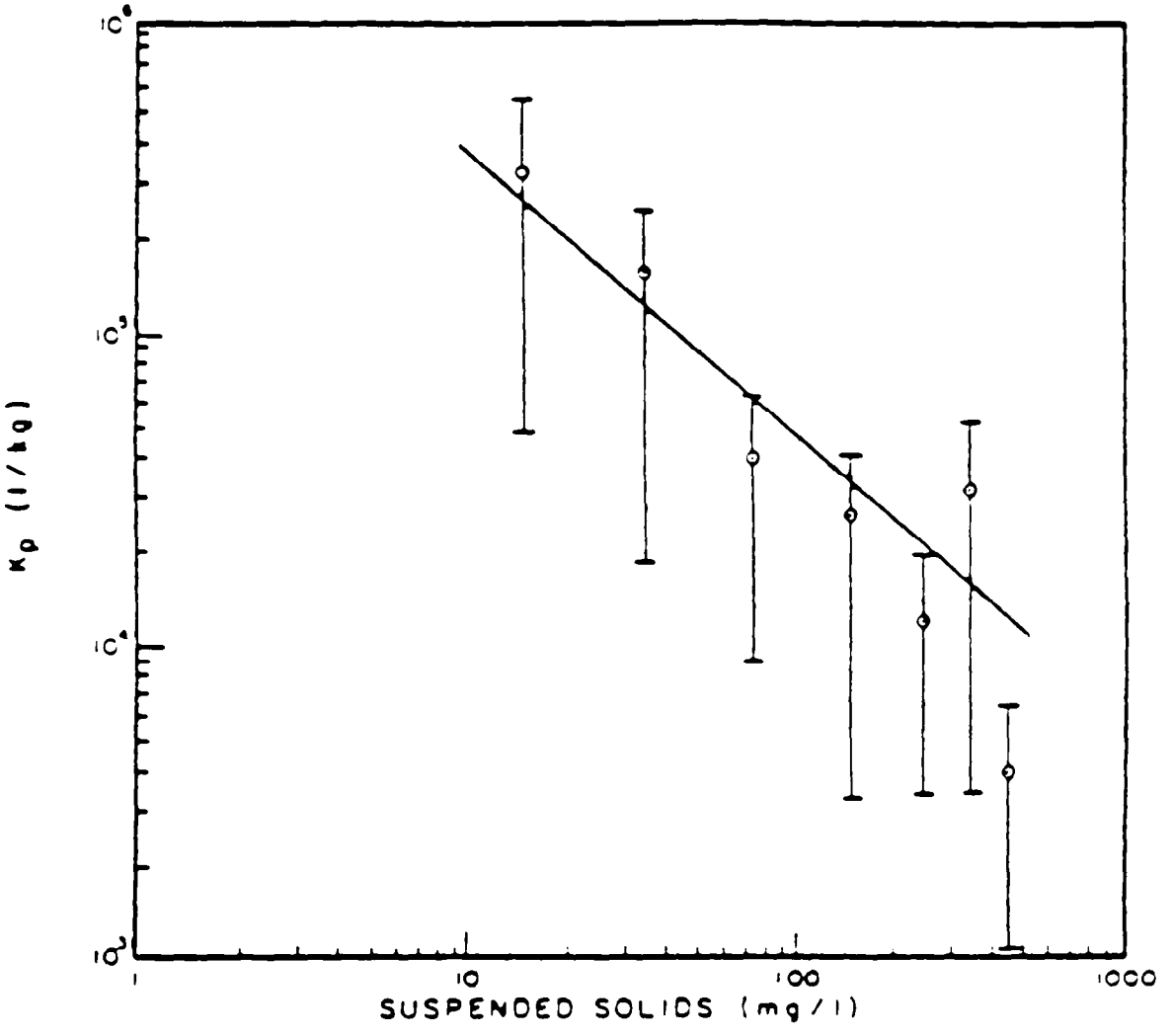


FIGURE A-12A

PARTITION COEFFICIENT AS FUNCTION OF SUSPENDED SOLIDS
CHROMIUM IN STREAMS

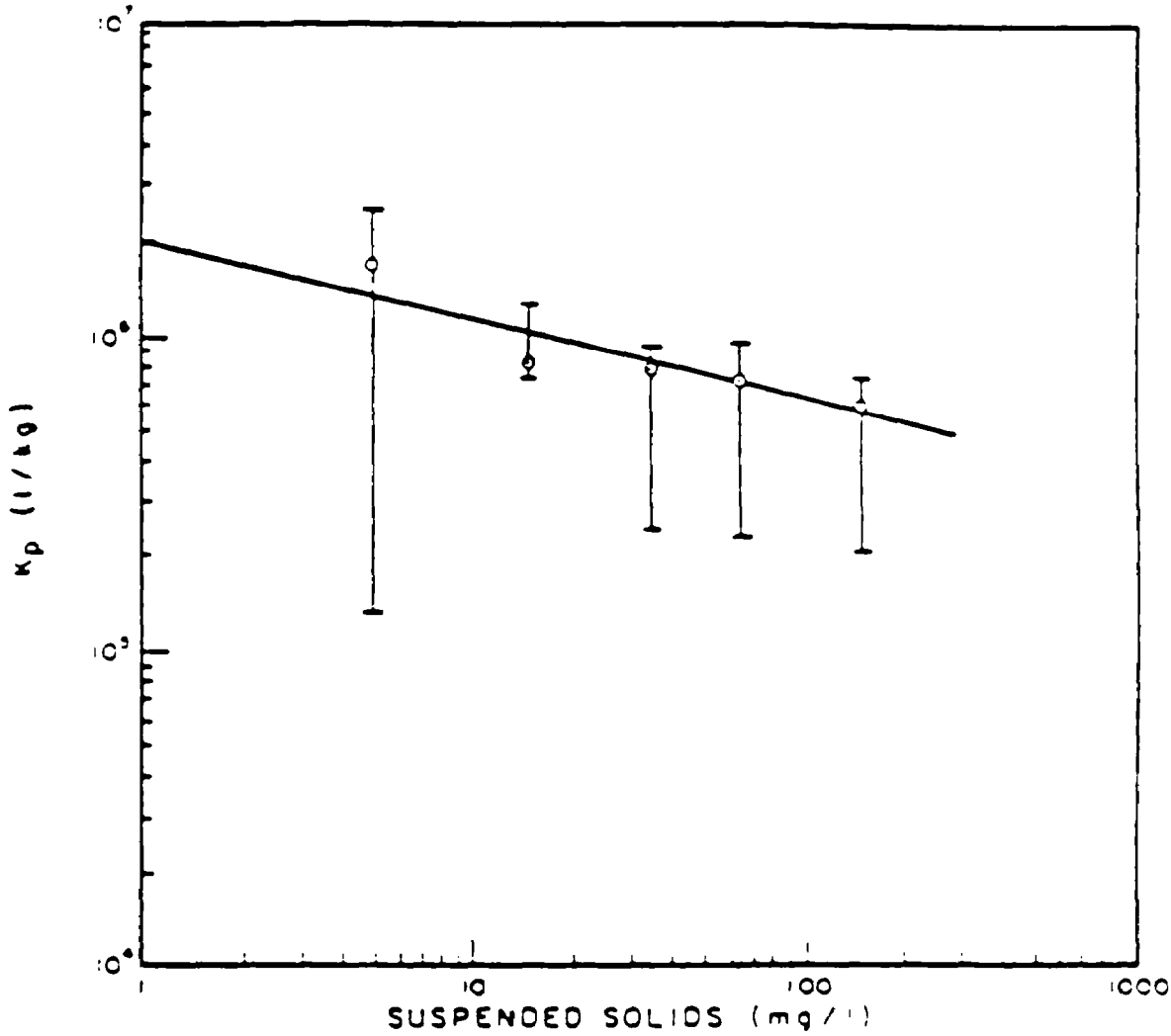


FIGURE A-12B

PARTITION COEFFICIENT AS FUNCTION OF SUSPENDED SOLIDS
CHROMIUM IN LAKES

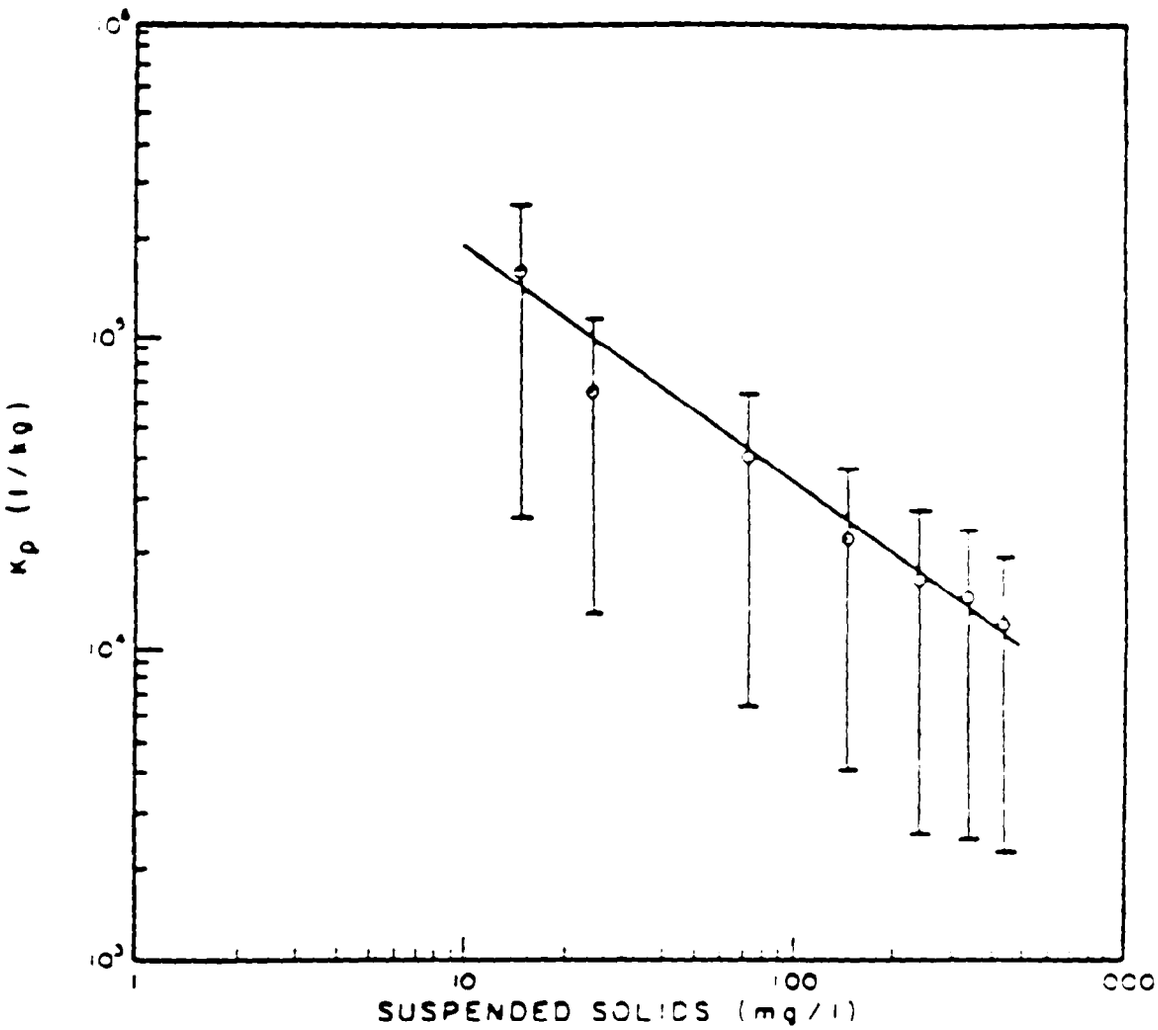


FIGURE A-13A

PARTITION COEFFICIENT AS FUNCTION OF SUSPENDED SOLIDS
COPPER IN STREAMS

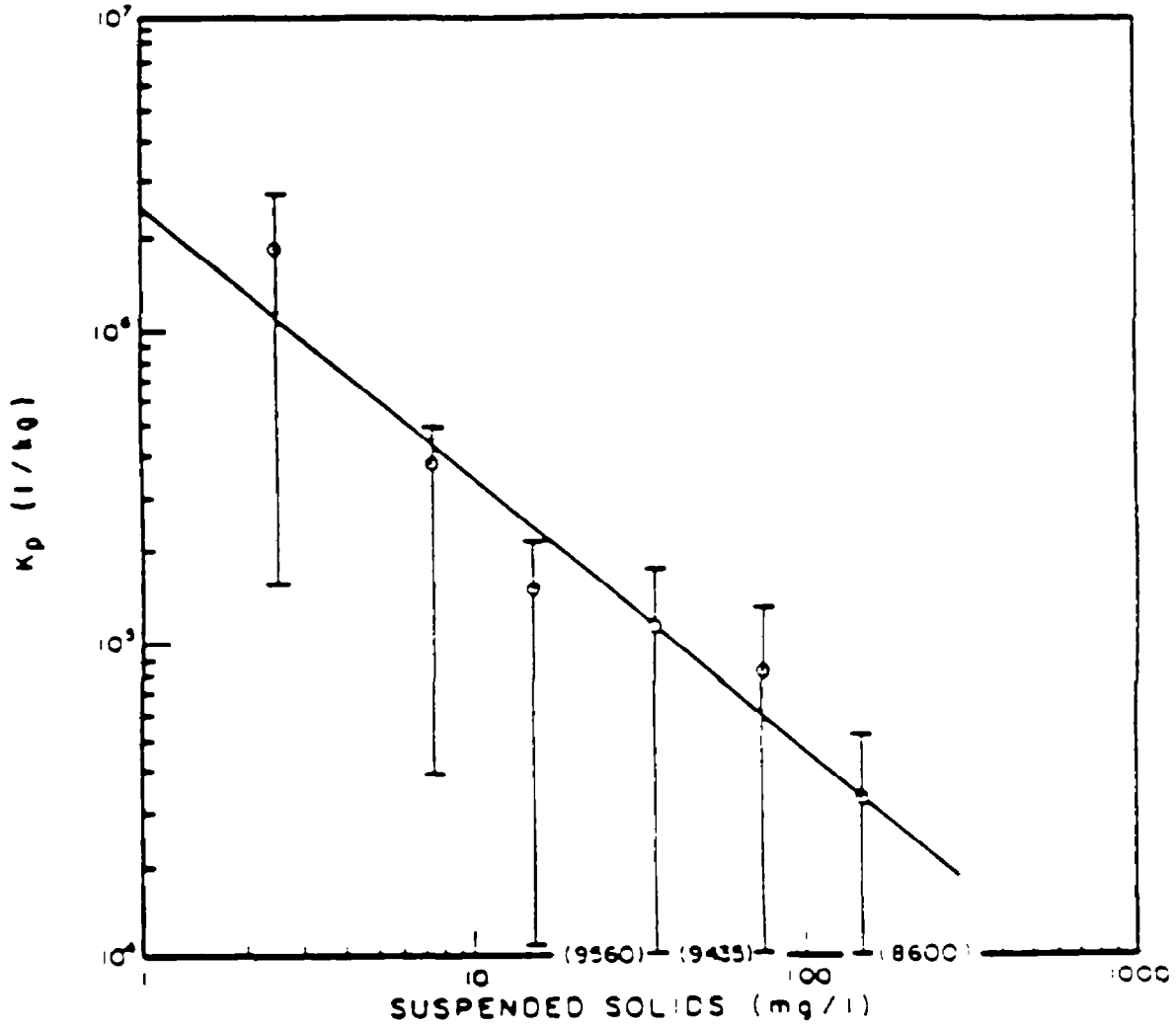


FIGURE A-13B

PARTITION COEFFICIENT AS FUNCTION OF SUSPENDED SOLIDS
COPPER IN LAKES

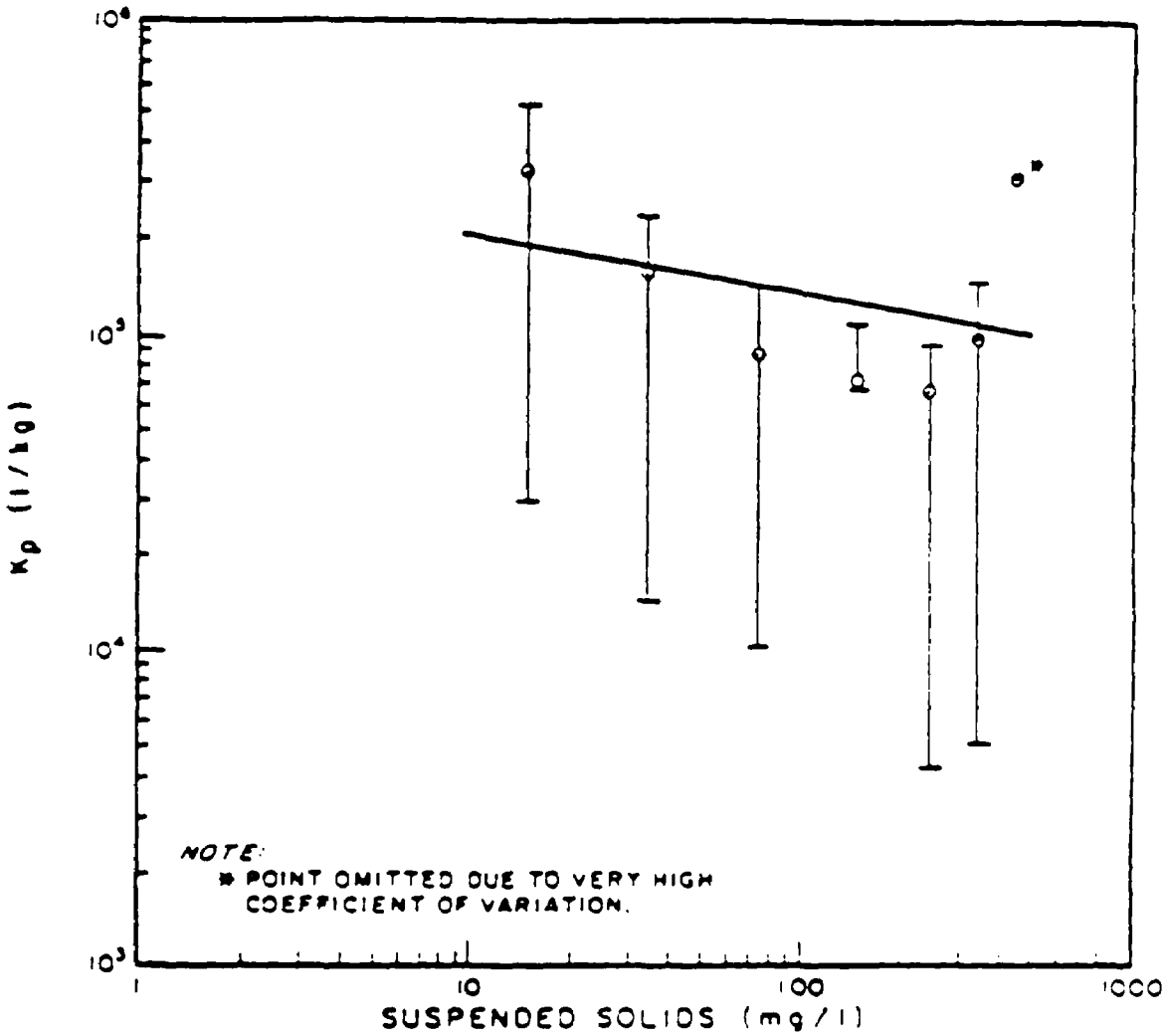


FIGURE A-14A

PARTITION COEFFICIENT AS FUNCTION OF SUSPENDED SOLIDS LEAD IN STREAMS

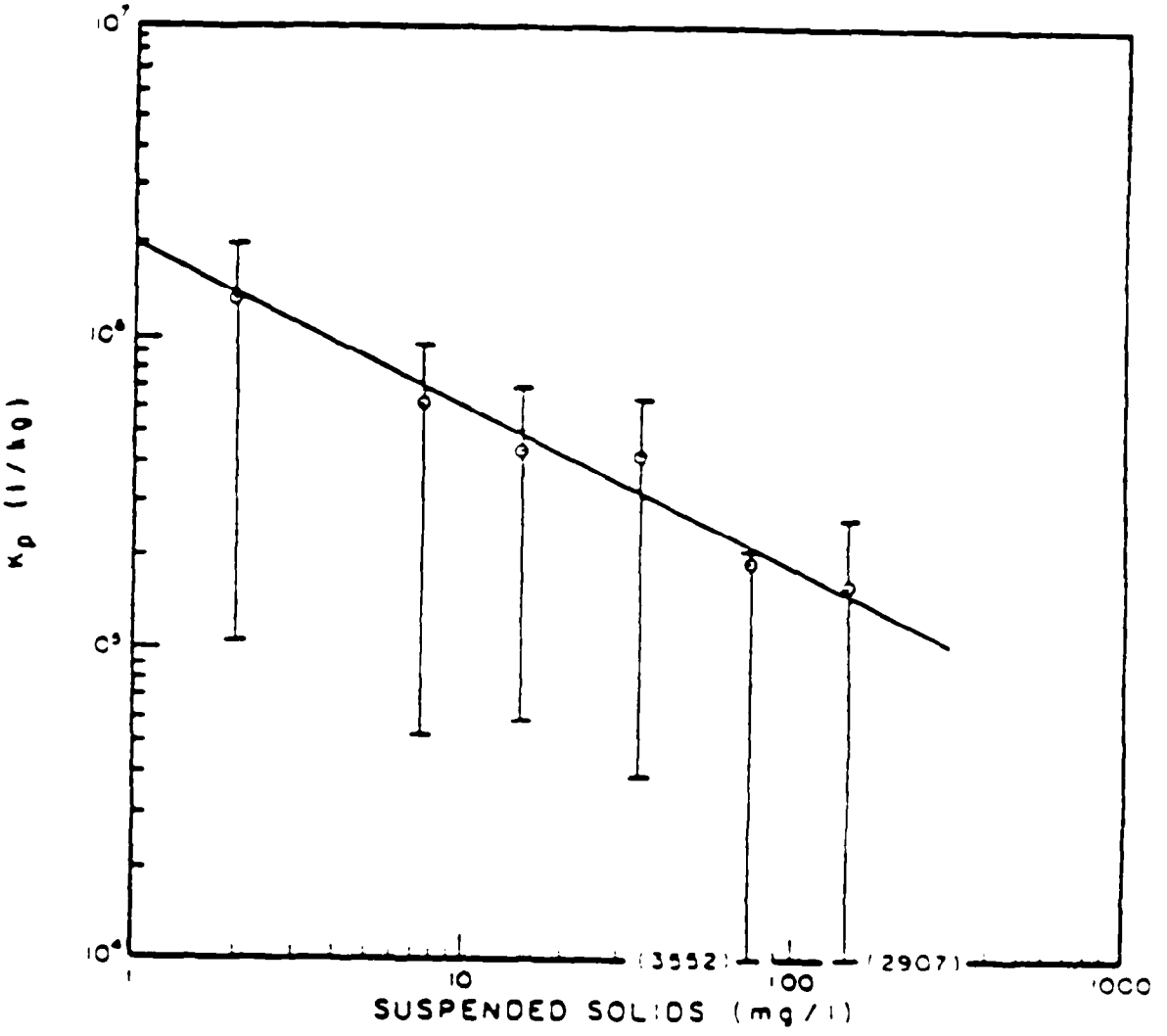


FIGURE A-14B

PARTITION COEFFICIENT AS FUNCTION OF SUSPENDED SOLIDS
LEAD IN LAKES

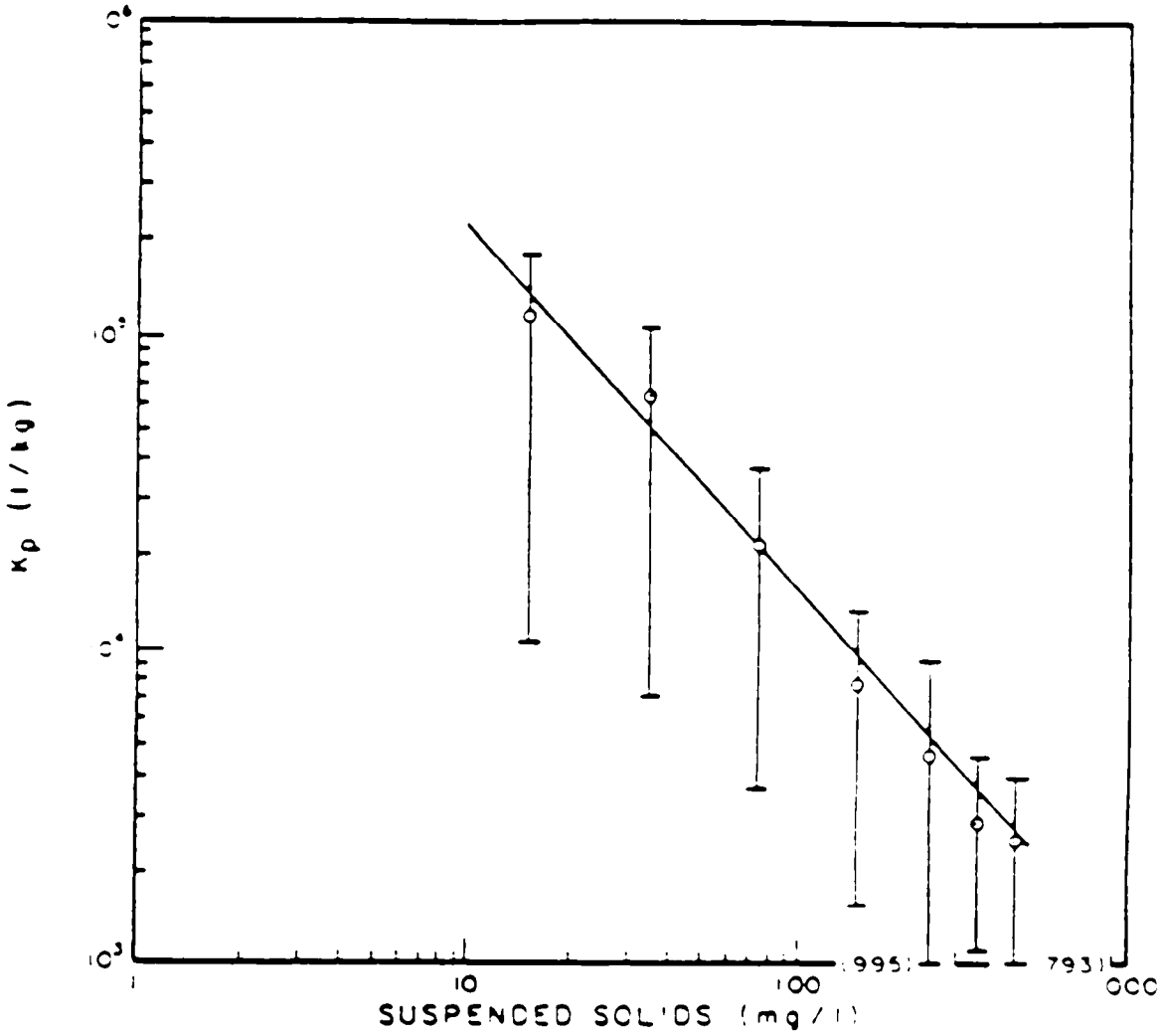


FIGURE A-15A

PARTITION COEFFICIENT AS FUNCTION OF SUSPENDED SOLIDS
MERCURY IN STREAMS

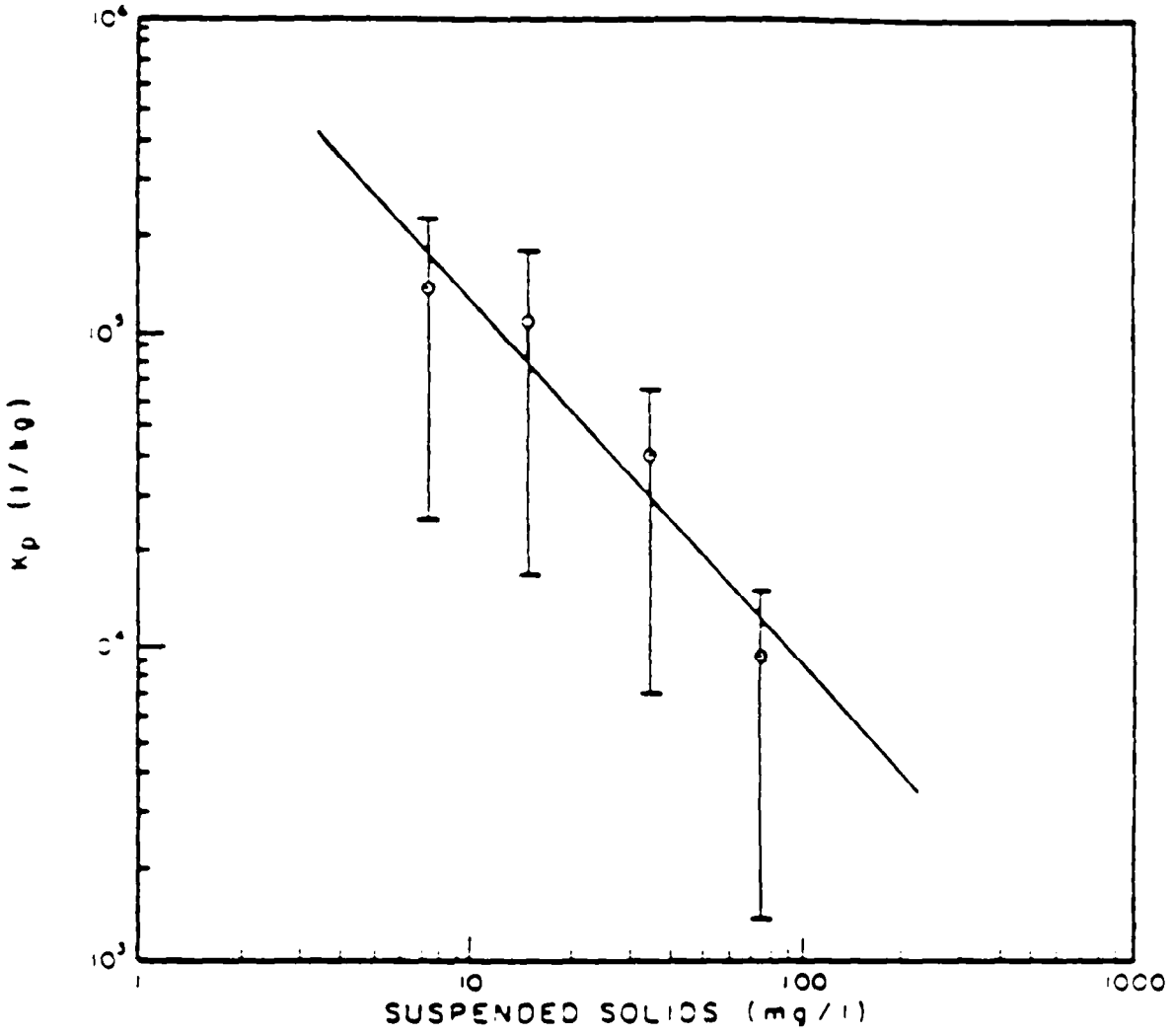


FIGURE A-15B

PARTITION COEFFICIENT AS FUNCTION OF SUSPENDED SOLIDS
MERCURY IN LAKES

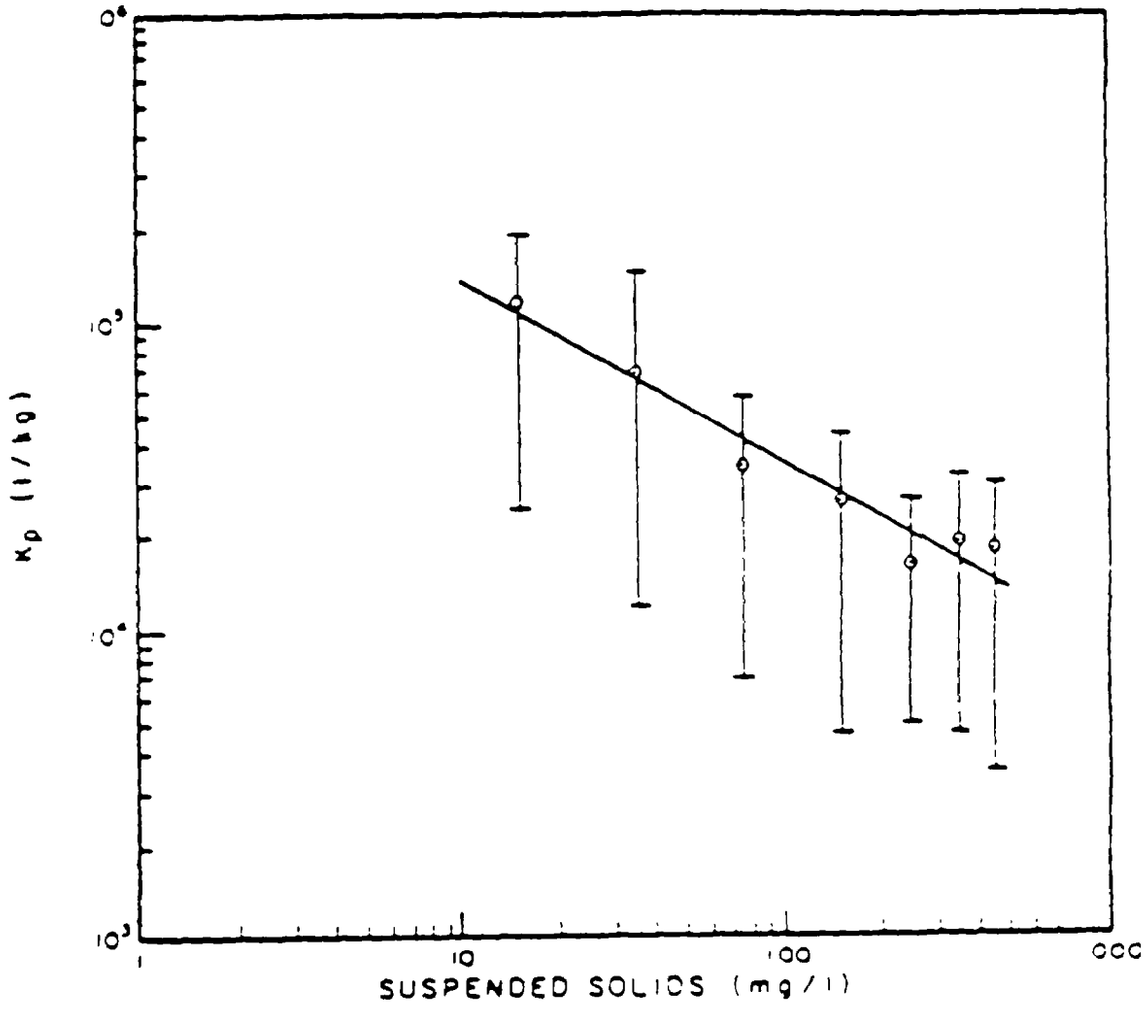


FIGURE A-16A

PARTITION COEFFICIENT AS FUNCTION OF SUSPENDED SOLIDS
NICKEL IN STREAMS

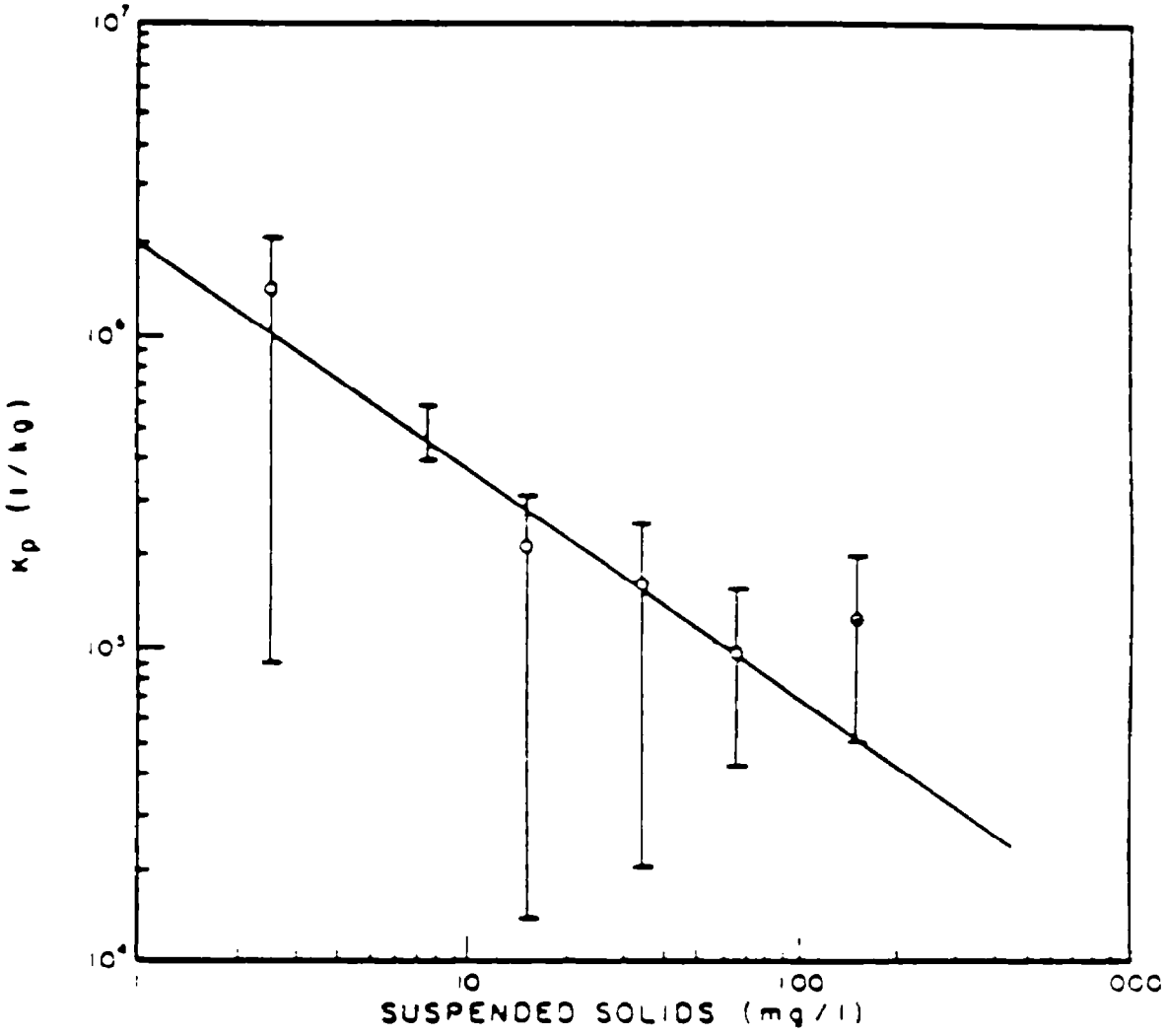


FIGURE A-16B

PARTITION COEFFICIENT AS FUNCTION OF SUSPENDED SOLIDS
NICKEL IN LAKES

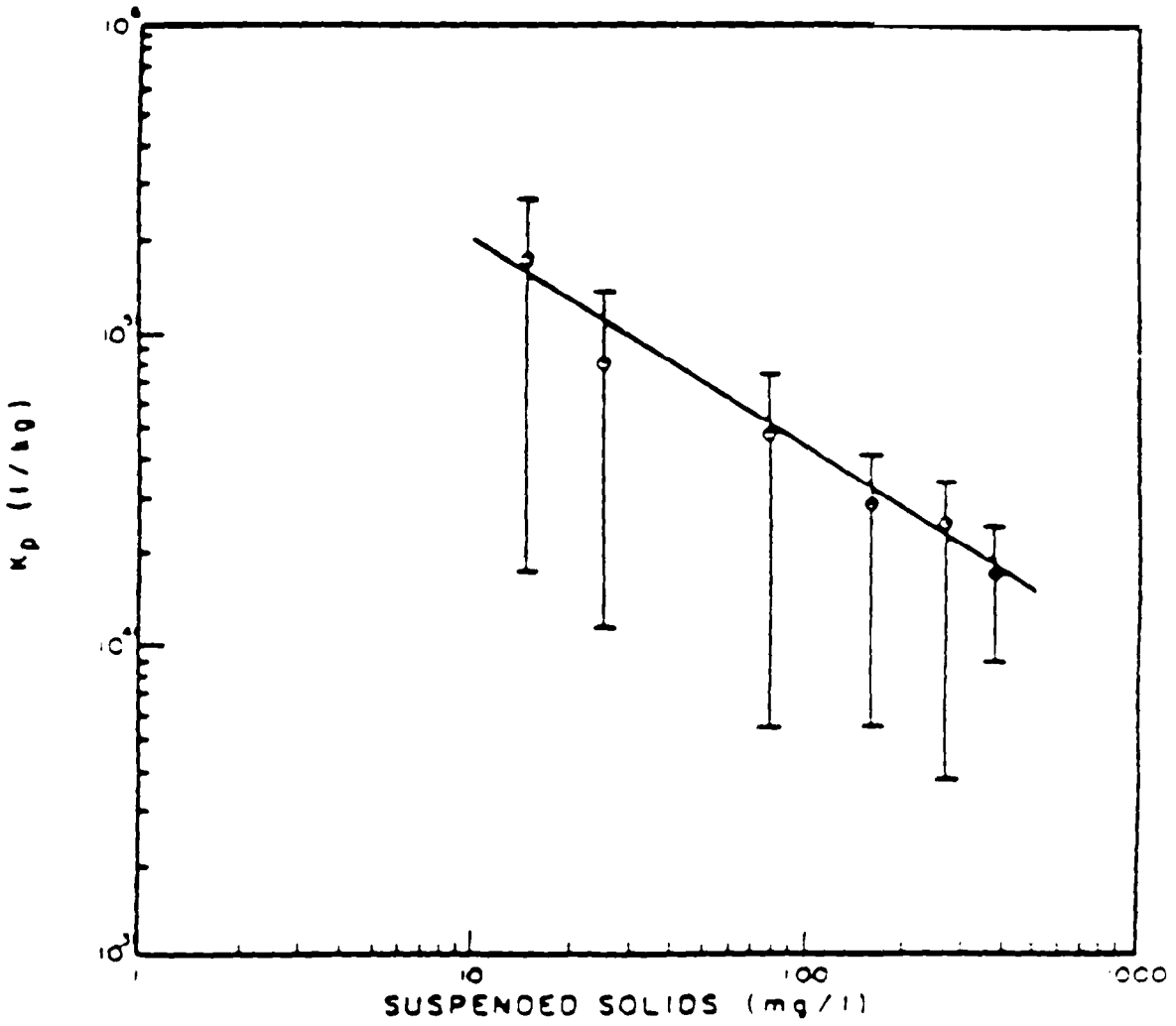


FIGURE A-17A

PARTITION COEFFICIENT AS FUNCTION OF SUSPENDED SOLIDS
ZINC IN STREAMS

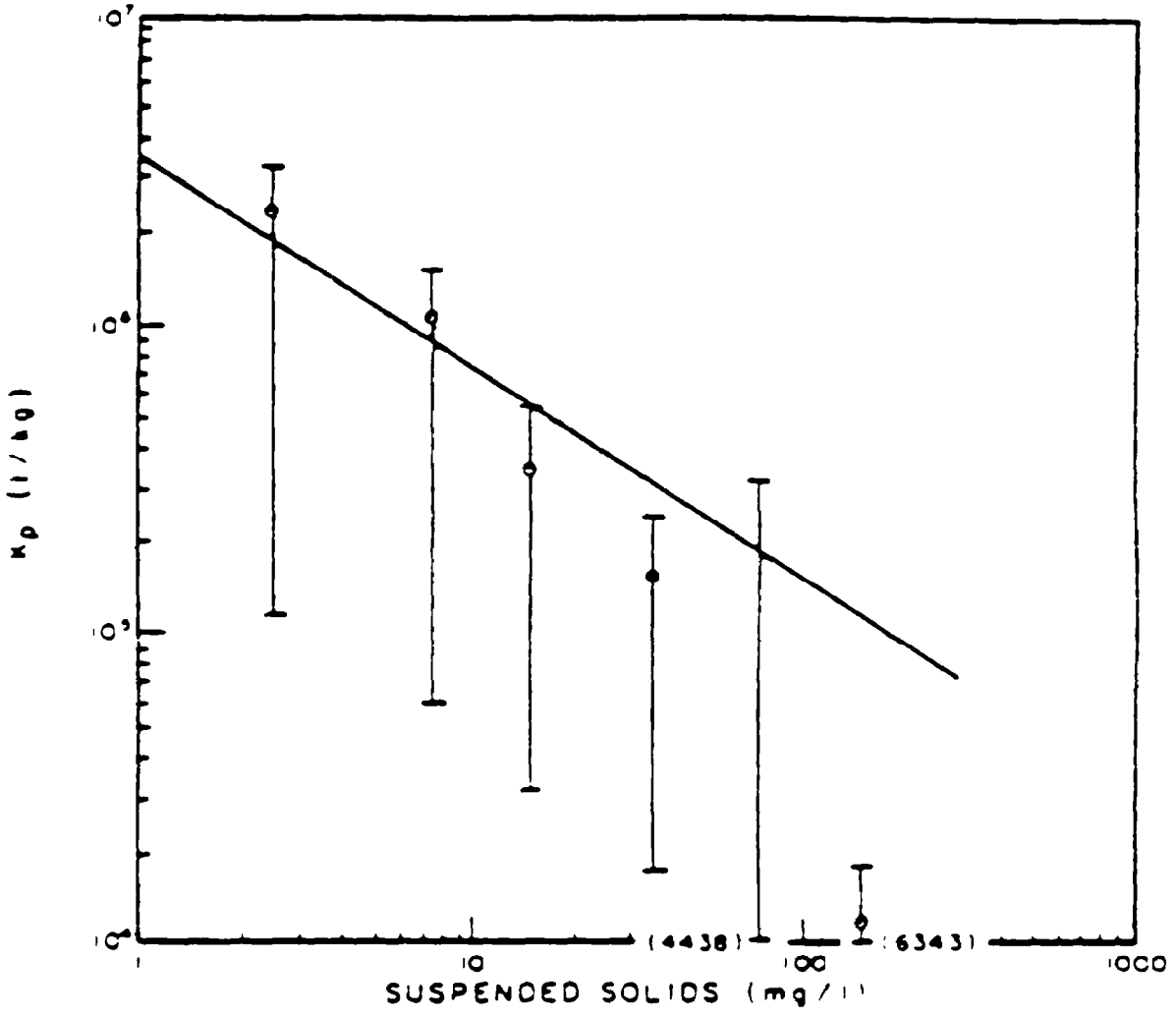


FIGURE A-17B

PARTITION COEFFICIENT AS FUNCTION OF SUSPENDED SOLIDS
ZINC IN LAKES

Catalogue of Waste Load Allocation Models for Toxic Compounds

EPA Contract No. 68-01-6160
Work Order No. 8

Prepared by:

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Prepared for:

U.S. Environmental Protection Agency
Monitoring and Data Support Division
Washington, D.C. 20460

April 1984

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Simple Desk Calculator Method

Introduction

Water quality based effluent limitations, as envisioned by Section 303 of the Clean Water Act, call for an analysis of the capabilities of water bodies to accept pollutant loadings without impairment of their beneficial uses. Ambient water quality standards indicate the pollutant concentrations allowable for attaining the use. Predicting the effluent loading restrictions needed to prevent violation of the ambient standards can be accomplished on a site-specific basis using mathematical models.

The desirability of controlling toxic pollutant discharges has lead to the recent development of a number of algorithms and computer codes which articulate the environmental transport and transformation processes relevant to toxicants. The purpose of this catalogue is to summarize the characteristics and capabilities of several of these simulation routines and thereby assist the potential user in identifying, selecting, and applying the documented and supported mathematical toxic pollutant fate models appropriate for the problem at hand. It is understood that final model selection will be a function of several important factors: complexity of the aquatic system simulated (e.g., number and nature of pollutant sources, system hydrodynamics, physico-chemical properties of pollutant, etc.); available resources (i.e., relevant data bases, technical expertise, economic, and hardware), and the ultimate use of the simulation results (e.g., permit writing vis-a-vis waste load allocation analysis, scientific research in pollutant behavior, etc). It is up to the analyst to prioritize each of these factors according to the constraints of his particular analysis.

The models discussed in this catalogue do not represent the universe of available toxic simulation routines; however, they do represent an adequate cross-section exhibiting a wide range of complexity and may be considered representative of the types of models likely to find use. Furthermore, this catalogue does not include models with toxicant simulation capabilities limited to the processes of pollutant delution and simple first-order decay in the water column.

All of the models listed here are general in nature; they take on the characteristics of a specific site only by specifying the parameter values appropriate to that site. They are all readily available and at least moderately well documented. All predict toxicant concentrations in the water column an in the bed sediment. As a group, they apply to streams, rivers, impoundments, lakes, estuaries, and coastal waters, although some individual models are limited to particular types of waters.

Each abstract summarizes the model's theoretical characteristics, input requirements, output information, primary strengths, limitations, and response requirements. It also indicates where the model has been applied, and how to obtain further information and user support.

Capsule Summary: WQAM
• *Far-field, steady state, 1-dimensional model* • *Procedures for assessing river, lake, and estuary water quality* • *First-order decay kinetics* • *Requires only a desk top calculator for calculations*

Summary

The Water Quality Assessment Methodology (WQAM) (Mills et al. 1982) was developed by Tetra Tech Inc. of Lafayette, California; Monitoring and Data Support Division, OWRS; and the Center for Environmental Research Information (CERI). The methodology was designed to perform preliminary (screening) assessments of surface freshwaters. The original methodology (Zison et al. 1977) addressed the identification of problems associated with sediment, nutrients, dissolved oxygen, and some urban pollutants in streams, lakes, and estuaries. The updated version now includes provisions for the assessment of toxic chemicals in the environment. WQAM is a simplified methodology in that all of the calculations are intended to be solved by a desk calculator.

The methodology was designed as a screening procedure that makes use of available generic data. The analyses require little external input since much of the needed information is provided by tables and figures within the manual. It predicts far field, average steady-state pollutant concentrations in rivers, lakes, and estuaries as a function of long term average maximum and minimum non-point source and point source loads.

Calculations performed by WQAM are divided into four sections. The first set is for waste load estimations of toxic and conventional pollutant loadings from both point and non-point sources. Procedures include load estimations for single event and annual loads from agricultural, forested, and urban areas. The Universal Soil Loss Equation (USLE) is used for agricultural areas; the URS Urban Water Quality Management procedure (Amy et al. 1974) and the Stormwater Management Model (SWMM) Level One Screening procedure are used for urban areas. The estimations may then be used to assess the water quality impacts in rivers, streams, lakes, and estuaries.

The response of rivers and streams to the release of pollutants is predicted by the second set of calculations. Variations in longitudinal pollutant concentrations are estimated. The calculations are based on steady-state, plug flow solutions to the conservation of mass equation. Conventional pollutant interactions presented include BOD, DO, temperature, coliforms, nutrients, and sediment transport. Procedures for toxic chemicals include methods for point and non-point sources as well as for large single event spills. The fate and transport of toxic chemicals are assessed using volatilization, sorption, and first order degradation.

Methods for assessing water quality and physical conditions in lakes are addressed in the third section. They are based on empirical stratification relationships and mass balances. In addition to toxic materials, sediment accumulation, thermal stratification, BOD-DO interactions, and eutrophication are covered. The fate of toxic pollutants is estimated with respect to biological uptake and bioconcentration in addition to the physico-chemical properties of the water and the chemical.

The last section provides methods for estuarine water quality assessment and prediction. The procedures include means for estuary classification (vertically stratified or vertically well mixed), turbidity, sedimentation, thermal pollution, transport of conservative and non-conservative pollutants, and flushing time prediction of pollutants. Analysis of longitudinal pollutant distribution is estimated by two different methods, the far field approach and the near field approach. The near field approach accounts for the buoyancy and momentum effects of the pollutant while the far field approach ignores them.

WQAM is designed to operate with minimum data, recognizing that the more data available, the more accurate the analysis. Although WQAM provides much information, most of it is general in nature.

Input Data Requirements

WQAM provides most of the data required for the calculations. In general, the only data not provided are climatic and hydrologic. Climatic data needed include precipitation, cloud cover, and humidity. The type of hydrologic information required includes runoff quantities, statistical flows such as 7Q10, stagnant regions, stratification, and estuarine tidal prism. Other basic information is also needed such as land use, stream lengths, lake depths and volumes, and estuary salinity distributions.

Output Descriptions

WQAM's output includes predicted concentrations of a pollutant (conservative and/or non-conservative) over distance from the input source. In addition to predicting pollutant concentrations, WQAM predicts:

- stream concentrations of BOD, DO, total N, total P, and temperature.
- lake nutrient concentrations, eutrophic status, and hypolimnion DO concentrations.
- estuarine concentrations of BOD, DO, and total N and P.

Advantages and Limitations

The major advantage of WQAM lies in its simplistic approach to waste load assessments. All the equations in the methodology are algebraic, and they c be solved using a desk calculator. This is a major advantage over other models in that the user does not need any programming experience. WQAM provides "typical" data which can be used in lieu of actual data for predicting chemical concentrations. Another advantage of WQAM is that it can be used for waste load assessments of estuaries as well as lakes and rivers.

Because of its simplistic approach, WQAM cannot include all the physico-chemical processes acting upon a pollutant. It is designed for long-term pollutant loading and average steady-state conditions and does not address the short-term effects that may be associated with toxics loadings. The methodology does cover the assumptions under which the algorithms are developed and provides the user the limitations of some of the tools presented.

WQAM closely relates the loading of conventional and toxic pollutants to receiving waters to the loss of soils and sediments and the amount of runoff. The non-point source loading section utilizes the Universal Soil Loss Equation for agricultural areas. It was developed primarily for croplands and does not predict erosion from streambanks, ditches beside roads, or gullies. The stream and river section is based on steady-state, plug flow solutions. It assumes dispersion to be small compared to advection. The calculations assume the lotic system to be vertically and laterally mixed and that any decay of the pollutant to be first order.

In estimating the fate and transport of pollutants in a lake, the methodology accounts for biodegradation, volatilization, and sedimentation. However, the model neglects several important physico-chemical processes (e.g., photolysis, oxidation, hydrolysis, coagulation-flocculation, and precipitation).

The transport of pollutants in estuaries assumes continuous, steady-state discharges of pollutants. The distribution of pollutants is based on the fraction of freshwater and/or modified tidal prism methods for calculating flushing times. The fraction of freshwater method assumes uniform salinity and uniform mixing of freshwater. The modified tidal prism method models for the entire estuary, regardless of where the pollutant source is located.

Model Applications

The original WQAM was applied and tested on the Sandusky River Basin and four Chesapeake Bay sub-basins: the Patuxent, Chester, Ware, and Occoquan. The model was used for simulating sedimentation, stratification, eutrophication, and DO depletion.

The modeling of toxic pollutants has been done using data from Coralville Reservior, Iowa. The insecticide dieldrin had accumulated in the reservior from its use on agricultural fields. The data from Schnoor's (1981) report on the reservior was used to test the accuracy of WQAM. The results showed WQAM to be in agreement with Schnoor (1981) for dieldrin concentration in both water and fish tissue.

Resource Requirements

All of the calculations in WQAM are algebraic expressions requiring only a hand calculator for solving. A programable calculator might be useful for the numerous advective-dispersion equations in the estuary section

User Support Activities

Copies of WQAM (EPA-600/6-82-004a-b) are available from the CERI, U.S. EPA, Cincinnati, Ohio, (534-684-7562).

User assistance may be obtained by contacting:

Robert Ambrose
USEPA
EPA Athens Environmental Research Laboratory
Center for Water Quality Modeling
Athens, Georgia 30613
FTS 250-3585 COM 404-546-3585

General References

Amy G, Pitt R, Singh R, Bradford WL, LaGraff MB. 1974. Water quality management planning for urban runoff. U.S. Environmental Protection Agency, Washington, D.C. EPA440/9-75-004; PB 241 689/AS.

Mills WB, Dean JD, Porcella DB, et al. 1982. Tetra Tech, Inc. Water quality assessment: a screening procedure for toxic and conventional pollutant Part .. Athens, Georgia: Environmental Research Laboratory. Office of Research and Development, U.S. Environmental Protection Agency. EPA-600/6-82-004a.

Mills WB, Dean JD, Porcella DB, et al. 1982. Tetra Tech, Inc. Water quality assessment: a screening procedure for toxic and conventional pollutants . Part 2. Athens, Georgia: Environmental Research Laboratory. Office of Research and Development, U.S. Environmental Protection Agency. EPA-600/6-82-004b.

Schnoor JL. 1981. Fate and transport of dieldrin in Coralville Reservior: residues in fish and water following a pesticide ban. Science 211:840-842. February 20.

Zison SW, Haven K, Mill WB. 1977. Tetra Tech, Inc. Water quality assessment: a screening methodology for nondesignated 208 areas. Athens, Georgia: Environmental Research Laboratory. Office of Research and Development, U.S. Environmental Protection Agency. EPA-600/9-77-023.

Steady State Models

Simplified Lake/Stream Analysis (SLSA)

Capsule Summary: SLSA
• *Steady state and time varying, 1-dimensional, compartment model.*
• *Freshwater, non-tidal aquatic systems.*
• *Simple first-order kinetics.*
• *Suitable for hand calculation or simple FORTRAN program.*
• *Easy to set up and use*

Summary

The Simplified/Lake Stream Analysis (SLSA (HydroQual 1982) is a simplified waste load assessment model developed by HydroQual Inc., Mahwah, New Jersey, for the Chemical Manufacturers Association, Washington, D.C. It analyzes organic and inorganic chemicals in simplified lake and stream settings. SLSA calculates the dissolved and sorbed steady state concentrations of a pollutant in the water column and bed sediment using an analytical solution. The model provides a less rigorous approach to pollutant simulation than complex computer programs. It is most applicable to single (or bunched) point source loadings. The intent of this model is to make the chemical fate of a pollutant in a freshwater system understandable to an unspecialized analyst

SLSA models streams and rivers as being well mixed in cross-section and as having a relatively constant flow and geometry. An analytical solution is given for pollutant concentration as a continuous function of distance downstream from the loading source. The model also estimates pollutant concentrations in the water column and bed sediment of unstratified impoundments or lakes. SLSA simplifies the hydrodynamics of the systems; aqueous transport is a function of the mean inflow rate of water, the depth and volume of the segment modeled, and the stream velocity or lake hydraulic retention time. Sedimentation and exchanging bed conditions are accounted for, however, the bed is assumed to be completely uniform.

SLSA only considers advection in the transport of a pollutant. Pollutant losses due to degradation processes are represented by simple first-order rate constants supplied by the user. The constants are then summed to yield an aggregate decay value. Practical methods for evaluating the interactions between the water column and bed sediment particulate sedimentation and resuspension and diffusive exchange are provided.

SLSA is essentially a 1-dimensional, steady-state model; however, it is capable of three quasi-time varying analyses of lakes in which the pollutant discharge rate is at steady state. The first time-variable evaluation pertains to the water column and bed sediment pollutant responses to an

instantaneous chemical load. The other two evaluations deal with the water column and bed sediment responses to either an initiation or cessation of long term pollutant loading.

SLSA is amenable to desk calculations, though a computer program is available for convenience. The program is written in FORTRAN IV level G and is convertible to most standard computer systems with FORTRAN compilers. The relatively small core requirements of the program and the speed of execution make the program very compatible with microcomputers.

Input Data Requirements

Input data requirements for SLSA are limited and are arranged in three groups:

- Pollutant input - pollutant loadings to the receiving water.
- Transport information - flow rates, water and sediment depths, length of stream, solids in water column and sediments, sedimentation and resuspension velocities, diffusive exchange.
- Transfers and kinetics - water column and sediment partition coefficients; water column photolysis, volatilization, hydrolysis, oxidation, and biodegradation first-order coefficients; sediment hydrolysis, oxidation and biodegradation rates.

The model defines the data requirements and explains how to evaluate and prepare it for use in the calculations.

Output Descriptions

SLSA output includes summations of the model's inputs and diagnostic information that aids in determining the relative importance of the transport mechanisms. The receiving water's response to the pollutant load is presented in tabular form. The response is presented in terms of pollutant concentrations in the water column and bed sediment. The concentrations can be further refined to estimate the dissolved and particulate concentrations of each phase as well.

Advantages and Limitations

The major advantage of SLSA is that it is a simple and easy-to-use model which can be applied using hand calculations or small microcomputers. SLSA requires only minimal data input. Model set up and

use can be accomplished in relatively short time as compared to other models.

SLSA has some time varying capabilities and can account for some interactions between the water column and bed sediment.

Because of SLSA's simplistic approach it has several limitations. Dispersive flow is not accounted for as in other models such as CTAP, thus limiting its use to relatively simplistic systems. The bed sediment is assumed to be completely mixed and undergoes no movement. Decay mechanisms are all first-order. Suspended solid concentration is kept constant at the input value and only a single particle size is considered. Only one reach with a single point source loading and no additional inflows are permitted.

Model Applications

SLSA has been applied to a 90 km reach of Rapid Creek in Rapid City, South Dakota. The study area was located downstream of a municipal wastewater treatment plant. The pollutant considered was the surfactant, linear alkylbenzene sulfonate (LAS). The treatment plant was the only known source of LAS.

The model was applied to reflect diurnal load variability for long-term loading. The predicted water column concentrations were slightly lower than the actual concentrations, but there was good agreement between the predicted and actual concentrations in the bed sediment.

Evaluation of the model inputs showed the accuracy and validity of these estimates to be good. There were however, discrepancies in the known flows and LAS concentrations. The known concentration values of the plant effluent were based on only five samples taken over a two-year period, necessitating calculations of alternative effluent concentrations. The estimates in those calculations probably contributed to any deviations between SLSA-computed concentrations and the actual concentrations.

Resource Requirements

SLSA requires a short (280 Bytes) FORTRAN program and a small storage capacity, if programming is desired.

User Support Activities

Copies of the SLSA user manual, as well as documentation, can be obtained from:

William Gulledge
Chemical Manufacturers Association
2581 M Street, N.W.
Washington, D.C. 20037
202-887-1183

Other assistance can be obtained by contacting:

John St. John
Domenic DiToro
HydroQual Inc.
1 Lethbridge Plaza
Mahwah, New Jersey 07430
201-529-5151

General References

HydroQual, Inc. 1981. Analysis of fate of chemicals in receiving waters Phase I. Prepared for: Chemical Manufacturers Association, Washington, D.C.

HydroQual, Inc. 1982. Application guide for CMA - HydroQual chemical fate models. Prepared for: Chemical Manufacturers Association, Washington, D.C.

Michigan River Model (MICHRIV)

Summary

Capsule Summary MICHRIV
• *Steady state, 1-dimensional*
• *Models rivers/streams*
• *Simple first-order kinetics*
• *Easy to set up and use*

The Michigan River Model (MICHRIV) (DePinto et al., n.d.) was developed at the EPA's Environmental Research Laboratory - Duluth, Large Lakes Research Station, Grosse Ile, Michigan, specifically for use in the waste load allocation program. MICHRIV simulates steady-state concentrations of pollutants from loadings into rivers for the water column and bed sediment. It has the ability to model successive reaches (instead of just one) using an analytical solution. It is fairly similar to SLSA but is less simplified and more flexible. MICHRIV is comparable to SLSA except for:

1) MICHRIV predicts particulate concentrations in the water column (state variable); SLSA treats it as an input data constant

2) MICHRIV can model successive reaches; SLSA can handle only one

3) MICHRIV is not intended for lakes whereas SLSA is.

MICHRIV simulates the advective transport of dissolved and adsorbed pollutants. The model employs first-order decay mechanisms for predicting pollutant distributions. An aggregate first-order loss rate coefficient, representing the sum of a number of processes, including volatilization, hydrolysis, photoylsis, oxidation, and biodegradation, is used in the model. Bed-water interactions include settling, resuspension, burial of particulates, and diffusion of dissolved constituents.

The model is written in FORTRAN, is user oriented, and provides guidance for input data preparation and model option selection. MICHRIV has flexible batch input routines suitable for multiple reaches.

Input Requirements

MICHRIV requires basic information for modeling:

- Loading rates of pollutants and solids to the receiving river.
- Flow rates, length of reach, water depth, and cross-sectional area.

- Partition and first-order decay coefficients for both the water column and bed sediment.

- Sediment/water exchange parameters; sediment solids concentration.

Output Description

MICHRIV predicts pollutant concentrations as a function of distance from the loading source. Total and dissolved pollutant concentrations for both the water column and bed sediment are reported. Suspended sediment concentrations are predicted as well.

Advantages and Limitations

MICHRIV was developed specifically for riverine waste load allocations; its level of complexity was intended to be suitable for widespread application. It requires less than two dozen input parameters per reach, therefore, model set up time is relatively rapid.

MICHRIV is designed for single river systems and is not appropriate for river networks, lakes, or estuaries without modifications. Other limitations of MICHRIV include:

- The model is steady-state with respect to flow and loads.

- Decay processes are first-order; it has no specialized second-order organic decay routines.

- Dispersion is assumed to be negligible.

- Sorption/desorption are assumed to be instantaneous.

- Bed load is not permitted.

Model Applications

MICHRIV was tested and applied to a 60 Km reach of the Flint River, Genesee County, Michigan. The application of the model dealt with the distribution of zinc, cadmium, and copper from point sources. The main purpose of the study was for calibration and field testing of the model. Calibrations were made on solids transport and water column partition coefficients to yield reasonable predictable total and dissolved metal concentrations. The results were reasonable enough to demonstrate MICHRIV's ability to accurately simulate sediment and water column concentrations of a pollutant.

Resource Requirements

MICHRIV is written in FORTRAN. The user manual and documentation are contained within an EPA draft report on technical guidance for waste load allocation studies.

User Support

MICHRIV is currently under review and should become available in the near future. Technical assistance for MICHRIV can be obtained by contacting:

Bill L. Richardson
US EPA
Environmental Research Laboratory - Duluth
Large Lakes Research Station
Grosse Ile, Michigan 48138

or

Joseph V. DePinto
Clarkson College of Technology
Potsdam, New York 13676

General References

DePinto JV, Richardson WL, Rygwelski K, et al. n.d. Technical guidance manual for performing waste load allocations. Draft report. Washington, DC: U.S. Environmental Protection Agency.

Chemical Transport and Analysis Program (CTAP)

Summary

The Chemical Transport and Analysis Program (CTAP) (HydroQual 1981) was developed by HydroQual Inc., Mahwah, New Jersey for the Chemical Manufacturers Association, Washington, D.C. CTAP is an extension of the Simplified Lake/Stream Analysis (SLSA), also developed by HydroQual and was designed for more complex problem settings.

Capsule Summary: CTAP
• *Steady-state, 3-dimensional compartment model.*
• *Streams, stratified rivers, lakes, estuaries, and coastal embayments.*
• *Multiple waste inputs.*
• *Simple first-order kinetics.*

CTAP, like SLSA, is designed to account for the dissolved and sorbed steady-state concentrations of organic and inorganic pollutants in both the water column and bed sediment. However, its greater complexity allows it to model stratified lakes, rivers, tidal rivers, estuaries, and coastal embayments. CTAP is essentially like SLSA in that it is a compartment model in which each compartment is equivalent to one SLSA "lake". However, CTAP is more complex in that these compartments (up to 425) may be arranged in any 1, 2, or 3-dimensional configuration (spatial concentration variations may exist in one, two, or three dimensions). Whatsmore, the compartments are interactive with each other via advective and dispersive transport. Mass balance equations are written for each compartment of both the water column and bed sediment and are interconnected to adjacent compartments. The result is a matrix of equations which are solved by digital computation.

CTAP accepts multiple chemical load inputs from different locales to the aquatic system. It can also account for tributary inflows and withdrawals as well.

CTAP can be used to simulate multi-dimensional bed sediment conditions. In addition, it allows for a moving bed, where the upper-most layers are subject to movement in the direction of water flow.

CTAP utilizes the same first-order reaction kinetics as SLSA. The coefficients for photolysis, hydrolysis, oxidation, and biodegradation are supplied by the user and then summed for an aggregate rec ; constant. The sorption-desorption mechanisms are assumed to occur instantaneously; a. it is assumed that soluble and particulate chemicals within each compartment are in a state of local equilibrium. Interactions between the water column and bed sediment include settling, resuspension, burial of particulates, and diffusive exchange of dissolved constituents.

Input Data Requirements

CTAP data requirements are more intensive than those of SLSA. In addition to the standard physico-chemical parameters of the aquatic system, CTAP requires:

- Sources and amounts of pollutant loading.
- Segment volumes and lengths.
- Segment flows per phase and dispersion rates.
- Solids types, distributions, loadings and concentration.
- Partition coefficients by phase and segment.
- First-order coefficients for - water column photolysis, volatilization, hydrolysis, oxidation, and biodegradation; sediment hydrolysis, oxidation, and biodegradation.

Data requirements are described by the model along with a discussion of how to prepare data for input.

Output Descriptions

The CTAP output presents less diagnostic information than SLSA, but prints out more computed chemical concentrations in the dissolved and particulate phases. The concentrations are presented in tabular form for both the water column and sediments. The output is also arranged so that the concentrations for each segment-compartment are reported.

Advantages and Limitations

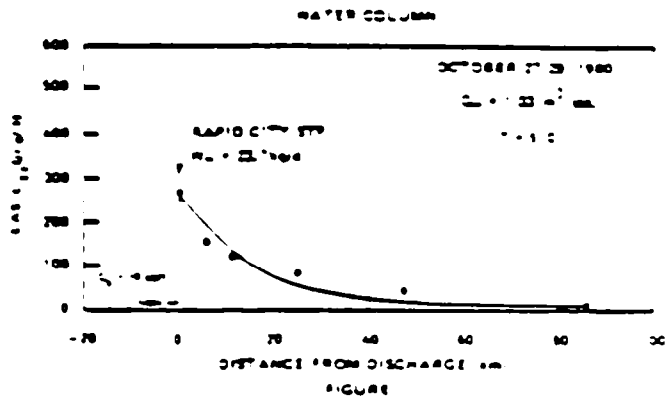
CTAP is a compartmental model, very flexible in configuration (up to three dimensions in both water column and bed sediment), and applicable to most types of water bodies. It can account for multiple point source waste inputs, but no non-point sources. Spatial variable flows can be handled, though the user must specify them since they are not predicted.

The model has no specialized organic decay routines of the type used in EXAMS; the user must specify first-order decay rates. A single decay rate, which is the sum of first-order coefficients of photolysis, hydrolysis, oxidation, biodegradation, and volatilization, is used to predict chemical fate. Bed-water interactions are articulated with an intermediate level of complexity. CTAP allows for up to five different particle sizes; it also allows for bed load.

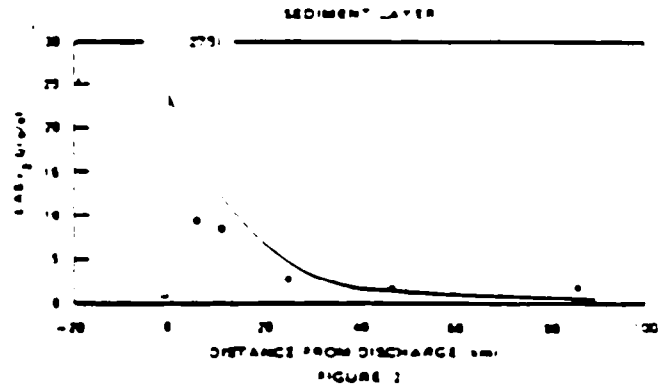
Model Applications

CTAP was applied to the data collected by Games (1981) from a 90-km reach of Rapid Creek, Rapid City, South Dakota. The study area was located downstream of a municipal wastewater treatment plant. The chemical considered was the surfactant linear alkylbenzene sulfonate (LAS). The treatment plant was the only known source of LAS. This is the same scenario used to apply the SLSA model.

The results of the CTAP modeling of long-term loading are shown in Figures 1 and 2 for concentrations in the water column and sediments, respectively. The circled points are the actual concentrations. The predicted concentrations in the water column were in close agreement with the actual; however, the predicted sediment values were slightly higher. When diurnal load variability was accounted for, the predicted sediment values were in better agreement.



Although not all the capabilities of CTAP were used in this application, the input was sufficient to accurately predict LAS concentrations. Evaluation of the inputs showed the accuracy and validity of these estimates to be good.



Resource Requirements

CTAP is written in Fortran IV and is suitable for operation, with slight modification, to the IBM 360/370, Univac 1108, CDC 6600 mainframe computers and to minicomputer systems such as the PDP 11/70, VAX 750/780, IBM 1130, and DSC Meta/4. The minicomputer version of CTAP requires 32K bytes of storage with subroutine overlay and disk scratch files for temporary storage.

User Support Activities

Copies of the CTAP user manual, as well as documentation, can be obtained for a fee from:

William Gulledge
Chemical Manufacturers Association
2501 M Street, N.W.
Washington, D.C. 20037
202-887-1183

Technical assistance can be obtained by contacting:

John St. John or
Domenic DiToro
HydroQual Inc.
1 Lethbridge Plaza
Mahwah, New Jersey 07430
201-529-5151

General References

HydroQual Inc. 1981. CTAP documentation - chemical transport analysis program. Prepared for the Chemical Manufacturers Association, Washington, D.C.

HydroQual Inc. 1982. Application guide for CMA-HydroQual chemical fate models. Prepared for the Chemical Manufacturers Association, Washington, D.C.

Games L. 1981. Practical applications and comparisons of environmental exposure assessment models. Presented at the ASTM Sixth Symposium of Aquatic Toxicology. St. Louis, Missouri.

Capsule Summary:	*EXAMS*
• *Steady state, 3-dimensional, compartment model.*	
• *Freshwater, non-tidal aquatic systems.*	
• *Comprehensive second-order kinetics for organic chemical decay.*	

Summary

The Exposure Analysis Modeling System (EXAMS) (Burns et al., 1982) is a steady-state water quality model designed by the U.S. Environmental Protection Agency's Environmental Research Laboratory in Athens, Georgia. The model was designed to allow for the rapid screening and evaluation of the behavior of synthetic organic chemicals in freshwater aquatic ecosystems. With a description of the physical and chemical properties of the compound of interest, and the relevant transport and physical/chemical characteristics of the aquatic system, EXAMS computes the exposure (steady-state environmental concentration), persistence (e.g., pollutant removal system half-life), and fate (distribution in the system and fraction consumed by each removal process) of each compound modeled. These calculations are based on the assumptions that the loadings are long term and time averaged.

The EXAMS program is an interactive modeling system that allows the user to specify and store the physical/chemical properties of both the chemical compounds and the aquatic environment.

The aquatic system is user specified and is represented by a set of segments or distinct compartments (water and sediment) in the system. As many as 100 compartments can be handled by EXAMS.

The program is based on a series of mass balances that give rise to a single differential equation for each compartment. Mass balances accounting for all compound mass entering and leaving are calculated by EXAMS as the algebraic sum of (1) external loadings, (2) transport processes that export the compound, and (3) transformation processes within the system that convert the chemical to daughter products. Working from the transport and transformation process equations, EXAMS compiles an equation for the net rate of change of chemical concentration in each compartment.

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EXAMS computes the kinetics of transformations attributable to direct photolysis, hydrolysis, biolysis, and oxidation reactions. The input chemical data for hydrolytic, biolytic, and oxidative reactions can be entered either as single valued second-order rate constants or as pairs of values defining the rate constant as a function of the environmental temperature specified for each segment. EXAMS includes two algorithms for computing the rate of photolytic transformation. The first requires an average pseudo-first-order rate constant applicable to near-surface waters; and the second computes the photolysis rate directly from the absorption spectra of the compound and its ions, measured values of the reaction quantum yields, and the environmental concentrations of competing light absorbence (chlorophyls, sediments, etc.).

Internal transport and export occur via advective and dispersive movement of dissolved, sediment-sorbed, and biosorbed materials, and by volatilization losses at the air-water interface. EXAMS provides a set of vectors that allows the user to specify the location and strength of both advective and dispersive transport pathways. EXAMS can compute transport of a chemical via whole-sediment bedloads, suspended sediment washloads, groundwater infiltration, transport through the thermocline of a lake, losses in effluent streams, etc.

External loadings of a chemical can enter the ecosystem via point sources, non-point sources, dry fallout or aerial drift, atmospheric wash-out, and groundwater seepage entering the system.

EXAMS is available in both a batch and interactive version.

Input Data Requirements

EXAMS requires an extensive amount of environmental data. However, the program can be run with a much reduced data set when the chemistry of a compound of interest precludes the existence of some of the transformation processes. For example, pH and pOH data can be omitted in the case of neutral organics that are not subject to acid or alkaline hydrolysis. Six "canonical" environments are included with most model versions and can be used for non-specific screening investigations.

Input parameters include:

- A set of chemical loadings on each sector of the ecosystem.
- Molecular weight, solubility, and ionization constants of the compound.

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- Sediment-sorption and biosorption parameters: Kp, Koc or Kow, biomasses, benthic water contents and bulk densities, suspended sediment concentrations, sediment organic carbon, and ion exchange capacities.

- Volatilization parameters: Henry's law constant or vapor pressure data, windspeeds, and reaeration rates.

- Photolysis parameters: reaction quantum yields, absorption spectra, surface scalar irradiance, cloudiness, scattering parameters, suspended sediments, chlorophyl, and dissolved organic carbon.

- Hydrolysis: 2nd-order rate constants or Arrhenius functions for the relevant molecular species: pH, pOH, and temperatures.

- Oxidation: rate constants, temperatures, and oxidant concentrations.

- Biotransformation: rate constants, temperatures, total and active bacterial population densities.

- Parameters defining strength and direction of advective and dispersive transport pathways.

- System geometry and hydrology: volumes, areas, depths, rainfall, evaporation rates, entering stream and non-point source flows and sediment loads, and groundwater flows.

Output Descriptions

EXAMS' 17 output tables include an echo of the input data, and tabulations giving the concentration, fate, and persistence of the chemical. Printer plots of longitudinal and vertical concentration profiles can be invoked by the interactive user.

Advantages and Limitations

The major technical strength of the EXAMS program lies in its ability to utilize well defined, chemically based fate process information in second-order rate expressions for the hydrolysis, photolysis, and oxidation processes. Volatilization is modeled in a way that is consistent with accepted mass transfer processes. Thus the model's strength is in evaluating the chemical's kinetics.

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From the user's standpoint, the model can be run in an interactive mode for rapid evaluation of scenarios reflecting varying system physical and chemical conditions. Furthermore, the model contains a built-in, on-line 'help-file' to explain the command options and required input data.

EXAMS is a steady-state model and as such was not designed to evaluate the short-term variations of an aquatic system.

EXAMS does not account for sediment and contaminant loss by burial in the benthic layer. Furthermore, it has only a single exchange coefficient lumping the process of water-sediment particle exchange and the process of water-pore water diffusion.

EXAMS has the capability to model ponds, rivers, and lakes. It does not have the capability of modeling estuarine aquatic environments.

- The model does not simulate sediment-pollutant loads from point and non-point sources. Solid concentrations must be derived from external sources.
- EXAMS evaluations do not include the effects of sediment-contaminant sorption/desorption kinetics on transport or transformation processes.

Model Applications

A field validation study of EXAMS was conducted for an anionic surfactant, linear alkylbenzene sulfonate (LAS), in Rapid Creek, South Dakota (Games, 1982). The single point source input to the creek is a sewage treatment plant located in Rapid City. Effluent to the creek is 7 to 8 mgd, which results in about a 3:1 dilution factor. Influent and effluent concentrations of LAS in the treatment plant were 3.7 mg/l and 0.51 mg/l, respectively, over the period 1978 to 1980.

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Simulations of LAS steady state concentrations in water and sediment were compared with observed concentrations. In a qualitative sense, agreement was good (see Figure 1). However, this agreement was only obtained by assigning an arbitrary value to the dispersion coefficient at the sediment/water interface. The value chosen was in the expected range, but little or no rationale for the value could be provided. Since this term is fairly important (as determined by a sensitivity analysis) and is seldom measured, it acquires the characteristics of a calibration parameter.

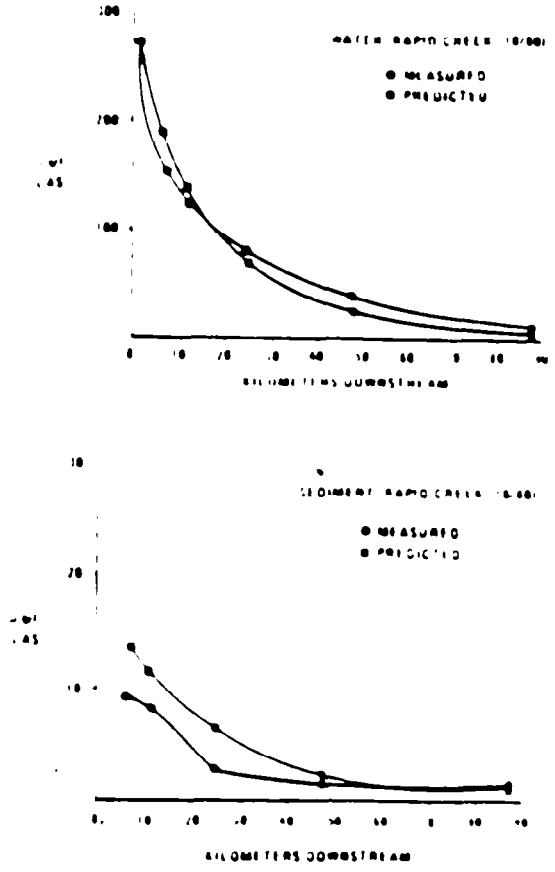


FIGURE 1 FIELD VALIDATION OF EXAMS IN A FLOWING STREAM

Model sensitivity analyses with respect to errors in measurement of creek flow rate, biodegradation rate constants, and adsorption coefficient were also conducted. Results indicated that model calculations are most sensitive to the least understood parameters, that is, the sediment/water exchange coefficient and the sediment biodegradation rate constant. However, this phenomena may be inherent in chemical and aquatic systems and may not be a problem unique to EXAMS.

In other applications, EXAMS has been successfully used to model volatilization of organics in specific field situations, and for a general assessment of the behavior of phthalate esters in aquatic systems. EXAMS has been implemented by a number of manufacturing firms for environmental evaluations of newly synthesized materials and has been used in an academic setting for both teaching and research.

Resource Requirements

EXAMS is available from the EPA Athens Environmental Research Laboratory in either a batch or an interactive version. The batch version requires 64K bytes (overlaid) of memory (for aquatic systems of up to 17 segments); this version does not require mass storage capabilities. The interactive version also requires 64K bytes (overlaid) of memory, plus an additional mass storage capability. The interactive version of EXAMS requires 100K bytes of mass storage for utility files, 2K bytes for each chemical in the active files, and 2.5K bytes for each active defined environment. An overlay capability is

required to implement EXAMS on small computers such as PDP-11 or HP 3000 systems. Execution times range from a few seconds to several minutes depending on the problem to be solved. The software is distributed on magnetic tape; the source code consists of about 16,000 card images.

It has been estimated that approximately one to two man-months of effort are required to setup the model (not including the effort required to evaluate the results). This estimate is based on the following assumptions: (1) all data necessary to meet the input requirements of the model are available and (2) qualified personnel are available to implement the model.

User Support Activities

Free copies of the user's manual and system documentation are available from ORD Publications, Center for Environmental Research Information, USEPA, Cincinnati, Ohio 45268 (Telephone: 513/684-7562; ask for publication No EPA-600/3-82-023). The computer tape of the program (provided for the requestor to copy and return) is available from Center for Water Quality Modeling, Environmental Research Laboratory, USEPA, College Station Road, Athens, Georgia 30613 (Telephone: 404/546-3123).

User assistance can be obtained by contacting:

Lawrence A. Burns
Environmental Systems Branch
U.S. Environmental Protection Agency
Environmental Research Laboratory
College Station Road
Athens, Georgia 30613
FTS 250-3123 COM 404/546-3123

David M. Cline
Automatic Data Processing
U.S. Environmental Protection Agency
Environmental Research Laboratory
College Station Road
Athens, Georgia 30613
FTS 250-3123 COM 404/546-3123

General References

Burns LA, Cline DM, Lassiter RR. 1982. Exposure analysis modeling system (EXAMS) user manual and system documentation. U.S. Environmental Protection Agency, Athens, Georgia. Publication No. EPA-600/3-82-023.

Games L M. 1982. Field validation of exposure analysis modeling system (EXAMS) in a flowing stream. In: Modeling the fate of chemicals in the aquatic environment. Dickson KL, Make AW, and Cairns J, Jr, eds. Ann Arbor Science Publishers.

Metals Exposure Analysis Modeling System (MEXAMS)

Capsule Summary: MEXAMS
• *Steady-state, 3-dimensional, compartment model.* • *Calculates speciation, and dissolved, adsorbed and precipitated metal concentrations.* • *Equilibrium constants and ancillary data available for a several metals in the models data base.*

Summary

The Metals Exposure Analysis Modeling System (MEXAMS) (Felmy et al. 1982) is a synthesis of two existing computer models that accounts for the chemical and physical processes affecting the fate and transport of metals in aquatic systems. This is accomplished by linking the geochemical model, MINTEQ, with the Exposure Analysis Modeling System (EXAMS) (Burns et al. 1982), an aquatic exposure assessment model. Combined, these models provide the capability to (1) estimate the quantities of metal likely to be in solution and (2) consider the effect of chemical speciation on adsorption or precipitation of metals, both of which can act to reduce the amount of metal in solution.

The chemical interactions are handled by MINTEQ, using thermodynamic equilibrium relationships and water quality data to calculate speciation, ar dissolved, adsorbed, and precipitated metal concentrations.

Speciation is calculated using an equilibrium constant approach wherein a series of mass action expressions are solved subject to mass balance constraints on each chemical component. An estimate of aqueous speciation is necessary to predict the quantity of metal that will be taken out of solution by precipitation and adsorption, and to evaluate environmental impacts. In the case of the latter, toxicity and bioavailability of individual metal species can vary by several orders of magnitude; therefore, estimates of metal speciation are required to predict aquatic impacts.

Adsorption is treated as being analogous to aqueous speciation. Therefore, mass action expressions can be formulated for adsorption reactions. MINTEQ contains six algorithms for calculating adsorption. It computes the mass of metal transferred into or out of solution as a result of the dissolution or precipitation of solid phases.

The migration and fate of the metal are handled by the aquatic exposure assessment model EXAMS, a steady-state transport model developed primarily for use with organic compounds (see EXAMS).

The coupling of MINTEQ and EXAMS was accomplished in such a way as to (1) retain all of the original EXAMS options and capabilities and (2) bypass unnecessary calculations or calculations either not applicable to metals or duplicated by MINTEQ. For instance, there is no need for EXAMS to compute adsorption since MINTEQ will provide the quantity of metal sorbed to sediments and biota. Another example is chemical degradation which is applicable to organics but not to metals. Through the proper specification of EXAMS inputs, most of these calculations can be bypassed. Thus, the user will not be required to maintain two versions of EXAMS, one for organics and one for metals.

MEXAMS was designed primarily to be used in performing screening level assessments using generally available water quality data. It can also be used to interpret data collected during bioassays and as a framework for guiding research related to the aquatic impacts of pollutant metals

The model is user oriented in that it contains an interactive program that assists the user in preparing data for input to MINTEQ and EXAMS.

At present, the model's data base contains data necessary for the evaluation of the following metals: arsenic, cadmium, copper, lead, nickel, silver, and zinc.

Input Data Requirements

MEXAMS requires input data for both the MINTEQ and EXAMS components of the model. The reader is directed to the EXAMS review in this catalogue for a discussion and list of EXAM's input requirements. MINTEQ requires two types of data: (1) thermodynamic data and (2) water quality data. The thermodynamic data are equilibrium constants, heats of reaction, and other information required to predict the formation of each species or solid phase. The water quality data are physical and chemical properties of the water body being analyzed (e.g., pH, pOH, temperature).

The user need only to generate the water quality data in order to implement MINTEQ. The thermodynamic data (for the specific metals currently handled by the model) are contained in a data base that accompanies the model.

Output Descriptions

The model output is divided between the EXAMS and MINTEQ components. EXAMS provides tabulations presenting estimates of the exposure, fate, and persistence of the metal. The MINTEQ outputs give details on the chemical interactions occurring in each compartment of the simulated aquatic system.

Advantages and Limitations

MEXAMS represents an improvement in metals modeling in that it accounts for the complex chemistry affecting the behavior of metals as well as the transport processes that affect their migration and fate. Specifically, MEXAMS considers the effect of chemical speciation on adsorption or precipitation of metals.

The modeling system is user oriented. It contains an interactive program that helps the user prepare water quality data for input to MINTEQ. It also queries the user to obtain user run information which is then used to control the operation of MINTEQ and EXAMS and the transfer of simulation results between the models.

The thermodynamic data base associated with MINTEQ contains equilibrium constants and ancillary data for only a limited number of pollutant metals (i.e., As, Cd, Cu, Pb, Ni, Ag, and Zu).

Organic complexation can have a significant impact on the speciation of metals. Although MINTEQ is capable of handling organic complexation, the thermodynamic data base does not contain the necessary equilibrium constants and ancillary data to evaluate this phenomena.

MINTEQ considers precipitation/dissolution, oxidation/reduction, and adsorption as equilibrium processes when in fact they may not be in equilibrium.

EXAMS does not describe vertical changes in pH, and oxidation-reduction reactions in the bed sediment. The latter can be very significant in simulating the fate of metals in lakes and polluted rivers.

The MEXAMS methodology is currently under development and has not been applied in the field.

Model Applications

Although MINTEQ and EXAMS have been applied independently, as they are currently linked in the MEXAMS program, they have not been applied in an environmental analysis.

Resource Requirements

MEXAMS will require a system with 32K memory. An overlay capability is required to implement MEXAMS on small computers such as a PDP 11/70 or HP3000 system.

User Support Activities:

Copies of the user manual and system documentation will be available sometime during the summer of 1983. At that time, it is anticipated that user support will be provided by the Center for Water Quality Modeling, ERL, USEPA, Athens, Georgia.

Additional information concerning the model can be obtained by contacting.

Yasuo Onishi
Battelle, Pacific Northwest Laboratories
Richland, Washington 99352

General References

Felmy AR, Brown SM, Onishi Y, Argo RS, Yabusaki SB. 1982. MEXAMS - The metals exposure analyses modeling system. Battelle, Pacific Northwest Laboratories, Richland, Washington. Contract No. 68-03-3089.

Burns LA, Cline DM, Lassiter RR. 1982. Exposure analyses modeling system (EXAMS): user manual and system documentation. U.S. Environmental Protection Agency, Athens, Georgia. Publication No. EPA-600/3-82-023.

Time-Variable Models

Estuary and Stream Quality Model (WASTOX)

Summary

WASTOX (Connolly 1982) was designed as a time-variable compartment model for simulating the transport and transformation of organic chemicals in the water column and the sediment of streams and estuaries; although the model is generally applicable to all types of water bodies.

Capsule Summary: WASTOX
▪ *Time-variable 3-dimensional compartment.*
▪ *Streams and estuaries, fresh and saline water*
▪ *Comprehensive second-order kinetics.*

WASTOX belongs to the WASP model (DiToro et al. 1981) family and therefore has capabilities and features similar to TOXIWASP (Ambrose et al. 1983). The major differences between WASTOX and TOXIWASP are: (1) WASTOX can account for three sediment size fractions; TOXIWASP accounts for one. (2) WASTOX sediment partition coefficients are expressed as a function of the solids concentration; TOXIWASP assumes a constant partitioning coefficient. (3) WASTOX assumes certain system properties being constant spatially; TOXIWASP accounts for a spatial distribution. (4) WASTOX employs a finite difference scheme for its mathematics; TOXIWASP employs the EXAMS compartment approach. (5) WASTOX does not separately account for pollutant oxidation, as TOXIWASP does. (6) In WASTOX, pollutant on sediment is transported via an advective sediment process; in TOXIWASP it is transported via the above process and an exchange (diffusive) process not requiring bedload (sedimentation) exchange between the water column and the sediment. (7) WASTOX has been mainly designed for 1- or 2-dimensional configurations of streams and tidal estuaries, and the kinetics of volatilization are oriented towards flowing systems. (8) An aquatic food chain routine is to be incorporated into the model.

WASTOX is a water/sediment quality program only, and as such, it requires the water body and sedimentation dynamics (e.g., flow, velocity, bed sedimentation velocity) as user inputs (see discussion in TOXIWASP model). WASTOX can be applied to time-variable simulations. Chemical kinetics are treated similarly to the EXAMS approach.

Input Data Requirements

Input requirements for WASTOX include:

- o Exchange coefficients and fields between segments (such as dispersion).

- Segment volumes and flows including time of flow duration, and velocities in compartments.

- Environmental and pollutant parameters such as geometry of the system, sedimentation transport/dynamics parameters, pH, temperature, concentration of compound degrading bacteria in water, second order biodegradation constants for dissolved and adsorbed toxicant, first- and second-order alkaline hydrolysis ratio, other first-order decay rates, Henry's constant, molecular weight of toxicants, temperature correcting parameters, solids dependent partitioning coefficients.

- Initial conditions, boundary conditions, and waste loads.

Output Descriptions

A finalized output format does not exist, since WASTOX is at a developmental stage. The output is expected to be similar to the WASP output, consisting of a listing of input data, and tabulations giving transport, fate, and persistence of the chemical in all water and sediment compartments of the water body.

Advantages and Limitations

The major advantages of WASTOX are its multi-dimensional capabilities which allow application to a variety of water bodies; capability to simulate time-variable loads and response; relatively sophisticated kinetics; and the capability to simulate the important features of sediment transport.

The technical limitations of WASTOX are similar to those of TOXIWASP. WASTOX has not been applied or validated yet and has not been formally released by the EPA. This may not be a limitation to model use, since the theory of WASTOX is conceptually sound and model predictions can be expected to be within certain limits. WASTOX, similar to most of the models described in this catalogue, requires detailed inputs regarding sediment transport characteristics of the water body. These requirements are difficult to meet from routinely available data.

Resource Requirements

WASTOX is available in a batch/tape version, is written in FORTRAN IV, and uses up to a 32K-byte user area on a PDP 11/70 machine. Execution times range from a few seconds to several minutes depending on the temporal and spatial resolution of the environment analyzed. At this stage, it is estimated that one to two man months of effort are required to have an operational model with a rough understanding of its overall behavior or performance.

User Support Activities

To obtain the WASTOX documentation along with sample data sets and support software, write or contact:

Dr. Parmely H. Prichard
Environmental Research Laboratory
Gulf Breeze, Florida 32561
(904) 932-5311

Dr. John P. Connolly
Environmental Engineering and Science
Manhattan College
Bronx, NY 10471
(212) 920-0276

General References

Ambrose R, Hill S, Mulkey L. 1983. User's manual for the chemical transport and fate model TOXIWASP, Version I. Draft document, U.S. EPA, Office of Research and Development. Athens Research Laboratory, Athens, Georgia.

Connolly TP. 1982. Preliminary estuary and stream version documentation of WASTOX. EPA Cooperative Agreement No. R807 827-02. EPA, Gulf Breeze, Florida. Manhattan College, Bronx, New York.

DiToro DM, Fitzpatrick JJ, Thomann RV. 1982. Water quality analysis simulation program (WASP) and model verification program (MVP) - documentation. Hydroscience, Inc., Westwood, NY. For U.S. Environmental Protection Agency. Duluth, MN, Contract No. 68-01-3872.

Chemical Transport and Fate Model (TOXIWASP)

Summary

The Toxics Water Analysis Simulation Program (TOXIWASP) (Ambrose et al. 1983) was designed as a time-variable compartment model for simulating the transport and transformation of organic toxic chemicals in the water column and the sediment of stratified lakes and reservoirs, large rivers, estuaries, and coastal waters.

Capsule Summary: TOXIWASP
• *Time-variable, 3-dimensional compartment model.* • *Rivers, lakes, estuaries* • *Comprehensive second-order kinetics.*

TOXIWASP was created by first adapting the kinetic structure of the EXAMS model (Burns et al. 1982) to the transport framework provided by the WASP program (DiToro et al. 1981), and by then adding simple sediment balance algorithms along with special input and output software.

Since TOXIWASP uses the compartment modeling approach, whereby segments can be arranged in a 0-, 1-, 2-, or 3-dimensional configuration. TOXIWASP is a water/sediment quality program only, and as such, it requires the water body and the sedimentation dynamics (e.g., flow, velocity, bed sediment velocity) as user inputs. TOXIWASP can be employed for analyses requiring more dynamic transport and loading capabilities than EXAMS, but less detailed and mechanistic sediment predictions than SERATRA (Onishi and Wise 1982).

The kinetic pollutant components of TOXIWASP were modified from EXAMS. EXAMS formulates a total transformation rate from the chemical characteristics of a compound and the environmental parameters of the system. In TOXIWASP and EXAMS this rate is based on a simple addition of the rate constant of each process, and the kinetic time derivative is calculated from this rate, yielding a time varying chemical concentration for a user-specified spatial network. EXAMS uses a kinetic structure that allows the study of five different ionic forms of a chemical, several ways to calculate photolysis, and other capabilities. In TOXIWASP, all those features have been aggregated in one formulation, but with an expanded library of kinetic subroutines. In that respect, TOXIWASP allows simulations of toxic organic chemical behavior in the aquatic environment resulting from loading pulses that cannot be modeled via steady-state codes.

Regarding the chemical transport and fate processes considered, TOXIWASP can account for volatilization, photolysis, hydrolysis, oxidation, biolysis, sorption on both sediment and biomass, advection, and diffusion. Sorption on sediments and biomass is calculated assuming local equilibrium using a constant partition coefficient and spatially varying environmental organic carbon fractions. For each compartment, one differential equation for the pollutant dissolved phase and one differential equation for the adsorbed phase are formulated and solved. As contrasted to WASTOX (Connolly 1982), the effective first-order decay rate can vary with time.

Exchange between the water column and the bed can occur by settling or resuspension of particulates, diffusion (of dissolved pollutant) between the water column and the pore water, by direct adsorption/desorption between the water column and the bed surface, and by percolation or infiltration. Within the bed, the pollutant can move vertically by diffusion, turnover (dispersion), percolation, and burial. Also within the bed, the pollutant cannot move horizontally (i.e., no bed load), in contrast with WASTOX.

Input Data Requirements

Input requirements for TOXIWASP include:

- Exchange coefficients between compartments such as dispersion between segments, water column and sediment, sediment and water in bed material.
- Segment volumes and flows.
- Boundary conditions.
- Environmental and pollutant characteristics such as number of constituents, temperature, cloudiness, bacterial population, biomass, hydroxide ion activity, molar concentration of oxidants, organic carbon, pH, decay coefficients, Arrhenius constants, second-order rate constants for biolysis in the benthic environment, octanol water partition coefficient, Henry's law constant, vapor pressure, and solubility.

Output Descriptions

Model output consists of a listing of input data and tabulations giving transport, fate, and persistence of the chemical in all water and sediment compartments of the water body.

Chemical Transport and Fate Model (TOXIWASP)

Summary

The Toxics Water Analysis Simulation Program (TOXIWASP) (Ambrose et al. 1983) was designed as a time-variable compartment model for simulating the transport and transformation of organic toxic chemicals in the water column and the sediment of stratified lakes and reservoirs, large rivers, estuaries, and coastal waters.

Capsule Summary: TOXIWASP
▪ *Time-variable, 3-dimensional compartment model*
▪ *Rivers, lakes, estuaries*
▪ *Comprehensive second-order kinetics.*

TOXIWASP was created by first adapting the kinetic structure of the EXAMS model (Burns et al. 1982) to the transport framework provided by the WASP program (DiToro et al. 1981), and by then adding simple sediment balance algorithms along with special input and output software.

Since TOXIWASP uses the compartment modeling approach, whereby segments can be arranged in a 0-, 1-, 2-, or 3-dimensional configuration, TOXIWASP is a water/sediment quality program only, and as such, it requires the water body and the sedimentation dynamics (e.g., flow, velocity, bed sediment velocity) as user inputs. TOXIWASP can be employed for analyses requiring more dynamic transport and loading capabilities than EXAMS, but less detailed and mechanistic sediment predictions than SERATRA (Onishi and Wise 1982).

The kinetic pollutant components of TOXIWASP were modified from EXAMS. EXAMS formulates a total transformation rate from the chemical characteristics of a compound and the environmental parameters of the system. In TOXIWASP and EXAMS this rate is based on a simple addition of the rate constant of each process, and the kinetic time derivative is calculated from this rate, yielding a time varying chemical concentration for a user-specified spatial network. EXAMS uses a kinetic structure that allows the study of five different ionic forms of a chemical, several ways to calculate photolysis, and other capabilities. In TOXIWASP, all those features have been aggregated in one formulation, but with an expanded library of kinetic subroutines. In that respect, TOXIWASP allows simulations of toxic organic chemical behavior in the aquatic environment resulting from loading pulses that cannot be modeled via steady-state code..

Regarding the chemical transport and fate processes considered, TOXIWASP can account for volatilization, photolysis, hydrolysis, oxidation, biolysis, sorption on both sediment and biomass, advection, and diffusion. Sorption on sediments and biomass is calculated assuming local equilibrium using a constant partition coefficient and spatially varying environmental organic carbon fractions. For each compartment, one differential equation for the pollutant dissolved phase and one differential equation for the adsorbed phase are formulated and solved. As contrasted to WASTOX (Connolly 1982), the effective first-order decay rate can vary with time.

Exchange between the water column and the bed can occur by settling or resuspension of particulates, diffusion (of dissolved pollutant) between the water column and the pore water, by direct adsorption/desorption between the water column and the bed surface, and by percolation or infiltration. Within the bed, the pollutant can move vertically by diffusion, turnover (dispersion), percolation, and burial. Also within the bed, the pollutant cannot move horizontally (i.e., no bed load), in contrast with WASTOX.

Input Data Requirements

Input requirements for TOXIWASP include:

- Exchange coefficients between compartments (such as dispersion between segments, water column and sediment, sediment and water in bed material.
- Segment volumes and flows.
- Boundary conditions.
- Environmental and pollutant characteristics such as number of constituents, temperature, cloudiness, bacterial population, biomass, hydroxide ion activity, molar concentration of oxidants, organic carbon, pH, decay coefficients, Arrhenius constants, second-order rate constants for biolysis in the benthic environment, octanol water partition coefficient, Henry's law constant, vapor pressure, and solubility.

Output Descriptions

Model output consists of a listing of input data and tabulations giving transport, fate, and persistence of the chemical in all water and sediment compartments of the water body.

Advantages and Limitations

TOXIWASP is designed for multi-dimensional, time-variable analyses, using sophisticated organic chemical decay kinetics. It does not incorporate a hydrodynamic simulation model; the user must input flows between compartments. Adsorption/desorption is instantaneous.

TOXIWASP is in a developmental stage and as such has not been applied or validated yet. This may not be an inherent limitation, since the basic science of the model originates from the EXAMS and the WASP packages for which some application experience exists.

TOXIWASP does not account for corrective bed load sediment transport between compartments.

Similar to most other models reviewed in this catalogue TOXIWASP input requirements are not easily met by routinely available data

Model Applications

TOXIWASP has not been applied to a real situation; however, the EXAMS model has been applied in numerous situations (see EXAMS description, and the WASP program, available since 1970, has been applied in more than 30 environments (DiToro et al. 1981).

Resource Requirements

TOXIWASP is not an interactive modeling package; rather, it is a standard software package in FORTRAN, operational via a standard CRT unit or a card deck. TOXIWASP requires an IBM 370 (OS/MVS Operating System), or a PDP 11/70 (IAS Operating System), programmed in FORTRAN IV+ or FORTRAN IV. The first version can accommodate 100 compartments, the second 50 compartments. The PDP 11/70 computer utilizes an IAS operating system and allocates a 32K word (64K byte) user area for execution of a program. TOXIWASP occupies at least 32K words of memory in either machine. Execution times range from a few seconds to several minutes, depending on the temporal and spatial resolution of the environment analyzed and the machine used. At this stage, it is estimated that one to two man-months of effort are required to have an operational model, with a rough understanding of its overall behavior/performance.

User Support Activities

TOXIWASP is available from the EPA Athens Environmental Research Laboratory in a batch/tape version. To obtain the TOXIWASP documentation along with sample data sets and support software, write or contact:

Mr. Robert Ambrose
Center for Water Quality Modeling
Environmental Research Laboratory
U.S. EPA, College Station Road
Athens, Georgia 30613
(404) 546-3546

General References

Ambrose R, Hill S, Mulkey L. 1983. User's manual for the chemical transport and fate model TOXIWASP, Version I. Draft document, U.S. EPA, Office of Research and Development. Athens Research Laboratory, Athens, Georgia.

Bonazountas M, Fiksel J, eds. 1982. Arthur D. Little, Inc. ENVIRO: Environmental mathematical modeling handbook/catalogue. Washington, D.C.: Office of Policy of Resource Management, U.S. Environmental Protection Agency.

Burns LA, Cline DM, Lassiter RR. 1982. Exposure analysis modeling system (EXAMS), user manual and system documentation. Athens, Georgia: U.S. Environmental Protection Agency.

Connolly TP. 1982. Preliminary estuary and stream version documentation of WASTOX. EPA Cooperative Agreement No. R807 827-02. EPA Gulf Breeze, Florida, Manhattan College, Bronx, New York.

DiToro DM, Fitzpatrick JJ, Thomann RV. 1981. Hydroscience, Inc. Water quality analysis simulation program (WASP) and model verification program (MVP) - documentation. Duluth, MN: U.S. Environmental Protection Agency. Contract No. 68-01-3872.

Onishi Y, Wise SE. 1982. User's manual for the instream sediment contaminant transport model, SERATRA. Athens, Georgia: U.S. Environmental Protection Agency. EPA-600/3-82-005 (in press).

Toxic Organic Substance Transport and Bioaccumulation Model (TOXIC)

Summary

The Toxic Organic Substance Transport and Bioaccumulation Model (TOXIC) (Schnoor and McAvoy 1981) is a quasi-dynamic water quality model designed to simulate the behavior of pesticides in a reservoir and bio-concentration of pesticides in aquatic life.

Capsule Summary: TOXIC
• *Quasi-dynamic, 3-dimensional compartment model*
• *Designed for reservoir and impoundment aquatic systems*
• *First-order kinetics with biological degradation and biouptake and depuration*

The quasi-dynamic approach utilitizes: (1) steady, annual average flow (from daily averages) for long-term simulations, (2) steady, annual average flow-weighted solids (from daily suspended solids measurements) and (3) time-variable toxicant loadings

TOXIC includes a routine which calculates a mass balance on sediments and the adsorbed chemical. Sediment deposition and scour are included, as is diffusion of toxics from sediment pore water to the overlying water. The model also computes contaminant uptake and depuration by fish.

TOXIC considers the aquatic system being simulated as being divided into a number of compartments (in one application of the model up to 100 compartments have been utilized). Each compartment is considered to be a completely mixed system.

The concentration of the contaminant through time is described by a set of ordinary differential equations, one for each compartment. The basic equation is written to include the sum of the first-order or pseudo-first order reactions (hydrolysis, biological degradation, biological uptake, photolysis, and volatilization) as well as adsorption and desorption kinetics as a function of particle size distribution. The coupled equations are then solved via a variable step size fourth order Runge-Kutta numerical technique.

Input Data Requirements

The inputs to the model can be classified under the following categories:

- Geometric properties, such as volumes of compartments, distances between them, surface areas, and locations with respect to other compartments.

- Flows between compartments and between each compartment and the outside of the system.
- Reaction rates, settling rate constants, and partition coefficients
- Solids concentrations in each compartment.
- Bulk dispersion coefficients between compartments.
- Simulation parameters such as step size and time of simulation.

Output Descriptions

Output from TOXIC includes:

- Solids balance description listing the concentration of the solids in the water column and in the sediment, and the net flux between the sediment and the water column over time
- Dissolved, particulate, and total concentration of the contaminant over time within each compartment.
- Description of the inflow and outflow volumes associated with each compartment.

Advantages and Limitations

TOXIC is intermediate between fully time-variable models (e.g., HSPF) and steady-state models (e.g., EXAMS). Flows and sediment loads are steady-state, while toxicant loading values are time-variable. It was designed as a pesticide transport model to be applied to reservoirs and impoundments. In addition to chemical reaction pathways, fish uptake and depuration (excretion and metabolism) are included in the model. Previous models have not combined fate and transport modeling with the biological effect (bioconcentration).

TOXIC includes a routine which calculates a mass balance on contaminant-sorbed and unsorbed sediments. Sediment deposition and scour are also included, as is the diffusion of toxics from sediment pore water to the overlying water.

Coefficients and rate constants must be supplied by the user thus requiring a working knowledge of kinetic processes, sediment transport mechanisms, and the ability to adjust the model's computer code.

The model's simulation capabilities was designed to be applied to reservoir or impoundment aquatic ecosystems and may therefore be unattractive for use in situations where multiple aquatic systems (e.g., rivers, streams, and impoundments) exist.

User support for the model is rather limited. A user's manual is unavailable at this time and the model is not currently supported by the Center for Water Quality Modeling, ERL, USEPA, Athens, Georgia.

Model Application

TOXIC has been applied to Iowa reservoir data to simulate the behavior of the insecticide dieldrin and the herbicides alachlor and atrazine. Steady-state analyses and quasi-dynamic simulations with time-variable flows and loadings were undertaken.

Laboratory measurements for alachlor were used in the model simulations with good agreement between model predictions and measured concentration. Laboratory measurements were also used in the atrazine and dieldrin simulations with the results well within an order of magnitude of field data.

Resource Requirements

The computer code for TOXIC is written in FORTRAN. TOXIC can be implemented in a batch mode on a IBM 370 or a TSO Prime system. No system overlay capabilities are required.

User Support Activities

The user's manual for the TOXIC methodology is not currently available, nor is its availability planned for the near future. However, copies of the model code (computer tape) and technical assistance on applying the model may be obtained by contacting:

J. L. Schnoor
Civil and Environmental Engineering
Energy Engineering Division
University of Iowa
Iowa City, Iowa 52248
(319) 353-7262

General References

Schnoor JL, McAvoy DC. 1981. A pesiticide transport and bioconcentration model. Journal Environmental Engineering Division. ASCE, Volume 17, No. EE5

Schnoor JL. 1981. Fate and transport of dieldrin in Coralville Reservoir: Residues in fish and water following a pesticide ban. Science, 211, pp. 840-842.

Schnoor JL. 1982. Field validation of water quality criteria for hydrophobic pollutants. In: Proceedings of the 5th symposium, Aquatic Toxicity, ASTM.

Schnoor JS. 1982. Fate and transport modeling for toxic substances. In: Modeling the fate of chemicals in the aquatic environment. Pellston Conference Proceedings, Ann Arbor Science Publishers.

Schnoor JL, et al. 1983. Verification of a toxic substance transport and bioaccumulation model. EPA 600/3-83-007. Environmental Research Laboratory, Athens, GA. 30613.

Channel Transport Model (CHNTRN)

Capsule Summary: CHNTRN
• *Time-varying, 1-dimensional compartment model.*
• *Models rivers, lakes, estuaries, coastal waters.*
• *Comprehensive second-order kinetics for organics.*
• *Complex and data intensive*

Summary

The Channel Transport Model (CHNTRN) (Yeh 1982) was developed by the Environmental Science Division of the Oak Ridge National Laboratory, Oak Ridge, Tennessee, for the EPA's Office of Pesticides and Toxic Substances. The purpose of CHNTRN is to simulate time varying distributions of sediments and chemicals in receiving waters. CHNTRN can model the transport and fate of a pollutant in a wide variety of aquatic systems, that include: tidal and non-tidal rivers, lakes, and reservoirs, streams, estuaries, and coastal seas. A particular feature of CHNTRN is its capability to deal with a network system that may consist of any number of joined and branched streams/rivers of comparable size. CHNTRN, combined with the Channel Hydrodynamic Model (CHNHYD) (Yeh 1982) which models the hydrodynamic computations of flows and water depths, constitutes a software package for predicting the transport, transfer, and transformations of organic pollutants in a stream/river system.

CHNTRN can model complex problem settings that can be approximated with 1-dimensional segments. Modification of the model to treat 2- and 3-dimensional problems is relatively easy because of the integrated compartment approach. The spatial scale of segments can vary from meters to kilometers, and the temporal scale can vary from seconds to hours.

CHNTRN uses the chemical kinetics of EXAMS (Exposure Analysis Modeling System) to account for hydrolysis, oxidation, photolysis, volatilization, biodegradation, and adsorption by biota. Consequently, other physico-chemical factors (e.g., temperature, DO, pH) are also required. Sediment transport, deposition, and scouring are simulated for three particle types, sand, silt, and clay. Provisions for adsorption/ desorption and pollutant accumulation in the bed sediment are included.

The model code is in basic FORTRAN language. It consists of a main program and 15 subroutines. The equations that govern the system's kinetics are derived from 3-dimensional mass balance equations. An integrated compartment method (Yeh 1981) is used to solve the differential equations. In this method, the link matrices are derived based on the fluxes of mass along each of the links that interline the compartments of the river system. The global matrix associated with spatial derivatives is assembled from these link matrices.

The result is a system of ordinary differential equations with respect to time that govern the dynamic evolution of suspended sediment, bed sediment, dissolved chemical concentration, particulate chemical concentration, and bed sediment chemical concentration. Chemical concentrations for both the wat column and bed sediment are solved by the time split scheme. Two options fo solution are provided; one is the explicit scheme for fast computation; the second is the implicit scheme which generates stable solutions for large time steps.

CHNTRN user manual and documentation are currently in draft form and it has yet to be field verified.

Input Data Requirements

CHNTRN is a sophisticated model requiring extensive data input. Before CHNTRN can be executed, hydrodynamic variables such as flow rates, water depth, cross-sectional area, width, and wet perimeter must be obtained from actual data if available; if not available, this information can be estimated using CHNHYD. Other data input includes:

- Environmental parameters - air temperature, solar radiation, wind speed, vapor pressure, water temperature, extinction coefficient, pH, pOH, oxidation radicals.
- Biological information - bacterial population density, biotemperature for activation energy, and the bacterial portion involved in degradation.
- Coefficients for photolysis, hydrolysis, oxidation, biodegradation
- Sediment types and distributions.
- Transport information - solids in water column and sediment, sedimentation and resuspension velocities, partition coefficients, dispersive coefficients between phases, and volatilization rates.
- System geometry - areas, depths, volume.
- Sources and amounts of pollutant.

Output Descriptions

CHNTRN calculates and presents the following for individual compartments in tabular form:

- Dissolved chemical concentration in the water column as a function of distance from the source.
- Particulate concentration in suspended and bed sediment.
- Suspended sediment concentration and amount of bed sediment remaining in a unit bed association.

Advantages and Limitations

The major advantage of CHNTRN is its capacity to simulate time-varying distributions in all types of water bodies. CHNTRN accounts for both advective and dispersive flows and the total flux of an aquatic system. The chemical kinetics are the second-order rate expressions of EXAMS.

CHNTRN is a complex model and as such is very data intensive. Considerable time might be needed for the acquisition of data not readily available. Computations for complex systems will also require large amounts of time for solution, as will the simulation execution time.

If hydrodynamic information is not available, it can be estimated by first using CHNHYD and then supplying the results to CHNTRN. Although CHNTRN would not be defined as "user-friendly", it does make provisions to allow the user to make some modifications.

CHNTRN has yet to be field validated.

Model Applications

CHNTRN has been applied to two river network sample problems for demonstration purposes. The first sample is a single river system, and the second is a network of five rivers. Typical data were used for the simulations. In each example, the rivers are divided up into compartments.

The first scenario produced seemingly unrealistic results. Closer analysis of the input data revealed it to be erroneous and illustrated the "garbage in, garbage out" results. The second scenario showed reasona results for clay, silt, sand, dissolved chemical, clay-adsorbed chemic silt-adsorbed chemical, and sand-adsorbed chemical concentrations. Because no analytical solutions were available, it is not possible to assess the accuracy of the results by comparing them with analytical results. However, the results intuitively indicate that the model can realistically simulate the behavior of the sediment and chemical variations in a stream/river network.

Resource Requirements

CHNTRN is written in FORTRAN IV and has been implemented on an IBM 3033 computer. Simulation execution time may be extensive.

User Support Activities

Copies of CHNTRN's draft user manual and documentation as well as assistance may be obtained from:

G. T. Yeh
Environmental Sciences Division
Oak Ridge National Laboratory
P.O. Box X
Oak Ridge, TN 33830
(615) 574-7285

References

Yeh GT. 1982. CHNTRN: A channel transport model for simulating sediment and chemical distribution in a stream/river network. Oak Ridge National Laboratory, Oak Ridge, TN. ORNL-5882.

Yeh GT. 1982. CHNHYD: A channel hydrodynamic model for simulating flows and water surface elevations in a stream/river network. Oak Ridge National Laboratory, Oak Ridge, TN. ORNL-5701.

Yeh GT. 1981. ICM: An integrated compartment method for numerically solving partial differential equations. Oak Ridge National Laboratory, Oak Ridge, TN. ORNL-5701.

Finite Element Transport Model (FETRA)

Capsule Summary: FETRA
• *Time-varying 2-dimensional (longitudinal, lateral)* • *Complex sediment transport capabilities* • *Comprehensive second-order kinetics for organic decay* • *River, estuary, and coastal systems*

Summary

The Finite Element Transport Model (FETRA) is a time-varying, 2-dimensional (longitudinal and lateral) transport model developed by Battelle Pacific Northwest Laboratories. FETRA utilizes a finite element solution technique and consists of three submodels coupled to simulate the transport of sediments and contaminants in rivers and estuaries through the mechanisms of advection, diffusion/dispersion, adsorption/desorption, and degradation/decay. FETRA can be applied to rivers, estuaries, coastal, and unstratified lake systems.

The sediment transport submodel simulates sediment movement for three sediment size fractions or sediment types. This submodel includes the mechanisms of: (1) advection and dispersion of sediments, (2) fall velocity and cohesiveness, and (3) deposition or erosion from the bed. It also calculates changes in bed conditions, including bed elevation changes due to scouring or deposition, and gives a 3-dimensional distribution of sediment sizes within the bed.

The dissolved contaminant transport submodel simulates the dissolved contaminant interaction with sediments in motion and with stationary bed sediments. The submodel includes the mechanisms of: (1) advection and diffusion/dispersion of dissolved contaminants; (2) adsorption of dissolved contaminants by both moving and stationary sediments or desorption from the sediments into water; and (3) chemical and biological degradation or radionuclide decay of contaminants.

The particulate contaminant transport submodel simulates the transport of sediment-attached contaminants for each sediment size fraction. It includes the mechanisms of: (1) advection and dispersion of particulate contaminants; (2) adsorption/desorption of dissolved contaminants with sediment; (3) chemical and biological degradation or radionuclide decay of contaminants; and (4) deposition of particulate contaminants on the bed or erosion from the bed.

The temporal scale of FETRA is on the order of minutes to hours. Hydrodynamic data are supplied by exterior models such as CAFE-I (ocean currents) and LO3D (wave refractions) for coastal waters applications, and EXPLORE-I (velocities and flow depths) for estuarine and riverine application

EXPLORE-I is a comprehensive mathematical water quality model to be used in river basin planning and water resource studies. This generalized river basin water quality model can predict the hydrodynamics and water quality dynamics for rivers and well mixed estuaries. The EXPLORE-I model is an extended and modified version of the Storm Water Management Model, receiving water component, which was developed for studies of DO/BOD dynamics. The model is capable of simulating a number of hydraulic regimes in either a dynamic or steady-state mode, and it has been set up, calibrated, and verified on a portion of the Willamette River Basin, consisting of major tributaries. EXPLORE-I was developed by Battelle-Northwest Laboratories for the EPA.

Input Data Requirements

The input data requirements for FETRA are quite extensive. The three submodel data requirements include:

- Common data requirements for all the submodels:
  - Channel geometry.
  - Discharges during the simulation period
  - Discharges of tributaries, overland runoff, and other point and non-point sources.
  - Lateral and longitudinal dispersion coefficients.
- Additional Requirements for sediment transport submodel:
  - Sediment size fraction.
  - Sediment density and fall velocities for sand, silt, and clay.
  - Critical shear stresses for erosion and deposition of cohesive sediment (silt and clay).
  - Erodibility coefficient of cohesive sediment.

- Sediment concentration for each sediment size fraction.

- Bottom sediment size fraction.

- Sediment concentration at the upstream end of the study reach.

- Contributions of sediments from over land, tributaries, and other point and non-point sources.

- Additional requirements for the dissolved contaminant and particulate contaminant transport submodels:

  - Distribution coefficients and transfer rates of contaminant with sediment in each sediment size fraction (i.e., sand, silt, and clay). If values of distribution coefficients are not available, it is necessary to know clay mineral and organic sediment content to estimate these values.

  - Second-order decay rates of contaminants

  - Boundary conditions.

  - Contributions of dissolved and particulate contaminant concentrations from tributaries, overland, and other point and non-point sources.

Output Descriptions

With the input data described above, FETRA simulates the following:

- Sediment simulation and longitudinal/lateral distributions of total sediment and size fractions and changes in bed elevation.

- Contaminant simulation and longitudinal/lateral distributions of dissolved contaminants, contaminants adsorbed by sediment and in the bottom sediment for each sediment size.

Advantages and Limitations

FETRA is designed for time-variable analyses of 1- or 2-dimensional (horizontal) water bodies. Its sediment transport routines are sophisticated and will predict the resuspension velocities and bed load given the sediment and hydraulic characteristics. The model can be coupled with a hydrodynamic model in order to generate flows and velocities.

Input data requirements for FETRA are extensive, and computational time for long term continuous simulations may be high. Resource requirements for set up and execution are expected to be substantial.

FETRA cannot discern water body stratification.

Model Applications

FETRA has been applied to the James River estuary in Virginia (Onishi 1981) and to the Irish Sea (Onishi et al. 1982). The purpose of the James River application was to simulate sediment movement and the transport of the pesticide Kepone which was discharged to the river in substantial quantities during the early 1970s. The purpose of the Irish Sea application was to evaluate exposure levels of radionuclides, heavy metals, and other toxic chemicals in coastal waters. Results of the Irish Sea application have not yet been published. A discussion of the James River application follows.

Figure 1.

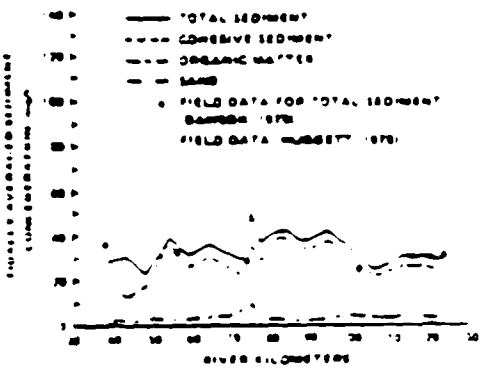
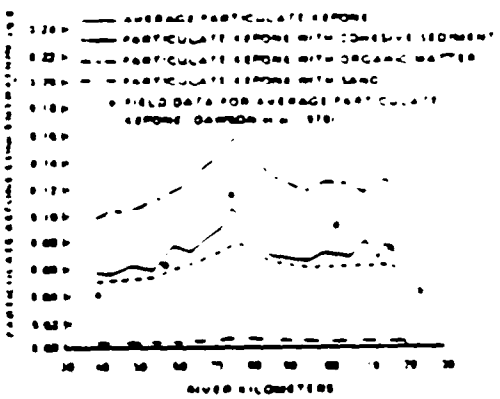


Figure 2.



The James River application was a calibration and verification study of FETRA. Sediment transport was modeled for three sediment types: (1) cohesive (silt and clay); (2) noncohesive (sand); and, (3) organic matter. These results (see Figure 1) were compared to field data which indicated that a considerable amount of particulate Kepone was transported by organic materials moving independently with other sediments. Predicted particulate Kepone concentrations associated with each type of sediment and weighted average particulate Kepone are shown together with measured field data of average particulate Kepone concentrations in Figure 2. The computed results and the field data closely agree in both Figures.

Resource Requirements

The computer program for FETRA is written in FORTRAN IV language. FETRA can be used on IBM, VAX, or CDC-7600 computers. Execution times and run costs vary, depending on the characteristics of the system to be modeled. For the James River application, computer time required to calculate all seven substances per computational mode per time step was 0.0028 cp second on the CDC-7600 computer.

User Support Activities

The user's manual and system documentation are still undergoing review at USEPA and are not yet available for publication. The FETRA model is operational, has been implemented in selected applications, and is available to the public.

Model information can be obtained by contacting:

Yasuo Onishi
Battelle - Pacific Northwest Laboratories
Richland, Washington 99352
FTS 444-8302 COM 509-376-8302

General References

Onishi Y. 1981. Sediment-contaminant transport model. Journal of the Hydraulics Division, ASCE, Vol. 107, No. HY9. Proc. Paper 16505. pp. 1089-1107.

Onishi Y, Mayer DW, Argo, RS. 1982. Sediment and toxic contaminant transport modeling in coastal waters. In: Finite Element Flow Analysis. Proc. Paper pp 733-740.

Onishi Y, et al. 1981. Critical review: Radionuclide Transport, Sediment Transport, and Water Quality Mathematical Modeling; and Radionuclide Adsorption/desorption Mechanisms. Richland, Washington: Pacific Northwest Laboratory, Battelle Memorial Institute. NUREG/CR-1322, PNL 2901.

USEPA. 1982. EPA Environmental Modeling Catalogue. Abstracts of Environmental Models. pp. 363-366.

Sediment-Contaminant Transport Model (SERATRA)

Capsule Summary: SERATRA
• *Time-varying, 2-dimensional (longitudinal, vertical)* • *Complex sediment transport capabilities* • *Comprehensive second-order kinetics* • *River, lake, and impoundment systems*

<u>*Summary*</u>

The Sediment-Contaminant Transport Model (SERATRA) (Onishi and Wise 1982a) is a time-varying 2-dimensional (longitudinal and vertical resolution in the water column and bed) sediment and contaminant transport model developed by Battelle-Pacific Northwest Laboratories. The model predicts distributions of sediments and toxic contaminants in rivers and some impoundments. The model consists of the following three coupled submodels which describe sediment-contaminant interactions and migration: (1) a sediment transport submodel; (2) a dissolved contaminant transport submodel; and (3) a particulate contaminant transport submodel.

The sediment transport submodel simulates transport, deposition, scouring and armouring for three size fractions (or sediment types) of cohesive and noncohesive sediments. The transport of particulate contaminants (i.e., contaminants absorbed by sediment) is also simulated for each sediment size. Dissolved contaminants are linked by the adsorption/desorption process to the sediment and particulate contaminants. The contaminant submodels account for (1) advection and dispersion of dissolved and particulate contaminants; (2) chemical resulting from hydrolysis, oxidation, photolysis, biological activities, and radionuclide decay where applicable; (3) volatilization; (4) adsorption/desorption; and (5) deposition and scouring of particulate contaminants. SERATRA also computes changes in riverbed conditions for sediment and contaminant distributions.

Required input includes channel and sediment characteristics and adsorption/desorption properties of the contaminants. In addition, SERATRA requires discharge and depth distributions which can be obtained by a hydrodynamic model such as EXPLORE-I. EXPLORE applications for use with SERATRA do not require reprogramming; however, some reformatting and recalculation of the input parameters may be required. EXPLORE is discussed in further detail in the FETRA summary.

SERATRA is similar to FETRA in that both consist of the same three coupled submodels; and provide time-varying, 2-dimensional transport simulation using comprehensive second-order decay kinetics. Both provide longitudinal resolution, whereas the other dimension for FETRA is lateral rather than vertical (as in SERATRA).

Input Data Requirements

SERATRA consists of the same three coupled submodels that comprises FETRA and therefore requires identical input data. Refer to the FETRA summary for discussion of SERATRA's input data requirements.

Output Descriptions

SERATRA provides output identical to the FETRA output except that longitudinal and vertical, rather than longitudinal and lateral, distributions and resolution are provided.

Advantages and Limitations

Like FETRA, SERATRA provides the capability of simulating the complex mechanisms involved in contaminant migration by coupling contaminant transport and degradation with sediment transport. SERATRA also handles time-variable analysis of stratified (2-dimensional) water bodies.

Adsorption/desorption mechanisms are expressed by a distribution coefficient and a transfer rate which describes the rate at which dissolved and particulate contaminant concentrations reach their equilibrium condition. Unlike most other models, SERATRA uses different distribution coefficients for adsorption and desorption and treats adsorption/desorption mechanisms as not being fully reversible.

SERATRA requires extensive input data, which may limit its applicability. It also requires rather extensive computer time, in which long-term, continuous simulations can be expensive.

The model cannot be applied to estuary systems because longitudinal diffusion is neglected and lateral sediment concentrations are assumed to be uniform. However, the model does handle vertical variations of longitudinal velocity to cause some longitudinal dispersal of sediment.

SERATRA requires an exterior hydrodynamic model to supply required hydrodynamic data. EXPLORE applications require adjustment of several parameters for use with SERATRA.

Model Applications

SERATRA has been applied under both steady and unsteady flow conditions and has also undergone field applications with calibration and verification data (Onishi et al. 1982). Also, SERATRA has been field tested as an integral component of the Chemical Migration Risk Assessment (CMRA) Methodology (Onishi et al. 1981).

Under steady flow conditions, SERATRA was applied to the Columbia River in Washington and the Clinch River in Tennessee (Onishi et al. 1982). The Columbia River application simulated the transport of sediments, radioactive 65Zn, and a heavy metal. The Clinch River application simulated instantaneous and continuous releases of radioactive 137Cs and 90Sr. Reasonably good agreement between predicted and measured results was obtained in both applications.

Under unsteady flow conditions, SERATRA was applied to two small streams with rapidly changing flows (Onishi et al. 1982). This application simulated migration and fate of a pesticide and stream sediments. No measured field data are available for comparison of the model's predicted results.

The calibration and verification application of SERATRA simulated the transport of sediment and four radionuclides in the Cattaraugus Creek watershed in New York (Onishi et al. 1982). Although there were some discrepancies between predicted and measured values, considering the complexity of the modeling system and field data accuracy, agreement between predicted and measured results were judged to be reasonable.

SERATRA, as part of CMRA, was applied to the Four Mile Creek watershed in Iowa for a three-year field study (Onishi and Wise 1982b). Migration and fate of a herbicide were simulated in this application. Simulation results revealed a strong seasonal pattern of herbicide transport.

Resource Requirements

The computer program for SERATRA is written in FORTRAN preprocessor language, FLECS. A standard FORTRAN IV version of SERATRA is also available. SERATRA can be implemented in a batch mode on VAX or PDP 11/70 computers. Execution time and run costs vary, depending on the characteristics of the system to be modeled. One cost estimate is $0.0088 per time step per segment. As part of the CMRA Methodology, four man-months were estimated to be required for the SERATRA component to be implemented at a cost of approximately $100 to $200 per run per one year simulation (for all four of the CMRA components). This time estimate is based on the following assumptions: (1) all data necessary to meet the input requirements are available; and (2) qualified personnel are available to implement the model.

User Support Activities

Copies of the user's manual are available from ORD Publications, Center for Environmental Research Information, USEPA, Cincinnati, Ohio 45268 (telephone 513/684/7562; ask for publication EPA-600/3-82-055)

User assistance can be obtained by contacting:

Robert Ambrose
USEPA
EPA Athens Environmental Research Laboratory
Center for Water Quality Modeling
Athens, Georgia 30613
(404) 546-3546

Model information can be obtained by contacting:

Yasuo Onishi
Battelle Pacific Northwest Laboratories
P.O. Box 999
Richland, Washington 99352
(509) 376-8302

The SERATRA model is operational, has been implemented in selected applications, and is available to the public.

References

Onishi Y, Wise SE. 1982a. User's Manual for the Instream Sediment-Contaminant Transport Model SERATRA. EPA 600/3-82-055, Environmental Research Laboratory, Office of Research and Development, USEPA, Athens, Georgia.

Onishi Y, Brown SM, Olsen AR, Parkhurst MA. 1981. "Chemical Migration and Risk Assessment Methodology." Proceedings of the Conference on Environmental Engineering, Proc. Paper, pp. 165-172.

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Transient One-Dimensional Degradation and Migration Model (TODAM)

Capsule Summary: TODAM
• *Time-varying, 1-dimensional* • *Complex sediment transport capabilities* • *Comprehensive second-order kinetics* • *River and estuary systems*

Summary

The Transient One-Dimensional Degradation and Migration Model (TODAM) is a time-varying, 1-dimensional (longitudinal) transport model developed by Battelle Pacific Northwest Laboratories in Richland, Washington. TODAM includes the longitudinal dispersion term and can handle river/stream systems estuaries, and dry bed conditions. The model is suitable for many rivers where vertical stratification is not a concern.

TODAM is a modified and simplified version of the 2-dimensional transport model, Sediment Contaminant Transport Model (SERATRA), also developed by Battelle. TODAM is composed of the following three submodels combined to describe sediment-contaminant interaction and migration:

- o Sediment transport
- o Dissolved contaminant transport
- o Sorbed contaminant (contaminants adsorbed by sediment) transport

These submodels solve an advection-diffusion equation using a finite element solution technique with decay and sink/source terms with appropriate initial and boundary conditions.

The sediment transport submodel simulates transport, deposition, and erosion of three sediment size fractions (or sediment types) of cohesive and noncohesive sediments. The dissolved contaminant transport submodel includes mechanisms of contaminant adsorption/desorption, as well as radionuclide decay and contaminant degradation resulting from hydrolysis, oxidation, photolysis, volatilization, and biological activity. The particulate contaminant transport submodel simulates transport, deposition, and erosion of contaminants associated with each sediment size fraction.

TODAM includes the mechanisms of advection and diffusion/dispersion of sorbed contaminants; adsorption (uptake) of dissolved contaminants by

sediments or desorption from sediments; radionuclide decay; deposition of sorbed contaminants to the river bed or resuspension from the river bed; and contributions of sorbed contaminants from point and non-point sources into the system. TODAM also computes changes in river bed conditions, including bed elevation, sediment size distribution, and sorbed contaminant distribution within the bed.

An exterior hydrodynamic model, such as EXPLORE, or the Distributed Kinematic Wave Model for Channel Flows (DKWAV), is required to provide channel flow, cross-sectional area, depth, shear stress, and wetted perimeter for use by TODAM. Reprogramming is not required if either EXPLORE or DKWAV is used. EXPLORE applications require some reformatting and recalculation of input parameters; whereas, DKWAV applications can be directly integrated for use with TODAM.

DKWAV, also developed by Battelle, is an unsteady, 1-dimensional, second-order, explicit, finite-difference model which simulates the hydrodynamics in dendritic river systems to obtain time varying distributions of depth and velocity in a channel. The model, which can be easily combined with overland flow models, routes flows through arbitrarily shaped channels in which the channel reach is divided into sections bounded by points called "nodes". Flow routing is performed from node to node by a marching solution. The equations of motion with the kinematic wave approximation are numerically analyzed via a modified version of the Lax-Wendroff, second-order, finite-difference scheme. Numerical stability is based upon the Courant conditions. Point inflow or continuous (or both) lateral inflow is included in which point inflow occurs at nodes or continuous lateral inflow occurs between nodes. Associated with each channel section is its own seepage velocity. A cross-sectional area versus discharge relationship exists for each segment between nodes. Based on this relationship, other characteristics parameters (flow depth, wetted perimeter, and so forth) of each section can also be obtained. Each channel section retains its own individual characteristics, which include a roughness parameter, lateral or point inflow rates, slope, seepage velocity, and natural cross-sectional shape.

The EXPLORE model is discussed in further detail in the FETRA summary.

Input Data Requirements

The following items are input data requirements of TODAM:

- Channel geometry

- Flow characteristics
  - Depth and velocity distributions
- Sediment characteristics
  - Sediment size distribution
  - Density
  - Critical shear stresses and erodibility coefficient for cohesive sediment
- Contaminant characteristics
  - Distribution coefficients
  - Transfer rates
  - Decay and degradation rates or associated parameters
  - Initial conditions
  - Boundary conditions

Output Descriptions

With the input data described above, TODAM provides the following output.

1. Sediment simulation and distributions of total sediment, sediment size fractions, and changes in bed elevation.
2. Contaminant simulation and distributions of dissolved contaminants, and concentrations adsorbed by each sediment size and within the bed.

Advantages and Limitations

The major strength of the TODAM model is that like FETRA and SERATRA, it has very sophisticated sediment resuspension and bed load predictive capabilities. Its 1-dimensional framework makes TODAM more tailored to river applications. TODAM's kinetics are comprehensive second-order.

Also, TODAM can handle reversible flow and dry bed conditions. TODAM, as a simplified version of SERATRA, can be substituted for SERATRA in estuarine applications.

TODAM requires extensive input data and computer time. The model can be used only in 1-dimensional applications.

Model Applications

TODAM was applied to Mortandad and South Mortandad Canyons in New Mexico to estimate in-stream flow, sediment transport, and radionuclide transport in intermittent streams. Transport of seven substances was simulated: sand, silt, clay, dissolved ^{239}Pu, and particulate ^{239}Pu adsorbed by each type of sediment. Results indicate that the grid size was too large and produced numerical approximations that were too coarse to obtain accurate solutions.

Resource Requirements

The computer program for TODAM is written in the FORTRAN preprocessor language, FLECS. A standard FORTRAN IV version of TODAM is also available. TODAM can be implemented in a batch mode on VAX or PDP 11/70 computers. Execution times and run costs vary, depending on the characteristics of the system to be modeled.

User Support Activities

The user's guide and system documentation are undergoing review at USEPA and are not yet available for publication. The TODAM model is in operation, has been implemented in selected applications, and is available to the public.

More information on this model can be obtained by contacting:

Yasuo Onishi
Battelle Pacific Northwest Laboratories
P.O. Box 999
Richland, Washington 99352
(509) 376-8302

References

Onishi Y, Whelan G, and Skaggs RL. 1982. Development of a Multimedia Radionuclide Exposure Assessment Methodology for Low-Level Waste Management. PNL-3370, Battelle-Pacific Northwest Laboratory, Richland, Washington.

Hydrological Simulation Program-FORTRAN (HSPF)

Summary

The Hydrological Simulation Program-FORTRAN (HSPF) (Johanson et al. 1980) is a series of fully integrated computer codes capable of simulating watershed hydrology and the behavior of conventional and organic pollutants in land surface runoff and receiving waters. Simulations are performed on a time-varying, 1-dimensional basis and can be performed for streams and non-tidal rivers and for well mixed, non-stratified reservoirs.

Capsule Summary: HSPF
• *Time-variable, 1-dimensional model for non-tidal rivers and lakes*
• *Systematic modular framework allows a variety of operating modes, including continuous hydrologic simulation*
• *Comprehensive second-order kinetics for organics decay*
• *Stream routing uses kinematic wave approximation*
• *Data intensive*

HSPF has been modified from the original version, which considered only conventional pollutants, to an updated version which also considers the chemical processes associated with the simulation of organic pollutants. Kinetic processes for organics include hydrolysis, oxidation, photolysis, volatilization, and biodegradation. A generalized first-order decay rate is included for sorbed substances. Furthermore, up to three organic pollutants can be simulated at any one time; up to two may be "daughter" chemicals, produced from the "parent" chemical (or the other "daughter") by any or all of the degradation processes.

Sediment transport, deposition and scour are modeled for sand, silt, and clay particle sizes; adsorption/desorption rates are computed for each size of suspended and bed sediment.

The model incorporates structured programming and top-down design for a set of integrated modules which allow for the continuous simulation of hydrologic and water quality processes. HSPF contains three application modules: PERLND, IMPLND, and RCHRES. It contains five utility modules: COPY, PLTGEN, DISPLY, DURANL, and GENER.

The watershed hydrologic algorithms follow the assumptions made in the Stanford Watershed Model. The dynamic and continuous processes that affect the storages and outflow of pesticides and nutrients from agricultural lands are derived from the Agricultural Runoff Model (ARM), and the land surface washoff algorithms are from the Non-point Source (NPS) Model. Stream routing uses the kinematic wave approximation, and the water quality algorithms apply second-order kinetics to a finite difference solution technique.

Sediment-contaminant runoff contributions from rural and urban land surfaces can be simulated through the execution of the appropriate non point source modules (user-specified) contained in the model code. These modules predict sediment-contaminant loadings associated with pervious and impervious land surfaces as a function of snow accumulation and melt, sediment production and removal, sediment-contaminant relationships, water budget, and soil infiltration rates.

The PERLND module simulates snow accumulation and melt, water movement, erosion processes, scour, and water quality in a pervious land segment with homogeneous hydrologic and climatic characteristics.

For impervious land segments where little or no infiltration occurs, module IMPLND can be applied.

Module RCHRES simulates the processes that occur in a single reach and one level of underlying bed sediment) of an open channel or a completely mixed lake.

The utility modules are designed to provide flexibility in managing simulation input and output. COPY is used by the user to change the form of the time series. A 5-minute rainfall record may be aggregated to an hourly time interval for example. The PLTGEN module creates a specially formatted segmental file for later access by a stand-alone plot program. DISPLY takes a time series and summarizes the data in a formatted table. DURANL computes several statistics on a time series. The GENER module is used to transform a time series to produce a new series or to combine two time series to create a new one.

An interactive editor to prepare input sequences for HSPF is under development and will be available from the Environmental Research Laboratory, Athens, Georgia.

Input Data Requirements

If fully implemented, the HSPF methodology requires an extensive amount of input data. However, if not all modules are selected for use in the simulation by the user, the amount of input data will be reduced accordingly. Furthermore, many parameters may be defaulted, but default values are not provided for the more sensitive, site-specific parameters. The time series, constant parameters, and water quality input requirements include:

- Time series inputs which include: air temperature, precipitation, evapotranspiration, channel inflow, surface and groundwater inflow, and wind movement.

- Constant parameter inputs which include: channel geometry, vegetative cover index, surface detention storage, groundwater storage volume, soil moisture content, overland flow slope, snow-pack data, infiltration index, and interflow index.

- Land sediment factors: soil detachment coefficients, sediment influx, surface cover, sediment washoff coefficient.

- Soil temperature data: air temperature time series, slope and intercept of land temperature to air temperature equation.

- Dissolved gas in land water: ground elevation, interflow and groundwater DO and CO_2 concentrations.

- Quality constituents associated with sediment: washoff potency factor, scour potency factor.

- Quality constituents concentrations in interflow and groundwater

- Agrichemical quality constituents: solute leaching factors, soil layer depths; soil densities; and pesticide and nutrient sorption parameters, solubility factors, degradation rates.

- Impervious land quality factors: surface runoff removal rates, solids washoff coefficient, rate of solids placement and removal on surface, and overland flow borne pollutant accumulation and storage rates.

- Reach and reservoir water quality characteristics, coefficients, and rates.

Output Description

HSPF output consists of multiple printouts including system state variables, pollutant concentrations at a point versus time, and yearly summaries describing pollutant duration and flux. The model also includes a frequency analyses which provides a statistical summary of time-varying contaminant concentrations and provides the link between simulated instream toxicant concentrations and risk assessment.

Advantages and Limitations

HSPF is designed for year-around simulation of river basin hydrology, pollutant runoff or discharge, and receiving water quality. Its modular structure allows it to be readily used in more restrictive ways, using streamflow and effluent time series inputs, without the complications of applying the rainfall runoff simulation module. HSPF provides a frequency distribution summary of the output, thereby providing a year-around perspective.

The sediment-contaminant kinetics routines have the same general characteristics as other complex water quality models; however, like EXAMS it has the added capability of simulating the production and interactions of contaminant daughter products.

HSPF contains a code to calculate the frequency of occurrence and duration of contaminant concentrations in the receiving waters.

Because of its 1-dimensional approach to pollutant simulation, HSPF does not discern stratification in the water column and bed sediments.

The model's code has been optimized for both mini- and mainframe computers. On minicomputers, usage of direct access files is maximized. On mainframes, maximum use is made of fast memory and direct access I/O is minimized. Versions of HSPF are available for both types of systems.

Data requirements to implement HSPF are potentially extensive (depending on the application modules invoked) and may, therefore, result in high data production costs and significant manpower requirements.

Model Applications

HSPF has been applied on numerous occasions where an evaluation of best management practices (BMP) for controlling non-point source pollution from surface land runoff was needed. In this context, the model was applied to the Occoquan River Basin in Virginia to project long-term receiving water quality impacts from existing and future land use patterns; the Clinton River Basin in Michigan to evaluate a proposed floodway, estimate the impact of developing wetlands, and investigate various lake operating procedures; and various EPA studies to evaluate its application and use as a planning tool in determining agricultural BMPs.

Resource Requirements

HSPF requires a FORTRAN compiler that supports direct access I/O Twelve external files are required. The system requires 128K bytes of instruction and data storage on virtual memory machines, or about 250K bytes with extensive overlaying on overlay-type machines. The system was developed on a Hewlett-Packard 3000 minicomputer and has been used on IBM 370 series computers. It has been installed on the following systems: IBM, DEC VAX and System 10/20, Prime 350 and above, Data General MV4000, CDC Cyber, HP3000 and HP1000, Burroughs and Harris. Installation notes are available for specific machines.

User Support Activities

HSPF is in the public domain and can be obtained from the Center for Water Quality Modeling, Environmental Research Laboratory, USEPA, College Station Road, Athens, Georgia 30613 (telephone 404 546-3583).

User assistance can be obtained by contacting:

Thomas O. Barnwell
U.S. Environmental Protection Agency
Environmental Research Laboratory
College Station Road
Athens, Georgia 30613
FTS 250-3175 COM 404-546-3175

General References

Donigian AS, et al. 1983. Guide to the Application of the Hydrological Simulation Program - FORTRAN (HSPF). Draft report, Environmental Research Laboratory, Athens, GA, 30613.

Johanson RC, Imhoff GC, Davis HH. 1980. User's manual for Hydrological Simulation Program--FORTRAN (HSPF). EPA 600/9-9-80-015, Environmental Research Laboratory, Athens, GA. 30613.

Johanson RC, and Kittle JL. 1983. Design, Programming, and Maintenance of HSPF, Journal of Technical Topics in Civil Engineering, Vol. 109. No. 1, pp. 41-57.

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