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PROCESSES, COEFFICIENTS, AND MODELS FOR SIMULATING TOXIC ORGANICS AND HEAVY METALS IN SURFACE WATERS

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FOREWORD

As environmental controls become more costly to implement and the penalties of judgment errors become more severe, environmental quality management requires more efficient analytical tools based on greater knowledge of the environmental phenomena to be managed. As part of this Laboratory's research on the occurrence, movement, transformation, impact, and control of environmental contaminants, the Assessment Branch develops management or engineering tools to help pollution control officials achieve water quality goals.

In this work, rate constants and coefficients for toxic organic chemicals and heavy metals used in pollutant fate modeling are compiled from a review of literature through 1986. The compilation is intended to meet the same data needs for organics and metals formulations as are provided for "conventional" pollutants in the popular, Athens-developed handbook Rates, Constants and Kinetics Formulations in Surface Water Quality Modeling. Also included in the handbook are evaluations of the EXAMS, TOXIWASP, HSPF, and MINTEQ models for simulating transport and transformation of organics and metals in the environment.

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ABSTRACT

This is a reference manual for users of models that compute the fate and transport of toxic organic chemicals and heavy metals in natural surface waters. The primary purpose of this document is to assist potential users in selecting proper models and to supply a literature review of rate constants and coefficients, to insure the wise application of the models. The manual describes basic concepts of fate and transport mechanisms, providing kinetic formulations that are common to these models. Development of generalized mathematical models and analytical solutions to the equations are demonstrated. The manual includes a brief general description of four models (EXAMS II, TOXIWASP, HSPF, and MINTEQ), example runs, and comparisons of these models. Rates and coefficients provided in the manual were collected through literature reviews through 1986.

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Finally, I would like to express my deepest gratitude to Ms. Jane Frank, whose word processing abilities exceed even my abilities for entropy production!

Jerry Schnoor
Iowa City, Iowa
April 17, 1987

SECTION 1

INTRODUCTION

There is an ever increasing need for water quality modeling in protection of the nation's waters. For the first time, it is possible to perform waste load allocations for some toxic organic and heavy metals pollutants in the development of National Pollutant Discharge Elimination System (NPDES) permits for water-quality limited stream segments, those segments which are not expected to satisfy water quality standards even with the implementation of best practicable control technology currently available. There exist river and stream segments which exceed water quality standards for some pesticides and heavy metals from nonpoint sources as well. Water quality managers need to determine what constitutes best management practices (BMP) in these cases and what improvements BMP's can achieve.

New water quality criteria are currently being promulgated to account for acute and chronic effects levels using frequency and duration concepts. These criteria could eventually result in water quality standards that are enforceable by law and would require the application of mathematical models for waste load allocations, risk assessments, or environmental impact assessments. On July 29, 1985, the U.S. Environmental Protection Agency (EPA) published a notice of final ambient water quality criteria documents in the Federal Register for nine toxicants: ammonia, arsenic, cadmium, chlorine, chromium, copper, cyanide, lead, and mercury (USEPA, 1985). The new criteria specify an acute threshold concentration and a chronic-no-effect concentration for each toxicant as well as tolerable durations and frequencies.

The new criteria state that aquatic organisms and their uses should not be affected unacceptably if two conditions are met: (1) the 4-day average concentration of the toxicant does not exceed the recommended chronic criterion more than once every three years on the average and (2) the 1-hour average concentration does not exceed the recommended acute criterion more than once every 3 years on the average. Criteria for other toxic pollutants will be published in the near future specifying the same durations and frequencies. The new criteria recognize that toxic effect is a function both of the magnitude of a pollutant concentration and of the organism exposure time to that concentration. A very brief exposure to a relatively high concentration may be less harmful than a prolonged exposure to a lower concentration.

The EPA is considering application of site-specific water quality criteria that also would require mathematical modeling to aid in determining water quality standards. For example, Carlson et al. (1986) have shown that copper exhibits much less toxicity and/or bioavailability in site-specific tests compared to single-specie laboratory bioassay testing. It is likely that aqueous copper forms strong complexes with ligands in-situ (organics ligands in particular) that are not as toxic or bioavailable to aquatic organisms. Because copper exceeds water quality criteria in some locations naturally, this is an extremely important issue. Publicly owned wastewater treatment plants often exceed wáter quality criteria for some heavy metals under extreme, low flow conditions. The likelihood of in-situ toxicity, either acute or chronic, becomes the point of primary concern. To provide the proper perspective, we must have valid exposure assessments. These assessments require the use of mathematical models. Hedtke and Arthur (1985) have demonstrated the techniques for development of a site-specific water quality criterion for pentachlorophenol.

1.1 OBJECTIVES

This publication has three primary objectives:

1) to describe four existing mathematical models (EXAMS, TOXIWASP, HSPF, and MINTEQ) that are supported by the Center for Water Quality Modeling at EPA's Environmental Research Laboratory, Athens, GA;
2) to aid the modeler in the proper choice of mathematical models, rate constants, and kinetic formulations that are available in the scientific literature; and
3) to present case studies that illustrate model capabilities, differences, and limitations.

The publication extends the discussion of chemical fate and transport to heavy metal reactions (as well as organic reactions) with the addition of MINTEQ. Based on a literature review through 1985 and selected references through 1986, it updates the chemical rate constant data of Callahan et al. (1979) and Mabey et al. (1982).

1.2 USE OF THIS DOCUMENT

Sections 2 through 4 present a review of the literature and a summary of available rate constants and equilibrium constants. Literature values were screened for applicability to natural water conditions. A range and summary of the constants are given in each Section; the Appendix includes all the values from a computerized literature search, The Appendix updates the work of Callahan et al. (1979) and Mabey et al. (1982) to 1985 for organic priority pollutants.

Section 5 describes the techniques involved in mathematical modeling of water quality including development of mass balance differential equations and simplified analytic solutions. These solutions, in many cases, can be used to understand the more detailed mathematical models and to check results.

Section 6 describes the EXAMS, TOXIWASP, HSPF, and MINTEQ models. TOXIWASP and HSPF can be applied to toxic organics or heavy metals, EXAMS was developed for organic pollutants only, and MINTEQ is for chemical equilibrium speciation of heavy metals. MINTEQ does not include transport or kinetics of these metals.

Section 7 gives an application and test case of EXAMS-II, HSPF, and MINTEQ employed for a waste load allocation. It allows the modeler to realize some of the data requirements for these models and compares the output of EXAMS and HSPF for a stretch of the Iowa River.

Each of these models is supported by EPA's Center for Water Quality Modeling at the Environmental Research Laboratory, Athens, GA. Support involves the distribution of code and documentation, the correction and updating of models through user experience, and the presentation of workshops and training courses.

1.2.1 Exposure Analysis Modeling System

EXAMS-II (Burns, Cline, and Lassiter, 1982; Burns and Cline, 1985), is á steady-state and dynamic model designed for rapid evaluation of the behavior of synthetic organic chemicals in lakes, rivers, and estuaries. An interactive program, EXAMS-II allows the user to specify and store the properties of chemicals and ecosystems, modify the characteristics of either via simple English-like commands, and conduct rapid, efficient evaluations of the probable fate of chemicals. EXAMS-II simulates the behavior of a toxic chemical and its transformation products using second-order kinetics for all significant organic chemical reactions. EXAMS-II does not simulate the solids with which the chemical interacts. The concentration of solids must be specified for each compartment; the model accounts for sorbed chemical transport based on solids concentrations and specified transport fields. Benthic exchange includes pore water advection, pore water diffusion, and solids mixing. The latter describes a net steady-state exchange associated with solids that is proportional to pore water diffusion.

1.2.2 Water Quality Simulation Program

TOXIWASP is related to two other models -- WASP3 and WASTOX. WASP3 (Di Toro et al., 1982; Ambrose et al., 1986) is a generalized modeling framework for contaminant fate and transport in lakes, rivers, and estuaries. Based on the flexible compartment modeling approach, WASP3 can be applied in one, two, or three dimensions given transport of fluxes between segments. WASP3 can read output files from the link-node hydrodynamic model DYNHYD3, which predicts unsteady flow rates in unstratified rivers and estuaries given variable tides, wind, and inflow. A variety of water quality problems can be addressed with the selection of appropriate kinetic subroutines. Two general toxic chemical modeling frameworks have been constructed from WASP - TOXIWASP and WASTOX. These separate frameworks will be combined in WASP4.

TOXIWASP (Ambrose et al., 1983), a subset of WASP3, combines a kinetic structure adapted from EXAMS with the WASP transport structure and simple

sediment balance algorithms to predict sediment and chemical concentrations in the bed and overlying waters. TOXIWASP predicts variable rate constants using second-order kinetics for all significant organic chemical reactions except ionization. Benthic exchange includes pore water advection, pore water diffusion, an empirical bioturbation-related dispersion, and deposition/scour. Net sedimentation and burial are calculated.

WASTOX (Connolly and Winfield, 1984) simulates a toxic chemical and up to three sediment size fractions in the bed and overlying waters. Second-order kinetics are used for all significant organic chemical reactions except ionization. Benthic exchange includes pore water advection, pore water diffusion, and deposition/scour. Net sedimentation and burial rates can be specified. An empirically based food chain model is linked to WASTOX for calculating chemical concentrations in biota and fish resulting from predicted aquatic concentrations (Connolly and Thomann, 1984).

1.2.3 Hydrological Simulation Program - FORTRAN

HSPF (Johanson et al., 1984) is a comprehensive package for simulation of watershed hydrology and water quality for both conventional and toxic organic pollutants. HSPF incorporates the watershed-scale ARM and NPS models into a basin-scale analysis framework that includes transport and transformation in one-dimensional stream channels. The result of this simulation is a time history of the runoff flow rate, sediment load, and nutrient and pesticide concentrations, along with a time history of water quantity and quality at any point in a watershed. HSPF simulates three sediment types (sand, silt, and clay) in addition to a single organic chemical and transformation products of that chemical. The transfer and reaction processes included are hydrolysis, oxidation, photolysis, biodegradation, volatilization, and sorption. Sorption is modeled as a first-order kinetic process in which the user must specify a desorption rate and an equilibrium partition coefficient for each of the three solids types. Resuspension and settling of silts and clays (cohesive solids) are defined in terms of shear stress at the sediment-water interface. For sands, the capacity of the system to transport sand at a particular flow is calculated and resuspension or settling is defined by the difference between the sand in suspension and the transport capacity. Calibration of the model requires data for each of the three solids types. Benthic exchange is modeled as sorption/desorption and deposition/scour with surficial benthic sediments. Underlying sediment and pore water are not modeled.

1.2.4 Geochemical Equilibrium Program

MINTEQ (Felmy et al., 1984a, Brown et al., 1987) is a geochemical model that is capable of calculating equlibrium aqueous speciation, adsorption, gas phase partitioning, solid phase saturation, and precipitation-dissolution of 11 metals (arsenic, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, thallium, and zinc). MINTEQ contains an extensive thermodynamic data set and contains 6 different algorithms for calculating adsorption. Proper application of MINTEQ requires some expertise because kinetic limitations at particular sites may prevent the thermodynamically possible reactions that are integral to the model.

Nevertheless, thoughtful application of MINTEQ may describe the predominant metals species at a site and thus give insight into potential biological effects. For waste load allocation problems, MINTEQ must be run in conjunction with one of the transport and transformation models described above. It has been linked and tested with EXAMS (Felmy et al., 1984b; Medine and Bicknell, 1986).

1.3 PROCESS FORMULATIONS AND DATA

To use mathematical models for environmental assessments, information is required on chemical fate processes. Fate of chemicals in the environment is determined by physical, chemical and biological processes which include transport, dispersion, sorption, volatilization, hydrolysis, oxidation, photo-transformations, biological transformations and bioconcentration. In Chapter 2 through 4, the mathematical formulations of these processes are presented with some theoretical background. Summary data tables are also presented with complete data sets given in Appendix A.

1.3.1 Transport

The transport of a dissolved chemical in surface waters is influenced by the velocity of the current or advective transport. Current velocities must be measured directly or calculated from a knowledge of flowrate and cross-sectional area through which it flows. Transport of an adsorbed chemical requires knowledge of sediment movement within the surface water, including sedimentation, resuspension/scour, and saltation along the bottom as bed load. The concentration of suspended solids multiplied times the flowrate of a river is a measure of the sediment transport or "wash load" of the river. Mixing of both dissolved chemicals and, to some extent, adsorbed chemicals occurs by dispersion in surface waters. Molecular diffusion of chemicals in surface water is generally too slow to be of importance except in pore waters of sediments. However, turbulent diffusion and dispersion are important processes in predicting the environmental transport of a chemical contaminant in surface waters.

1.3.2 Dispersion

Dispersion results from the mixing of surface waters under turbulent conditions. It is enhanced when turbulence is coupled with temporal and spatial variations in velocity within the water body. Dead zones (areas with very still, quiescent waters) cause back-mixing of water and the eventual "spread" of dissolved chemical pulses that is characteristic of dispersion. Chemical concentrations could not be accurately simulated without some knowledge of dispersion and mixing characteristics of the water body.

1.3.3 Sorption

Chemicals that are dissolved in water can become sorbed to sediment and suspended solids in the water body. Mechanisms of sorption include physical adsorption (by attractive coulombic forces), chemisorption (chemical binding to a specific site or ligand on the surface of the solids), and absorption

(a solution phenomena of organic chemicals dissolving in a like phase or organic matrix). The fate of a chemical in water is significantly affected by its partitioning between solids and water. In general, for organic chemicals, the more polar is the chemical, the more it tends to partition into the aqueous phase. Conversely, the more nonpolar it is, the more it tends to partition into the organic or solid phase. We estimate the tendency for an organic chemical to sorb by use of its octanol/water partition coefficient or K_{ow}. The greater is K_{ow}, the larger is its potential to sorb to the solid phase (sediment and suspended solids) in the water body.

1.3.4 Volatilization

Some chemicals evaporate (volatilize) from the water to the atmosphere by gas transfer reactions. Volatile chemicals are characterized by a high Henry's constant, H, that describes their tendency to partition into the gas phase rather than the aqueous phase at chemical equilibrium. The rate that chemicals volatilize is also dependent on their molecular properties in the solvent (water) including molecular size, polarity and functional groups. Chemical volatilization is often compared relative to that of dissolved oxygen and reaeration rates in natural waters.

1.3.5 Hydrolysis

Hydrolysis reactions occur between chemicals and water molecules (H_2O, OH^-, or H_3O^+), resulting in the cleaving of a molecular bond and the formation of a new bond with components of the water molecule. Tendency of an organic chemical to undergo hydrolysis reactions depends on its susceptibility to a nucleophilic attack. Organic esters, amides, amines, carbamates, and alkyl halides are often hydrolyzed in natural waters.

1.3.6 Oxidation

Some chemicals can undergo a strict chemical oxidation in natural waters due to their reducing potential. Oxidation may occur with dissolved oxygen as a reactant or, more commonly, a free radical (such as •OH, ROO•) that is generated at low concentrations from other redox reactions involving hydrogen peroxide, singlet oxygen, or ozone.

1.3.7 Photo-transformation

Photolysis is a light-induced degradation reaction that occurs when photons strike organic molecules and excite them to a higher electron state. Transformation of a chemical in natural waters may involve direct or indirect photolysis depending upon whether the chemical of interest is itself excited by the quantum of energy (photon) or whether it is transformed by another light-energized molecule.

1.3.8 Biological Transformation

Perhaps the most universal and important reactions occurring in natural waters are biological. Transformation reactions of organics and heavy

metals are often caused or enhanced by microorganisms, especially bacteria, fungi, and algae. Extra-cellular and intracellular enzymes catalyze a variety of reactions including hydrolysis and chemical oxidation. For example, many organo-phosphate ester pesticides are known to undergo spontaneous strict chemical hydrolysis reactions, but in the presence of microorganisms the reactions are greatly catalyzed. The reaction products and reactants are the same, but the rate that the reaction proceeds is much faster.

1.3.9 Bioconcentration

The capacity for a chemical to be taken-up from the aqueous phase by biota in natural waters is termed, "bioconcentration". It correlates quite well with the hydrophobic (lipophilic) nature of the chemical. Because some chemicals that are hydrophobic accumulate in the fatty tissue of fish and other organisms, bioconcentration is an important process that can contaminate fisheries. Like sorption to suspended solids, bioconcentration correlates with the tendency for chemicals to dissolve into octanol, as opposed to water. One measures this tendency as the octanol/water partition coefficient or K_{ow}.

1.4 CHEMICAL FATE MODELING

The fate of chemicals in the aquatic environment is determined by two factors: their reactivity, and the rate of their physical transport through the environment. All mathematical models of the fate of chemicals are simply useful accounting procedures for the calculation of these processes as they become quite detailed. To the extent that we can accurately predict the chemical, biological, and physical reactions and transport of chemical substances, we can "model" their fate and persistence and the inevitable exposure to aquatic organisms.

Figure 1.01 is a schematic of a mass balance modeling approach to chemicals in the environment. Key elements are:

- a clearly defined control volume
- a knowledge of inputs and outputs which cross the boundary of the control volume
- a knowledge of the transport characteristics within the control volume and across its boundaries
- a knowledge of the reaction kinetics and rate constants within the control volume.

A control volume can be as small as an infinitesimally thin slice of water in a swiftly flowing stream or as large as the entire body of oceans on the planet earth. The important point is that the boundaries are clearly defined with respect to their location so that the volume is known and mass fluxes across the boundaries can be determined. Within the control volume, the transport characteristics (degree of mixing) must be known either by measurement or an estimate based on the hydrodynamics of the system. Likewise, the transport in adjacent or surrounding control volumes may

contribute mass to the control volume, so transport across the boundaries of the control volume must be known or estimated.

A knowledge of the chemical, biological, and physical reactions that the substance can undergo within the control volume is the subject of Sections 3 and 4 in this manual. If there were no degradation reactions taking place in aquatic ecosystems, every pollutant which was ever released to the environment would still be present. Fortunately, there are natural processes that serve to degrade some wastes and to ameliorate aquatic impacts. One must understand these reactons from a quantitative viewpoint in order to assess the potential damage to the environment from pollutant discharges and to allocate allowable limits for these discharges.

A mass balance is simply the accounting of the mass inputs, outputs, reactions and accumulation as described by the following equation.

$$\text{Accumulation w/in the control volume} = \text{Mass Inputs} - \text{Mass Outflows} \pm \text{Reactions} \qquad (1)$$

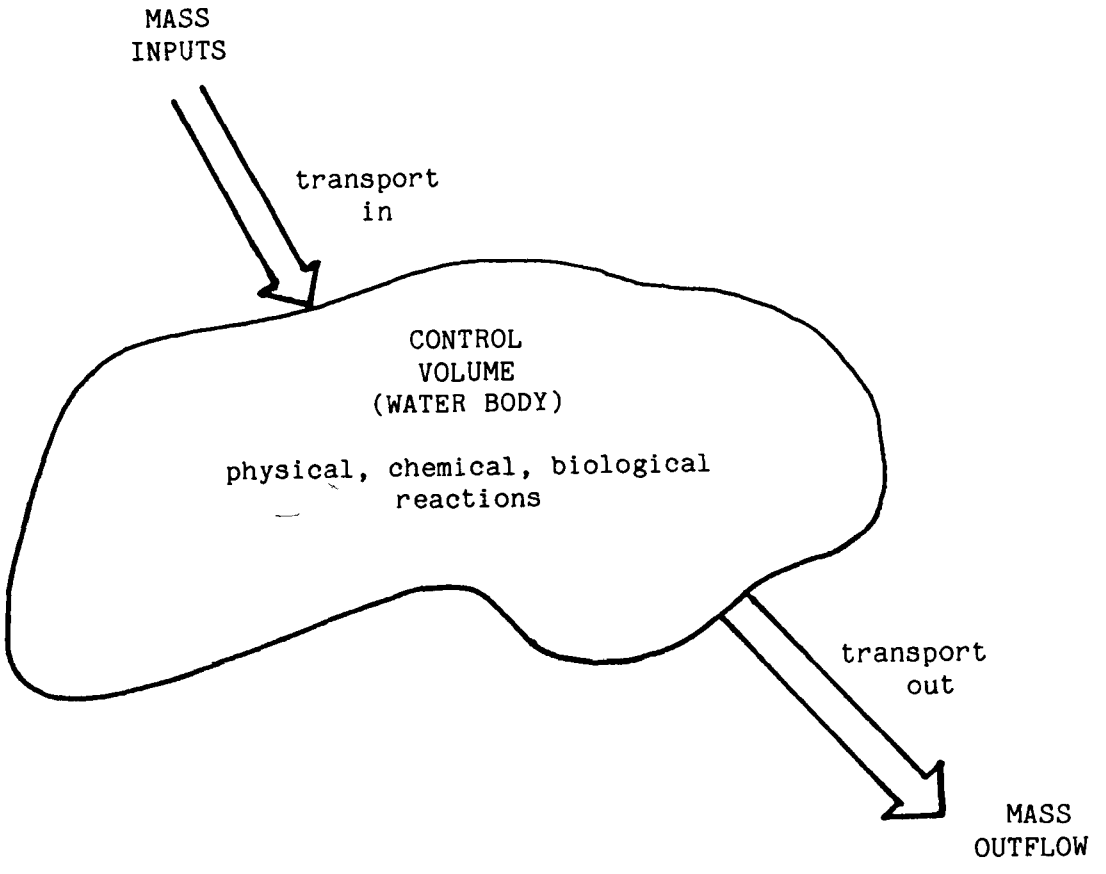

Figure 1.01. Generalized approach for mass balance models utilizing the control-volume concept and transport across boundaries.

If the substance is being formed or grown within the control volume such as the combination of two reactants to form a product P (A + B → P), then the algebraic sign in front of the "Reactions" term is positive. If the substance is being transformed or degraded within the control volume, then the algebraic sign of the "Reactions" term is negative. If the substance is conservative (i.e., non-reactive or inert), then the "Reactions" term is zero.

To perform mathematical modeling of toxic chemicals, four ingredients are necessary: 1) field data on chemical concentrations and mass discharge information, 2) a mathematical model formulation, 3) rate constants and coefficients for the mathematical model, and 4) some performance criteria with which to judge the model.

One cannot stress enough the importance of field data. Depending on the ultimate use of the model, the amount of field reconnaissance varies. If the model is to be used in a waste load allocation for NPDES permits, there should be enough field data to be confident of model results. Usually this requires two sets of field measurements, one for model calibration and one for verification under somewhat different circumstances.

Model calibration involves a comparison between simulation results and field measurements. Model coefficients and rate constants should be chosen initially from literature or laboratory studies. (In this manual, you may use Appendix A if the chemical in which you are interested is listed.) Discharge rates are also needed as input to drive the model. After you run the model, a statistical comparison is made between model results for the state variables (chemical concentrations) and field measurements. If errors are within an acceptable tolerance level, the model is considered calibrated. If errors are not acceptable, rate constants and coefficients must be systematically varied (tuning the model) to obtain an acceptable simulation. Thus the model is calibrated.

To verify the model, a statistical comparison between simulation results and a second set of field data is required. Coefficients and rate constants cannot be changed from the model calibration. This procedure provides some confidence that the model is performing acceptably. Performance criteria may be as simple as, "model results should be within one order of magnitude of the field concentrations at all times," or as stringent as, "the mean squared error of the residuals (difference between field measurements and model results) should be a minimum prescribed or optimal value". Performance criteria depend on the use of the model, but criteria should be determined a priori, in the advance of the modeling exercise.

In this manual, Sections 3 and 4 and Appendix A can aid in the initial selection of model rate constants and coefficients. Sections 5, 6, and 7 and Appendix B can aid in the understanding and use of four models highlighted here and supported by Athens Environmental Research Laboratory. Table 1.01 gives the general characteristics of the four models to aid in selection for your particular application.

TABLE 1.01 GENERAL CHARACTERISTICS OF FATE MODELS

Model	Water Body	Time Domain	Chemical	Availability
EXAMS-II	L,R,E	S,D	O	A,PC
TOXIWASP, WASTOX	L,R,E	D S,D	O,M	A,PC
HSPF	R	D	O,M	A,PC
MINTEQ	L,R,E	S	M	A,PC
	Lake, River, Estuary	Steady-State, Dynamic	Organic Metal	Athens EPA, Personal Computer Version

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SECTION 2

TRANSPORT PHENOMENA

2.1 INTRODUCTION

The reactions that a chemical may undergo are an important aspect of a chemical's fate in the environment, but an equally important process has to do with the rate of a chemical's transport in the aquatic environment. In this chapter, we shall discuss three processes of mass transport in aquatic ecosystems: transport by the current of the water (advection), transport due to mixing within the water body (dispersion), and transport of sediment particles within the water column and between the water and the bed.

Toxic organic chemicals, at low concentrations in natural waters, exist in a dissolved phase and a sorbed phase. Dissolved substances are transported by water movement with little or no "slip" relative to the water. They are entirely entrained in the current and move at the water velocity. Likewise, organics that are sorbed to colloidal material or fine suspended solids are essentially entrained in the current, but they may undergo additional transport processes such as sedimentation and deposition or scour and resuspension. These processes may serve to retard the movement of the sorbed substances relative to the water movement. Thus in order to determine the fate of toxic organic substances, we must know both the water movement and sediment movement.

The importance of a good water budget cannot be understated. Physical transport of water in a clearly defined control-volume is accounted for by a water balance. Seldom are all of the terms in the water balance measured accurately, so errors are generated in the water accounting procedure. A complete water balance is presented below.

$$\text{Accumulation of } H_2O = \text{Inflows} + \text{Direct Precipitation} - \text{Outflows} - \text{Evaporation}$$

$$+ \text{Infiltration} - \text{Exfiltration} + \text{Overland Runoff}$$

Water can be stored within lakes or rivers by a change in elevation or stage. Inflows and outflows should be gaged or measured over the period of investigation. Precipitation gages and evaporation pans can provide sufficiently accurate data. In the best of situations, it is possible to achieve an annual water balance within 5 percent (total inflows are within

5% of total outflows). Confounding factors include infiltration, exfiltration, and overland runoff.

2.1.1 Transport of Chemicals in Water

The transport of toxic chemicals in water principally depends on two phenomena: advection and dispersion. Advection refers to movement of dissolved or fine particulate material at the current velocity in any of three directions (longitudinal, lateral or transverse, and vertical). Dispersion refers to the process by which these substances are mixed within the water column. Dispersion can also occur in three directions. A schematic for advection, turbulent diffusion, and dispersion in a stream is given in Figure 2.01. Three processes contribute to mixing (dispersion):

1. Molecular diffusion. Molecular diffusion is the mixing of dissolved chemicals due to the random walk of molecules within the fluid. It is caused by kinetic energies of molecular vibrational, rotational, and translational motion. In essence, molecular diffusion corresponds to an increase in entropy whereby dissolved substances move from regions of high concentration to regions of low concentration according to Fick's laws of diffusion. It is an exceedingly slow phenomenon, such that it would take on the order of 10 days for 1 mg/ℓ of dissolved substance to diffuse through a 10-cm water column from a concentration of 10 mg/ℓ. It is generally not an important process in the transport of dissolved substances in natural waters except relating to transport through thin and stagnant films at the air-water interface or transport through sediment pore water.

2. Turbulent Diffusion. Turbulent or eddy diffusion refers to mixing of dissolved and fine particulate substances caused by micro-scale turbulence. It is an advective process at the microscale level caused by eddy fluctuations in current velocity. Shear forces within the body of water are sufficient to cause this form of mixing. It is several orders of magnitude larger than molecular diffusion and is a contributing factor to dispersion. Turbulent diffusion can occur in all three directions, but is often anisotropic (i.e., there exist preferential directions for turbulent mixing due to the direction and magnitude of shear stresses).

3. Dispersion. The interaction of turbulent diffusion with velocity profiles in the water body causes a still greater degree of mixing known as dispersion. Transport of toxic substances in streams and rivers is predominantly by advection, but transport in lakes and estuaries is often dispersion-controlled. Velocity gradients are caused by shear forces at the boundaries of the water body, such as vertical profiles due to wind shear at the air-water interface, and vertical and lateral profiles due to shear stresses at the sediment-water and bank-water interfaces (Figure 2.02). Also velocity gradients can develop within the water body due to channel morphology, sinuousity and meandering of streams, and thermal or

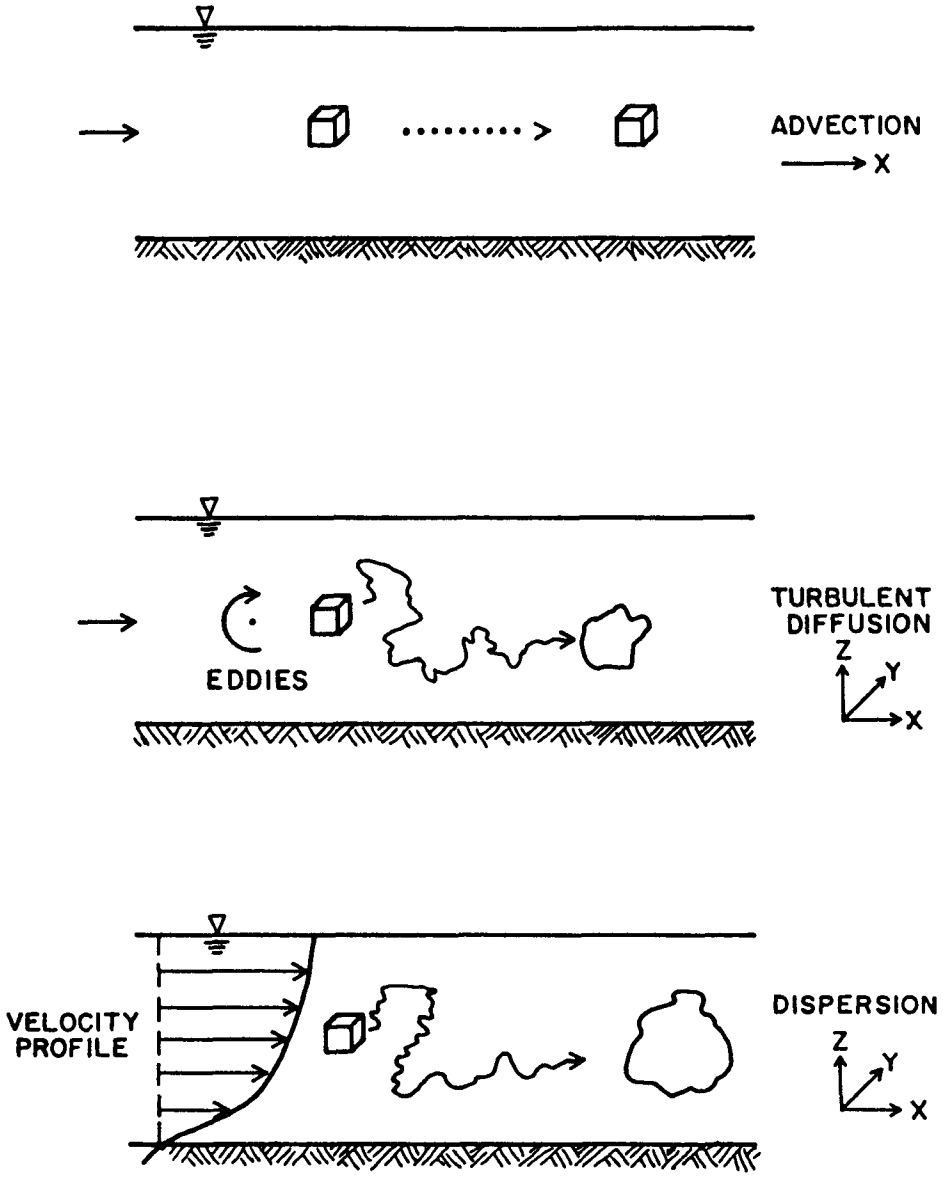

Figure 2.01. Schematic of transport processes: 1) Advection, movement of chemical entrained in current velocity; 2) Turbulent diffusion, spread of chemical due to eddy fluctuations; 3) Dispersion, spread of chemical due to eddy fluctuations in a macroscopic velocity gradient field.

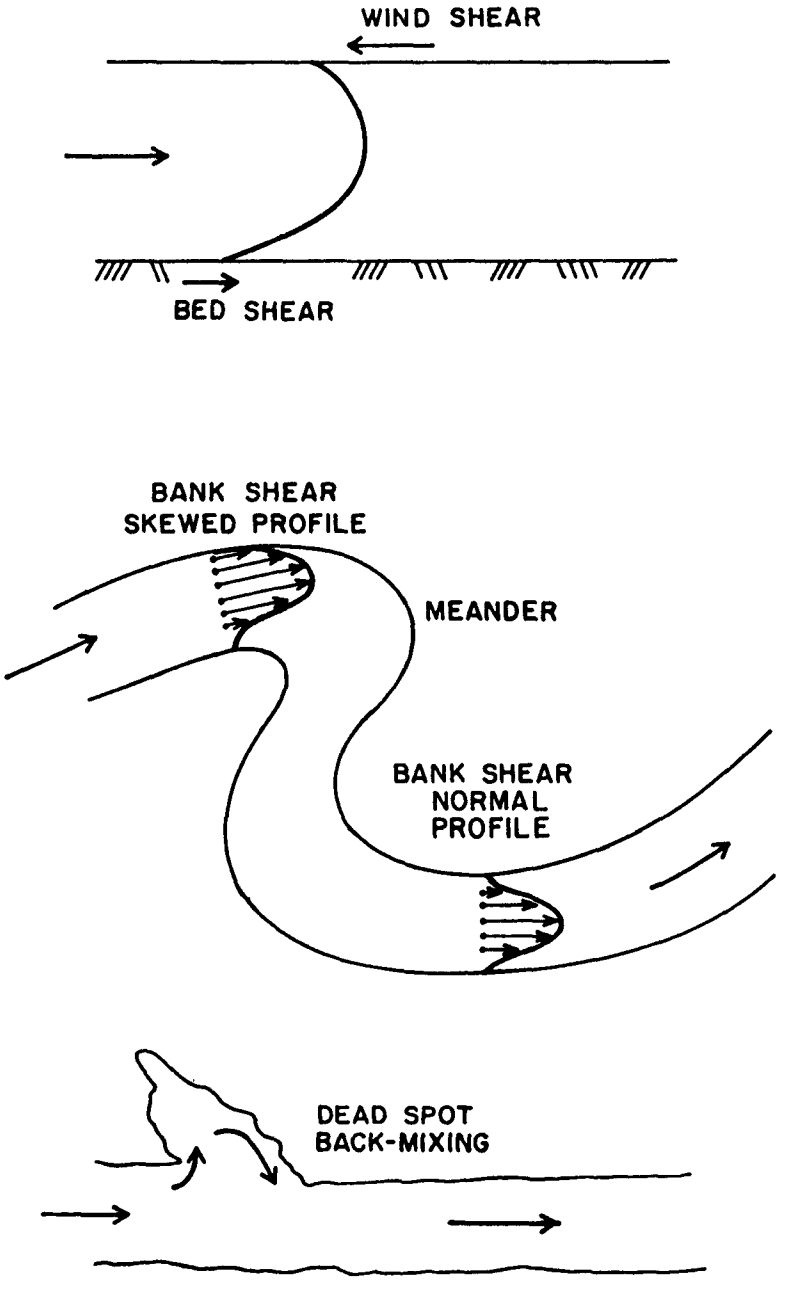

Figure 2.02. Schematics of velocity gradients created by shear stresses at the air-water, bed-water, and bank-water interfaces.

density stratification and instabilities in lakes and estuaries. Morphological causes of dispersive mixing in rivers include dead spots, side channels, and pools where back-mixing occurs. When turbulent diffusion causes a parcel of fluid containing dissolved substances to change position, that parcel of fluid becomes entrained in the water body at a new velocity, either faster or slower. This causes the parcel of fluid and the toxic substance to mix forward or backward relative to its neighbors. The mixing process is called dispersion and results in a mass flux of toxic substances from areas of high concentration to areas of low concentration. The process is analagous to molecular diffusion but occurs at a much more rapid rate. The steady state mass flux rate can be described by Fick's first law of diffusion:

$$J = - K A \frac{dc}{dx} \qquad (2.1)$$

where J = mass flux rate, M/T
K = diffusion or dispersion coefficient, L^2/T
A = cross sectional area through which diffusion occurs, L^2, and
$\frac{dc}{dx}$ = concentration gradient, M/L^3-L.

The rate of movement of chemical is proportional to the cross sectional area and the concentration gradient, which is the driving force for diffusion.

2.1.2 Advective-Dispersive Equation

The basic equation describing advection and dispersion of dissolved matter is based on the principle of conservation of mass and Fick's law. For a conservative substance, the principle of conservation of mass can be stated:

Rate of change of mass in control volume	=	Rate of change of mass in control volume due to advection	+	Rate of change of mass in control volume due to diffusion	-	Transformation Reaction Rates (Degradation)

$$\frac{\partial C}{\partial t} = - u_i \frac{\partial C}{\partial x_i} + \frac{\partial}{\partial x_i} \varepsilon_i \frac{\partial C}{\partial x_i} - R \qquad (2.2)$$

where C = concentration, M/L^3
t = time, T
u_i = average velocity in the i'th direction, L/T
x_i = distance in the i'th direction, L, and
R = reaction transformation rate, M/L^3-T.

ε_i is the diffusion coefficient in the i'th direction. For laminar flow, $\varepsilon_i = \varepsilon_M$, the coefficient of molecular diffusion. For turbulent flow, $\varepsilon_i = \varepsilon_T + \varepsilon_M$, where ε_T is the coefficient of turbulent diffusion. In Fickian diffusion theory, it is assumed that dispersion resulting from

turbulent open-channel flow is exactly analogous to molecular diffusion. The dispersion coefficients in the x, y, and z directions are assumed to be constants, given by K_x, K_y and K_z. The resulting equation, expressed in Cartesian coordinates, is:

$$\frac{\partial C}{\partial t} + u_x \frac{\partial C}{\partial x} + u_y \frac{\partial C}{\partial y} + u_z \frac{\partial C}{\partial z} = K_x \frac{\partial^2 C}{\partial x^2} + K_y \frac{\partial^2 C}{\partial y^2} + K_z \frac{\partial^2 C}{\partial z^2} \qquad (2.3)$$

The solution of equation (2.3) depends on the values of K_x, K_y and K_z. Various authors have arrived at equations to approximate the values of the dispersion coefficients (K) in the longitudinal (x), lateral (y), and vertical (z) directions.

2.2 EVALUATING COEFFICIENTS

2.2.1 Longitudinal Dispersion Coefficient in Rivers

Liu (1977) used the work of Fischer (1967) to develop an expression for the longitudinal dispersion coefficient in rivers and streams (K_x, which has units of length squared per time):

$$K_x = \beta \frac{u_x^2 B^3}{U_* A} = \beta \frac{Q_B^2}{U_* D^3} \qquad (2.4)$$

where Liu (1978) defined,

$$\beta = 0.5 \frac{U_*^2}{u_x}$$

D = mean depth, L
B = mean width, L
U_* = bed shear velocity, L/T
u_x = mean stream velocity, L/T
A = cross sectional area, L^2, and
Q_B = river discharge, L^3/T.

β does not depend on stream morphometry but on the dimensionless bottom roughness. Based on existing data for K_x in streams, the value of K_x can be predicted to within a factor of six by equation (2.4). The bed shear velocity is related empirically to the bed friction factor and mean stream velocity:

$$U_* = \sqrt{\frac{\tau_o}{\rho}} = \sqrt{\frac{f}{8} u_x^2} \qquad (2.5)$$

in which τ_o = bed shear stress, $M/L\text{-}T^2$

f = friction factor ≈ 0.02 for natural, fully turbulent flow
ρ = density of water, M/L^3

2.2.2 Lateral Dispersion Coefficient in Rivers

Elder (1959) proposed an equation for predicting the lateral dispersion coefficient, K_y:

$$K_y = \phi D U_* \tag{2.6}$$

where ϕ is equal to 0.23. The value of $\phi = 0.23$ was obtained by experiment in long, wide laboratory flumes.

Many authors have since investigated the value of ϕ in both laboratory flumes and natural streams. Sayre and Chang (1968) reported $\phi = 0.17$ in a straight laboratory flume. Yotsukura and Cobb (1972) report values of ϕ for natural streams and irrigation canals varying from 0.22 to 0.65, with most values being near 0.3. Other reported values of ϕ range from 0.17 to 0.72. The higher values for ϕ are all for very fast rivers. The conclusions drawn are: 1) that the form of equation (2.6) is correct in predicting K_y, but ϕ may vary, and 2) that application of Fickian theory to lateral dispersion is correct as long as there are no appreciable lateral currents in the stream.

Okoye (1970) refined the determination of ϕ somewhat by use of the aspect ratio, $\lambda = D/B$, the ratio of the stream depth to stream width. He found that ϕ decreased from 0.24 to 0.093 as λ increased from 0.015 to 0.200.

The effect of bends in the channel on K_y is significant. Yotsukura and Sayre (1976) reported that ϕ varies from 0.1 to 0.2 for straight channels, ranging in size from laboratory flumes to medium size irrigation channels; from 0.6 to 10 in the Missouri River; and from 0.5 to 2.5 in curved laboratory flumes. Fischer (1968) reports that higher values of ϕ are also found near the banks of rivers.

2.2.3 Vertical Dispersion Coefficient in Rivers

Very little experimental work has been done on the vertical dispersion coefficient, K_z. Jobson and Sayre (1970) reported a value for marked fluid particles of:

$$K_z = \kappa U_* z \left(1 - \frac{z}{D}\right) \tag{2.7}$$

for a logarithmic vertical velocity distribution. κ is the von Karman coefficient, which is shown experimentally to be approximately = 0.4 (Tennekes and Lumley, 1972). Equation (2.7) agrees with experimental data fairly closely.

2.2.4 Vertical Eddy Diffusivity in Lakes

Vertical mixing in lakes is not mechanistically the same as that in rivers. The term "eddy diffusivity" is often used to describe the turbulent diffusion coefficient for dissolved substances in lakes. Chemical and thermal stratification serve to limit vertical mixing in lakes, and the eddy diffusivity is usually observed to be a minimum at the thermocline.

Many authors have correlated the vertical eddy diffusivity in stratified lakes to the mean depth, the hypolimnion depth, and the stability

frequency. Mortimer (1941) first correlated the vertical diffusion coefficient with the mean depth of the lake. He found the following relationship.

$$K_z = 0.0142\ Z^{1.49} \tag{2.8}$$

in which K_z = vertical eddy diffusivity, m^2/day, and

Z = mean depth, m.

Vertical eddy diffusivities can be calculated from temperature data by solving the vertical heat balance or by the simplified estimations of Edinger and Geyer (1965). Schnoor and Fruh (1979) have demonstrated that the mineralization and release of dissolved substances from anaerobic sediment can be used to calculate average hypolimnetic eddy diffusivities. This approach avoids the problem of assuming that heat (temperature) and mass (dissolved substances) will mix with the same rate constant, i.e., that the eddy diffusivity must equal the eddy conductivity. A summary of dispersion coefficients and their order of magnitude appears below.

	Dispersion Coefficient, cm^2/sec
Molecular Diffusion	10^{-5}
Compacted Sediment	10^{-7} - 10^{-5}
Bioturbated Sediment	10^{-5} - 10^{-4}
Lakes - Vertically	10^{-2} - 10^{1}
Large Rivers - Lateral	10^{2} - 10^{3}
Large River - Longitudinal	10^{4} - $10^{5.5}$
Estuaries - Longitudinal	10^{6} - 10^{7}

A literature summary of longitudinal dispersion coefficients for streams and rivers is reported in Table 2.01. The wide range of values reflects the site-specific nature of longitudinal dispersion coefficients and the many hydrologic and morphologic properties which affect mixing processes. An excellent reference for mixing processes in natural waters is that of Fischer et al. (1979).

Vertical dispersion coefficients in lakes (eddy diffusivities) have most commonly been determined by the heat budget method (Edinger and Geyer, 1965; Park and Schmidt, 1973; Schnoor and Fruh, 1979) or by McEwen's method (1929). Radio-chemical methods also have been used with success (Quay et al., 1980; Imboden et al., 1979; Torgersen et al., 1977). Table 2.02 gives some literature values for the vertical dispersion coefficient at the thermocline (minimum value), and Table 2.03 reports the mean vertical dispersion coefficient for the entire water column. Vertical dispersion is a function of the depth and morphometry of the lake, fetch-to-wind direction relationship, solar insolation and light penetration, and other factors. Example calculations for lake dispersion coefficients are presented at the end of this chapter; data for these calculations were taken from actual field measurements.

TABLE 2.01. SUMMARY OF DISPERSION MEASUREMENTS IN STREAMS

Reach	Depth m	Width m	U* cm/sec	Slope	Velocity or Flow - m/sec (m^3/sec)	Longitudinal Dispersion Coefficient m^2/sec	Reference
Missouri R., IA-NB					96.6	5.6×10^4	Sayre, 1973
Chicago Ship Canal	8.07	48.8	1.91			3	Fischer, 1973
Sacramento R.	4.00		5.1			15	"
River Derwent Australia	.25		14			4.6	"
S. Platte R., NB	.46		6.9			16.2	"
Yuma Mesa Canal	3.45		3.45			0.76	"
Green-Duwamish R., WA	1.10	20	4.9			6.5-8.5	"
Copper Creek, VA	.49	16	8			20	"
	.85	18	10			21	"
	.49	16	8			9.5	"
	.40	19	11.6			9.9	"
Clinch R., TN	.85	47	6.7			14	"
	2.10	60	10.4			54	"
	2.10	53	10.7			47	"
Powell R., TN	.85	34	5.5			9.5	"
Clinch R., VA	.58	36	4.9			8.1	"
Coachella Canal, CA	1.56	24	4.3			9.6	"
Monocacy R., MD		35.1		0.0006	0.11 (2.41)	4.6	McQuivey & Keefer, 1974
		36.6			0.21 (5.21)	13.9	"
		47.6			0.38 (18.41)	37.2	
Antietam Cr. MD		15.9		0.0001	0.20 (1.98)	9.3	"
		19.8			0.27 (4.36)	16.3	"
		24.4			0.42 (8.92)	25.6	"
Missouri R. NB-IA		182.9		0.0002	0.91 (379.50)	464.7	McQuivey & Keefer, 1974
		201.2			1.24 (911.92)	836.4	"
		196.6			1.48 (934.58)	1,487.0	"
Clinch R. TN		47.3		0.0006	0.21 (9.20)	13.9	"
		53.4			0.44 (50.98)	46.5	"
		59.5			0.65 (84.96)	55.8	"
Bayou Anacoco LA		19.8		0.0005	0.21 (2.44)	13.9	"
		25.9			0.34 (8.21)	32.5	"
		36.6			0.40 (13.45)	39.5	"
Nooksack R. WA		64.0			0.68 (32.57)	34.9	"
		86.0		0.0098	1.3 (303.03)	153.3	"
Wind/Bighorn Rivers WY		67.1		0.0013	0.89 (59.33)	41.8	"
		68.6			1.56 (230.81)	162.6	"

TABLE 2.01 (continued)

Reach	Depth m	Width or Area m (m^2)	U* cm/sec	Slope	Velocity or Flow - m/sec (m^3/sec)	Longitudinal Dispersion Coefficient m^2/sec	Reference
Elkhorn R., NB		32.6		0.00073	0.34 (4.25)	9.3	"
John Day River		25.0		0.00355	(14.16)	13.9	"
OR		34.1		0.00135	(69.10)	65.1	"
Comite R.		12.5		0.00078	0.23 (0.99)	7.0	"
LA		15.9			0.35 (2.41)	13.9	"
Amite R.		36.6		0.00061	0.24 (8.64)	23.2	"
LA					0.36 (14.16)	30.2	"
Sabine R., LA		42.4		0.00015	0.57 (118.95)	316.0	"
		127.4			0.65 (389.41)	669.1	"
Yadkin R., NC		70.1		0.00044	0.44 (70.80)	213.8	"
Muddy Creek		13.4		0.00083	0.30 (3.96)	13.9	"
NC		19.5			0.38 (10.62)	32.5	"
Sabine R., TX		35.1		0.00018	0.18 (7.36)	39.5	McQuivey & Keefer, 1974
White R., IN		67.1		0.00036	0.30 (12.74)	30.2	"
Chattahoochee R. GA		65.5		0.0052	0.34 (0.03)	32.5	"
Susquehanna R. PA		202.7		0.00032	0.33 (0.10)	92.9	"
Miljacka R.,	0.285	11.28	5.5		0.342/1.02	2.22	Bajraktarevic, 1982
	0.3	8.6	6.6		0.368/1.02		"
	0.29	10.53	6.2		0.35/1.02	5.66	"
	0.295	12.0	49		0.332/1.02	0.07	"
Uvas Creek, CA		(0.3)			(0.0125)	0.12	Bencala & Walters, 1983
		(0.45)			(0.0125)	0.48	"
		(0.30)			(0.0125)	0.12	"
		(0.42)			(0.0125)	0.15	"
		(0.72)			(0.0133)	0.24	"
		(0.82)			(0.0136)	0.31	"
		(2.08)			(0.0140)	0.40	"
Copper Creek, VA	0.49	15.9			(1.53)	19.5	Fischer, 1968
	0.85	18.3			(8.50)	21.4	"
	0.49	16.2			(1.36)	9.5	"
	0.40	18.6			(13.68)	9.9	"
Clinch R., TN	0.85	47.0			(9.15)	13.9	"
	2.13	59.5			(84.96)	53.9	"
	2.10	53.4			(50.98)	46.5	"
Powell R., TN	0.85	33.8			(3.96)	9.5	"
Clinch R., VA	0.58	36.0			(6.80)	8.1	"
Coachella Canal, CA	1.55	24.4			(26.90)	9.6	"

TABLE 2.02. VERTICAL DISPERSION COEFFICIENT FOR LAKES ACROSS THERMOCLINE

Site	Month	Vertical Dispersion cm^2/sec	Thermocline Depth m	Data from	Reference
Lake Zurich, Switz.	April	0.71	5	temp	Li, 1973
	May	0.14	10	temp	"
	June	0.064	10	temp	"
	July	0.039	12.5	temp	"
	Aug	0.026	10	temp	"
	Sept	0.020	10-12.5	temp	"
	Oct	0.074	20	temp	"
L. Greifensee, Switz.		0.25	10	PO_4	Imboden & Emerson, 1978
L. Baldeggersee, Switz.	May	0.0021	9	temp	Imboden, et al., 1979
(limno-corral)	June	0.08	8	temp	"
	July	0.003	7-9	temp	"
	Aug	0.08	7-9	temp	"
	Sept	0.0013	9	temp	"
	June	0.08	7	Rn	"
	Aug	0.09	6	Rn	"
	Sept	0.05	9.5	Rn	"
	Oct	0.05	9.5	Rn	"
L. Onondaga Lake, N.Y.	May	0.04	11.5	temp	Wodka, et al., 1983
	June	0.09	10.5	temp	"
	July	0.03	11.5	temp	"
	Aug	0.005	11.5	temp	"
	Sept	0.008	12.5	temp	"
	Oct	0.015	--	temp	"
L. Baikal, U.S.S.R.		2.5-7.4		temp	Snodgrass & O'Melia, 1975
L. Tahoe, Nevada		0.178		temp	"
L. Ontario		0.125, 0.063		temp	"
L. Cayuga, N.Y.		0.178, 0.25		temp	"
L. Luzern, Switz.		0.10		temp	"
L. Zurich, Switz.		0.03		temp	"
L. Washington, WA		0.03		temp	"
L. Tiberias, Israel		0.063		temp	"
L. Sammamish, WA		0.03		temp	"
L. ELA 305, Ontario		0.01		temp	"
L. Mendota, WI		0.025		temp	"

TABLE 2.02 (continued)

Linsley Pond, CT		0.003		temp	"
ELA 240, Ontario		0.004		temp	"
ELA 227, Ontario		0.003		temp	"
Cayuga Lake, NY		0.253	21	temp	Powell & Jassby, 1974
Castle Lake, CA	July	0.011	6	temp	Jassby & Powell, 1975
	July	0.0091	6	temp	"
	July	0.0069	7	temp	"
	July	0.0068	7	temp	"
	July	0.0068	7	temp	"
	July	0.0042	7	temp	"
	August	0.0004	9	temp	"
	August	0.0062	9	temp	"
	August	0.0041	9	temp	"
	August	0.0061	9	temp	"
	August	0.0036	9	temp	"
	August	0.0076	9	temp	"
	Sept	0.0077	9	temp	"
ELA 227, Ontario		0.0017	8	tritium	Quay, et al., 1980
ELA 224, Ontario		0.018	18	tritium	"
Lake Valencia, Venezuela		0.114	20	temp 1983	Lewis, Jr.,
Lake Erie		0.21	16	δ^3 He	Torgersen, et al., 1977

TABLE 2.03. WHOLE LAKE AVERAGE VERTICAL DISPERSION COEFFICIENT

Site	Month	Vertical Dispersion cm^2/sec	Data from	Reference
Lake Erie		0.58	δ^3 He	Torgersen, et al., 1977
Lake Huron		1.16	δ^3 He	"
Lake Ontario		3.47	δ^3 He	"
Wellington Reservoir, Australia		1.00	temp	Imberger, et al., 1978
White Lake, MI		0.4		Lung & Canale, 1977
Lake LBJ, Texas	Feb-April	0.18	temp	Park & Schmidt, 1973
	May-June	0.12	temp	"
	July-Jan	0.01	temp	"
Lake Erie		15	temp	Heinrich, et al., 1981
Lake Huron	(no stratification)	1.16	temp	DiToro & Matystik, 1979
Lake Erie	Unstratified	102		DiToro & Conolly, 1980
	stratified	0.05-0.25		"
	fall turnover			"
Cayuga Lake		2.31	temp	Bedford & Babajimopoulos, 1977
L. Greifensee	April	0.2	^{222}Rn	Imboden, 1979
	May-Aug	0.15	^{222}Rn	"
	Sept-Nov	0.05	^{222}Rn	"

Modeling hydrophobic chemical contaminants (e.g., DDT, PCB, kepone, dioxin, dieldrin) that are strongly sorbed to sediments requires knowledge of the diffusion and release rates from contaminated sediments into overlying waters. Radio-tracers that occur naturally and from bomb-testing have been used with success in analyzing sediment pore-water diffusion rates. Table 2.04 reports some values found in the literature. Most pore water diffusion coefficients are on the order of molecular diffusion coefficients ($\sim 10^{-5}$ cm^2/sec) or smaller. Bioturbation by benthic fauna or fish may significantly increase pore water transfer to overlying water.

TABLE 2.04. INTERSTITIAL SEDIMENT PORE WATER DIFFUSION COEFFICIENTS

Site	Vertical Dispersion cm^2/sec	Data from	Reference
White Lake, MI	2×10^{-6}		Lung & Canale, 1977
Lake Erie	4×10^{-6}	^{90}Sr	Lerman & Lietzke, 1975
	2×10^{-5}	^{137}Cs	"
Lake Ontario	2×10^{-5}	^{90}Sr	"
	2×10^{-6}	^{90}Sr	"
	2×10^{-5}	^{137}Cs	"
Green Bay, Lake Michigan	1.3×10^{-7}	^{210}Pb	Christensen, 1982
	6.3×10^{-9}	^{210}Pb	"
L. Greifensee	10^{-10}	^{230}Th	Imboden & Emerson, 1976
	10^{-9}	^{226}Ra	"
	0.8×10^{-5}	^{222}Rn	"

2.3 COMPARTMENTALIZATION

2.3.1 Choosing a Transport Model

It is possible to estimate the relative importance of advection compared to dispersion with the Peclet number:

$$Pe = uL/K \tag{2.9}$$

in which Pe = Peclet number, dimensionless

u = mean velocity, L/T

L = segment length, L, and
K = dispersion coefficient, L^2/T.

If the Peclet number is significantly greater than 1.0, advection predominates; if it is much less than 1.0, dispersion predominates in the transport of dissolved, conservative substances.

If there is a significant transformation rate, the reaction number can be helpful:

$$\text{Rxn No.} = \frac{kK}{u^2} \tag{2.10}$$

where k is the first order reaction rate constant, T^{-1}. If the reaction number is less than 0.1, then advection predominates and a model approaching plug flow is appropriate. If the reaction number is greater than 10, then dispersion controls the transport and the system is essentially completely mixed. Otherwise a plug flow with dispersion model or a number of compartments in series will best simulate the prototype water body.

2.3.2 Compartmentalization

Compartmentalization refers to the segmentation of model ecosystems into various "completely mixed" boxes of known volume and interchange. Interchange between compartments is simulated via bulk dispersion or equal counterflows between compartments. Compartmentalization is a popular assumption in pollutant fate modeling because the assumption of complete mixing reduces the set of partial differential equations (in time and space) to one of ordinary differential equations (in time only). Nevertheless, it is possible to recover some coarse spatial information by introducing a number of interconnected compartments.

A completely mixed flow-through (CMF) compartment contains an ideal mixing of fluid in which turbulence is so large that no concentration gradients can exist within the compartment. This corresponds to the assumption that $K_{x,y,z} = \infty$. Equation (2.3) reduces to:

Accumulation of Mass w/in Compartment j	=	Mass Inflows to j	+	Dispersive Inflows to j	-	Mass Outflows from j	-	Dispersive Outflows from j	-	Transformation Reactions within j

$$V_j \frac{dC_j}{dt} = \sum_{k=1}^{n} Q_{j,k}C_k + \sum_{k=1}^{n} Q'_{j,k}C_k - \sum_{k=1}^{n} Q_{k,j}C_j - \sum_{k=1}^{n} Q'_{k,j}C_j - kC_jV_j \tag{2.11}$$

in which V_j = volume of j compartment, L^3
C_j = concentration within j compartment, M/L^3
t = time, T
n = number of adjacent compartments to j
$Q_{j,k}$ = inflow from compartment k to compartment j, L^3/T
C_k = concentration in compartment k, M/L^3
$Q'_{j,k}$ = dispersive (interchange) flow from k to j, L^3/T
$Q_{k,j}$ = outflow from j to k, L^3/T

$Q'_{k,j}$ = dispersive (interchange) flow from j to k, L^3/T
k = pseudo-first order rate constant for transformation, T^{-1}

and $Q'_{j,k}$ = $Q'_{k,j}$ a symmetric matrix with zero diagonal.

Equation (2.11) can be rewritten in terms of bulk dispersion coefficients:

$$V_j \frac{dC_j}{dt} = \sum_{k=1}^{n} Q_{j,k}C_k - \sum_{k=1}^{n} Q_{k,j}C_j + \sum_{k=1}^{n} K'_{j,k}A_{j,k}(C_k-C_j)/\ell_{j,k} - kC_jV_j \qquad (2.12)$$

where K' = bulk dispersion coefficient, L^2/T
$A_{j,k}$ = interfacial area between compartments j and k, L^2, and
$\ell_{j,k}$ = distance between midpoints of compartments, L.

There is one mass balance equation (e.g. equation 2.12) for each of j compartments. This set of ordinary differential equations is solved simultaneously by numerical computer methods.

Bulk dispersion coefficients between compartments are dependent on the scale chosen for the compartments. They are not equivalent to measured dispersion coefficients from dye studies, which are usually derived from the continuous partial differential equations. The very nature of the compartmentalized system introduces considerable mixing into the model. Such mixing or numerical dispersion is in addition to the bulk dispersion specified by the bulk dispersion coefficient.

Streams and swift-flowing rivers may approach a 1-D plug flow system (i.e. the water is completely mixed in the lateral and vertical dimensions, but there is no mixing in the longitudinal dimension). In an ideal plug flow system, the longitudinal dispersion coefficient is equal to zero because no forward or backward mixing occurs. For this case, an infinite number of compartments (of infinitestimal length in the longitudinal direction) would be required in order to produce zero longitudinal mixing. Because it is impossible to specify an infinite number of compartments, one chooses a finite number of compartments and accepts the artificial dispersion that accompanies that choice. One method of estimating the artificial or numerical dispersion of a compartmentalized model for an ideal, plug flow system is given by equation (2.13).

$$E_x = \frac{u\Delta x}{2}\left(1 - \frac{u\Delta t}{\Delta x}\right) \qquad (2.13)$$

where E_x = artificial numerical dispersion coefficient, L^2/T
u = mean longitudinal velocity, L/T
Δx = longitudinal length of equally spaced compartments, L, and
Δt = time step for numerical computation, T.

One approach would be to set the artificial dispersion coefficient equal to the measured or estimated dispersion coefficient from equation (2.4). With this approach, it is not necessary to use bulk dispersion

coefficients; rather, one allows the artificial dispersion of the model to account for the actual dispersion of the prototype.

Another approach is to adjust the time step to minimize E_x while preserving stability:

$$\Delta t = \min_i \left(\frac{\Delta x_i}{U_i}\right)$$

where i refers to the physical compartments.

In general, most river simulations require many compartments due to their nearly plug flow nature, as indicated by their large Peclet number (equation 2.9). The greater the number of compartments, the greater the tendency towards plug flow conditions. It is a poor practice to simulate a riverine environment with one completely mixed compartment.

Lakes, reservoirs, and embayments may require a number of compartments if one desires some spatial detail, such as concentration profiles. These compartments should be chosen to relate to the physical and chemical realities of the prototype. For example, a logical choice for a stratified lake is to have two compartments: an epiliminion and a hypolimnion (Figure 2.03). Mixing between compartments can be accomplished by interchanging flows:

$$J = Q_{ex}C_{epi} - Q_{ex}C_{hypo} \qquad (2.14)$$

or

$$= Q_{ex}\,(C_{epi} - C_{hypo})$$

where J = net mass flux from epilimnion to hypolimnion due to vertical mixing, M/T
Q_{ex} = exchange flow, L^3/T, and
C = concentration of organic, M/L^3.

The magnitude of the interchange flow, Q_{ex}, can be determined from tracer studies or from temperature profiles and simulations. Bulk dispersion coefficients can then be calculated based on the interchange flow as $K' = Q_{ex}\ell_{epi/hypo}/A$, where $\ell_{epi/hypo}$ is the distance between centroids of two adjacent compartments.

Sometimes only coarse information is required for a given use of a model. The literature offers many examples of modeling efforts based on very simple transport models. The Great Lakes have often been simulated as single compartment, completely mixed lakes in series (O'Connor and Mueller, 1970; Chapra, 1977; Schnoor and O'Connor, 1980). Toxic chemical screening methodologies are usually based on organic chemical properties that are known only within an order of magnitude. In such cases it may not be necessary to simulate transport with great accuracy. A distinct trade-off exists between errors in transport formulations and errors in reaction rate constants as shown in Table 2.05. If the sum of the pseudo-first order reaction rate constant is accurately determined in the field or laboratory, then an accurate model simulation will require a realistic transport formulation. If the reaction rate constant and/or the detention time are

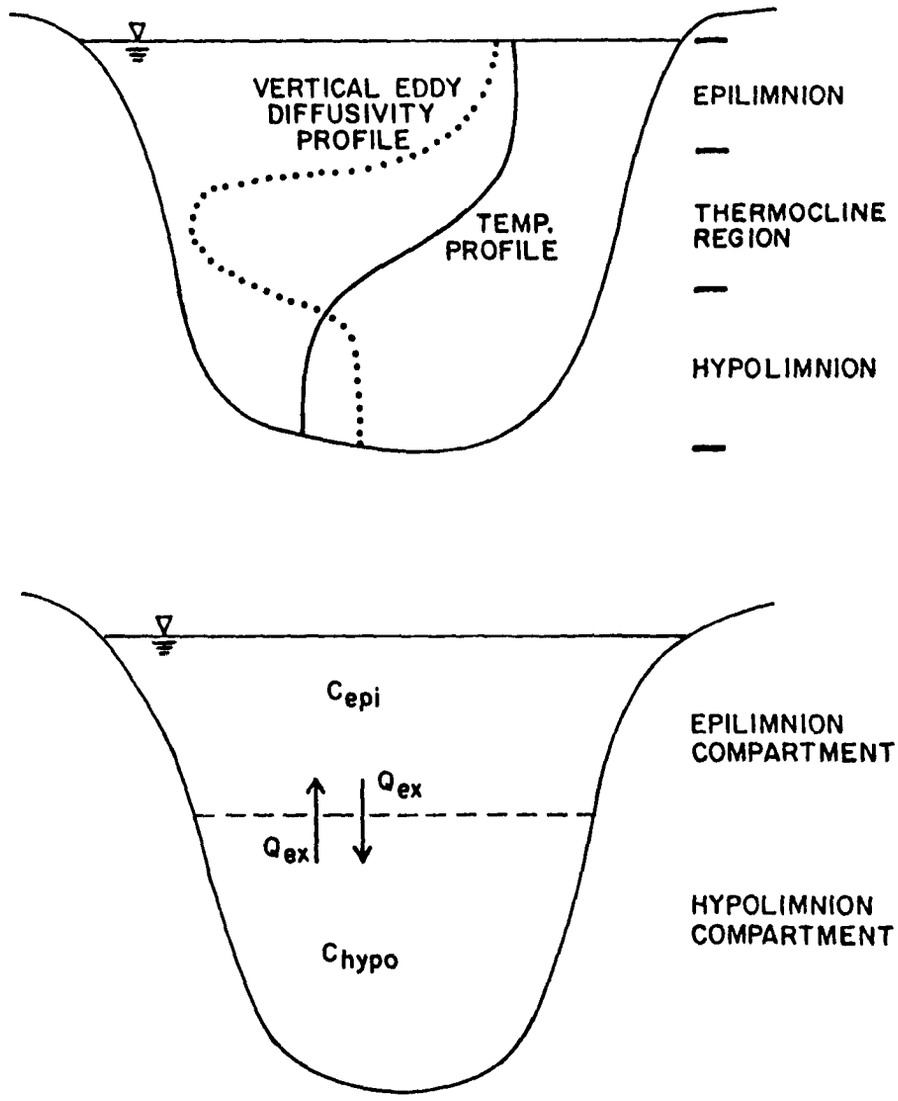

Figure 2.03. Thermal stratification in a lake and the assumption of mixing between two compartments.

low ($k\tau$ = 0.01), the choice of the number of compartments is not very critical. Errors in outflow concentration of greater than 10 percent will occur, however, if the dimensionless number $k\tau$ becomes greater than 1.0.

For example, consider a hypothetical lake whose steady-state outlet concentration of a toxic chemical is determined to be 0.01 times the inflow concentration. Suppose the hydraulic detention time, τ, of the lake is 10 days, and the transformation reaction rate constant is determined to be 1.0/day ($k\tau$=10). The lake is behaving like three compartments in series according to Table 2.05. The model calibration, however, would have required a reaction rate constant of 10/day in order to obtain the observed result of C/Co = 0.01 if only the completely mixed compartment had been assumed.

TABLE 2.05. OUTFLOW CONCENTRATION DIVIDED BY INFLOW CONCENTRATION AT STEADY STATE AS A FUNCTION OF NUMBER OF COMPARTMENTS AND $k\tau$.

	C/Co VALUES				
	Rate Constant x Detention Time				
	$k\tau$=0.01	$k\tau$=0.1	$k\tau$=1	$k\tau$=10	$k\tau$=100
CMF* Completely Mixed (1-compartment)	0.99	0.91	0.50	0.09	0.01
3-compartment+	0.99	0.91	0.42	0.01	2×10^{-5}
10-compartment+	0.99	0.91	0.39	1×10^{-3}	4×10^{-11}
PF† Plug Flow (∞ compartment)	0.99	0.90	0.37	5×10^{-5}	4×10^{-44}

* $C/Co = 1/(k\tau+1)$ where τ = total hydraulic detention time
k = first order reaction rate constant

\+ $C/Co = 1/((k\tau/n)+1)^n$ where n = number of compartments

† $C/Co = \exp(-k\tau)$

If better than order-of-magnitude accuracy is required in the model, one should estimate the dispersion coefficients from dye studies, temperature simulations, or equations (2.4) through (2.8). This allows the proper compartmental configuration to be selected, including consideration of numerical dispersion based on equation (2.13).

2.4 SEDIMENT TRANSPORT

2.4.1 Partitioning

A chemical is partitioned into a dissolved and particulate adsorbed phase based on its sediment-to-water partition coefficient, K_p (Karickhoff et al., 1979). The dimensionless ratio of the dissolved to the particulate concentration is the product of the partition coefficient and the concentration of suspended solids, assuming local equilibrium:

$$Cp/C = K_p M \tag{2.15}$$

where Cp = particulate chemical concentration, μg/ℓ
C = dissolved chemical concentration, μg/ℓ
K_p = sediment/water partition coefficient, ℓ/kg, and
M = suspended solids concentration, kg/ℓ.

The particulate and dissolved concentrations can be calculated from knowledge of the total concentration, C_T, as stated in equations (2.16) and (2.17).

$$Cp = \frac{K_p M}{1 + K_p M} C_T \tag{2.16}$$

$$C = \frac{1}{1 + K_p M} C_T \tag{2.17}$$

These concentrations can be calculated for the water column or the bed sediment, by using the concentration of suspended solids in the water (M) or in the bed (M_b), where $M_b = M/n$, the bed sediment concentration in kg/ℓ of pore water, and n = the porosity of the bed sediment.

2.4.2 Suspended Load

The suspended load of solids in a river or stream is defined as a flow rate times the concentration of suspended solids, e.g., kg/day or tons/day; the mean load is greatly affected by peak flows. Peak flows cause large inputs of allochthonous material from erosion and runoff as well as increases in scour and resuspension of bed and bank sediment.

The average suspended load is not equal to the average flow times the average concentration, as stated in equation (2.18),

$$\overline{Q} \times \overline{C} \neq \overline{QC} \tag{2.18}$$

but is calculated as stated in equation (2.19):

$$\overline{QC} = (\overline{Q} \times \overline{C}) + \overline{Q'C'} \tag{2.19}$$

The mean fluctuation of mass, $\overline{Q'C'}$, is usually greater than the first term of equation (19) and contributes greatly to the average suspended load. These equations hold true for the mass of suspended solids as well as the mass of adsorbed chemical.

2.4.3 Bed Load

Several formulae have been reported to calculate the rate of sediment movement very near the bottom. These equations were developed for rivers and noncohesive sediments, i.e., fine-to-coarse sands and gravel. It is important to note that it is not sands, but rather silts and clays, to which most chemicals sorb. Therefore, these equations are of limited predictive value in environmental exposure assessments. Generally, bed load transport is a small fraction of total sediment transport (suspended load plus bed load). In estuaries, however, bed load transport of fine silts and clays may be an important contributor to the fate of chemical contaminants. Unfortunately, predictive equations have not been developed for bed load transport in such applications. Bed load consists of those particles that creep, flow, or saltate very near to the bottom (within a few particle diamters). Figure 2.04 is a schematic of bed load and suspended load in a stream or river.

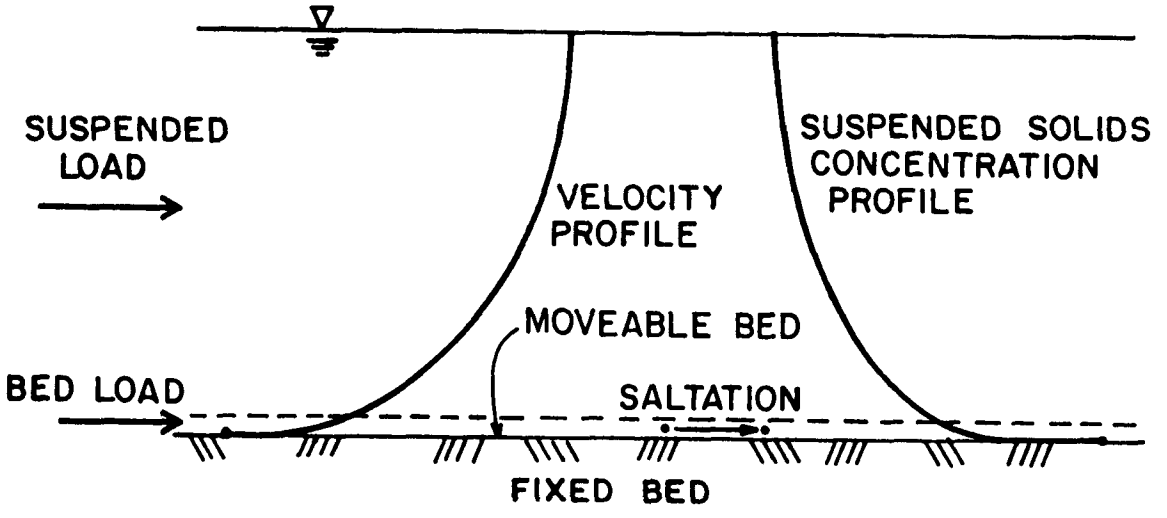

Figure 2.04. Suspended Load and Bed Load. Bed load is operationally defined as whatever the bed load sampler can measure. Bed load occurs within a few millimeta of the fixed bed.

2.4.4 Sedimentation

Suspended sediment particles and adsorbed chemicals are transported downstream at nearly the mean current velocity. In addition, they are transported vertically downward by their mean sedimentation velocity. Generally, silt and clay-size particles settle according to Stoke's Law, in proportion to the square of the particle diameter and the difference between sediment and water densities:

$$W = 8.64 \left(\frac{g}{18\mu}\right) (\rho_s - \rho_w)\, d_s^{\,2} \qquad (2.20)$$

in which

W = particle fall velocity, ft/sec

ρ_s = density of sediment particle, 2-2.7 g/cm^3

ρ_w = density of water, 1 g/cm^3

g = gravitational constant, 981 cm/sec^2

d_s = sediment particle diameter, mm

μ = absolute viscosity of water, 0.01 poise (g/cm-sec) @ 20°C

Generally, it is the washload (fine silt and clay-size particles) that carries most of the mass of adsorbed chemical. These materials have very small fall velocities, on the order of 0.3-1.0 m/day for clays of 2-4 μm nominal diameter and 3-30 m/day for silts of 10-20 μm nominal diameter.

Once a particle reaches the bed, a certain probability exists that it can be scoured from the bed sediment and resuspended. The difference between sedimentation and resuspension represents net sedimentation. Often it is possible to utilize a net sedimentation rate constant in a pollutant fate model to account for both processes. In many ecosystems where the bed is aggrading, sedimentation is much larger than resuspension (Schnoor and McAvoy, 1981). The net sedimentation rate constant can be calculated as follows

$$k_s = \frac{W}{H} - k_u \approx \frac{W}{H} \tag{2.22}$$

where k_s = net sedimentation rate constant, 1/T

W = mean particle fall velocity, L/T

H = mean depth, L, and

k_u = scour/resuspension rate constant, 1/T.

2.4.5 Scour and Resuspension

Quantitative relationships to predict scour and resuspension of cohesive sediments are difficult to develop due to the number of variables involved. Sayre and Chang (1968) reported on the vertical scour and dispersion of silt particles in flumes. Di Toro et al. (1982) recommended a resuspension velocity (W_{rs}) of about 1 to 30 mm/yr based on model calibration studies. The turbulent vertical eddy diffusivity for sediment (ε_s) is also related to the scour coefficient and/or resuspension velocity.

Under steady-state conditions, the sedimentation of suspended sediment must equal the scour and resuspension of sediment.

$$w\bar{C} + \varepsilon_s \frac{\partial \bar{C}}{\partial z} = 0 \qquad (2.23)$$

where w = sedimentation velocity, L/T
ε_s = suspended sediment vertical eddy diffusivity, L^2/T, and
$\bar{C}$ = concentration of suspended sediment, M/L^3.

Under time-varying conditions, however, the boundary condition at the bed-water interface is more complex. According to Onishi and Wise (1979), the following equation applies, based on the work of Krone (1962) and Partheniades (1965).

$$pw\bar{C} + \varepsilon_s \frac{\partial \bar{C}}{\partial z} = S_D - S_R \qquad (2.24)$$

where p = probability that descending particle will "stick" to the bed

$$S_D = \frac{2w\bar{C}}{h}\left(1 - \frac{\tau_o}{\tau_{cD}}\right) = \text{rate of bed deposition, } M/L^2\text{-}T$$

$$S_R = M_j\left(\frac{\tau_o}{\tau_{cR}} - 1\right) = \text{rate of bed scour, } M/L^2\text{-}T$$

M_j = erodibility coefficient, M/L^2-T
τ_{cR} = critical bed shear required for resuspension, $M/L\text{-}T^2$
τ_{cD} = critical bed shear stress which prevents deposition, $M/L\text{-}T^2$, and
h = ratio of depth of water to depth of active bed layer.

Equation (2.24) shows that the bed can either be aggrading or degrading at any time or location depending on the relationship between S_D and S_R.

2.4.6 Desorption/Diffusion

In addition to sedimentation and scour/resuspension, an adsorbed chemical can desorb from the bed sediment. Likewise dissolved chemical can adsorb from the water to the bed. Both pathways can be presented by a diffusion coefficient (K_b) and a concentration gradient or difference between pore water and overlying dissolved chemical concentrations.

Sediment mass balances must include terms for advection, sedimentation, scour/resuspension, and possibly vertical or longitudinal dispersion. At the bottom, bed load movement may be included. Processes that affect the fate of dissolved substances include desorption from the bed (or adsorption from the water column), advection, dispersion, and transformation reactions. Adsorbed particulate chemical is removed from the water column by sedimentation and returned to the water column by scour. Models used to evaluate transport and transformation should include these processes.

Often, it is possible to neglect the kinetics of adsorption and desorption in favor of a local equilibrium assumption. Over the time scales of interest, this may be a good assumption. Bed load movement is sometimes small relative to wash load movement and can be neglected. Under steady-state conditions, net sedimentation rates are often used to simplify the

transport of sedimentation and scour. All of these assumptions have their applications but should be carefully considered in each model application.

2.5 LAKE DISPERSION CALCULATIONS

The steps for calculating vertical dispersion across the thermocline in a lake from temperature data are presented below for three different methods. These methods were derived from the heat dispersivity equation, assuming that E does not vary much with depth over the region of interest, particularly the thermocline:

$$\frac{d\theta}{dt} = E \frac{d^2\theta}{dx^2} \tag{2.25}$$

where θ is temperature, t is time, E is thermal dispersivity, and x is distance. It is assumed that no heat has entered the lower part of the water column under consideration by any mechanism other than vertical turbulent transport, E. The assumption is made that mass transfer through dispersion occurs at the same rate as heat transfer. The analogy is applied by substituting concentration or mass (c) into the equation, thus

$$\frac{dc}{dt} = E \frac{d^2c}{dx^2} \tag{2.26}$$

For more information on the theory, the reader is referred to G. Evelyn Hutchinson, (1957). Actual data are presented for Lake Clara, Wisconsin, and Linsley Pond, Connecticut.

2.5.1 McEwen's Method

This method of computing lake dispersion is based on fitting an exponential curve to the mean temperature data in the thermocline and hypolimnion. If the data are of a linear or otherwise nonexponential shape, this method is inappropriate. The reader is referred to Hutchinson (1941). Two examples are provided for Lake Clara, Wisconsin, in the summer of 1982 and Linsley Pond, Connecticut.

Step 1: Compile temperature data by date and depth (see Figure 2.05 and Table 2.06).

Step 2: Average temperature data at each depth for the period June-August: $\bar{\theta}_z$. $\bar{\theta}_z$ vs. depth is plotted in Figure 2.06.

Step 3: Compute the change in temperature over the summer data period at each depth: $\Delta\theta_z/\Delta t$.

Step 4: Compute C

a (graphical): C is the temperature that the data approach in the hypolimnion (see Figure 2.06).

b (computational): Find C by linear regression using

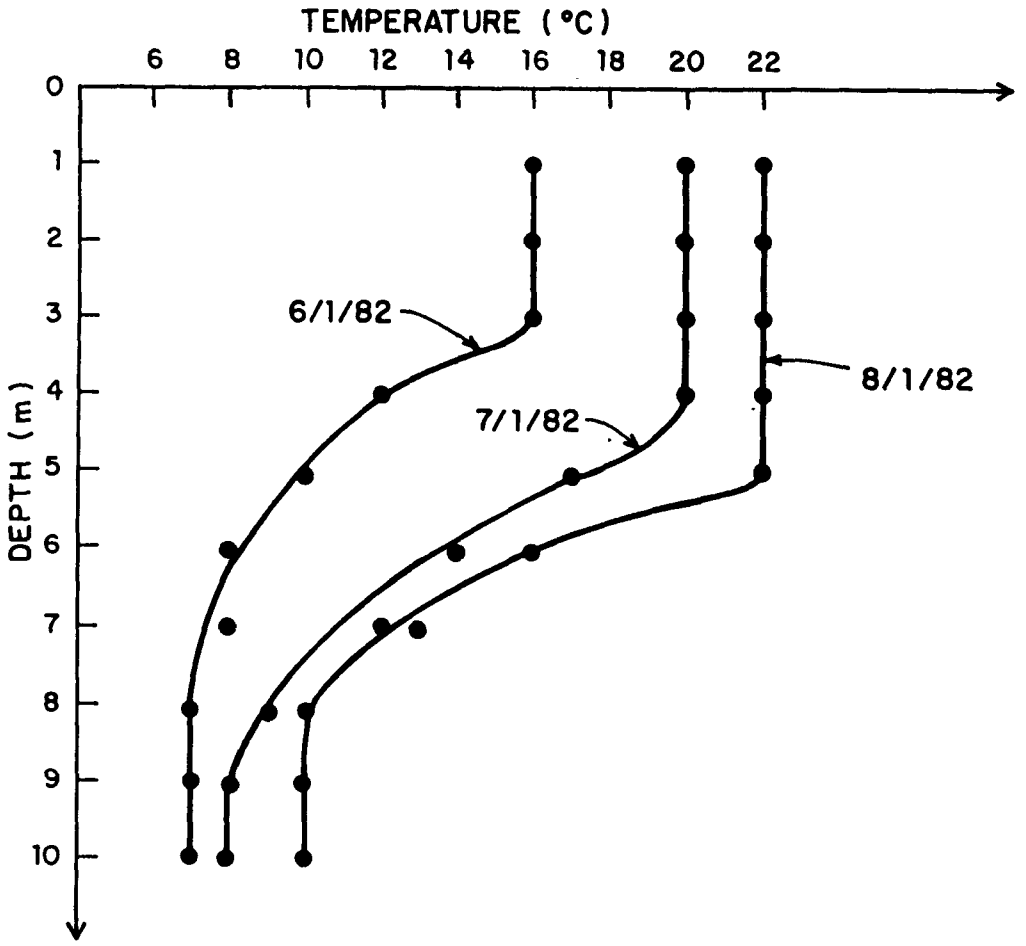

Figure 2.05. Lake Clara, Wisconsin, temperature profile - Summer 1982.

TABLE 2.06 LAKE CLARA TEMPERATURE DATA

Depth (m)	6/1/82 (°C)	7/1/82 (°C)	8/1/82 (°C)	$\bar{\theta}$ (°C)	$\Delta\theta/\Delta t$ (°C/month)
1	16	20	20	18.67	2.00
2	16	20	20	18.67	2.00
3	16	20	20	18.67	2.00
4	12	20	20	17.33	4.00
5	10	17	20	15.67	5.00
6	8	14	16	12.67	4.00
7	8	12	13	11.00	2.50
8	7	9	10	8.67	1.50
9	7	8	10	8.33	1.50
10	7	8	10	8.33	1.50

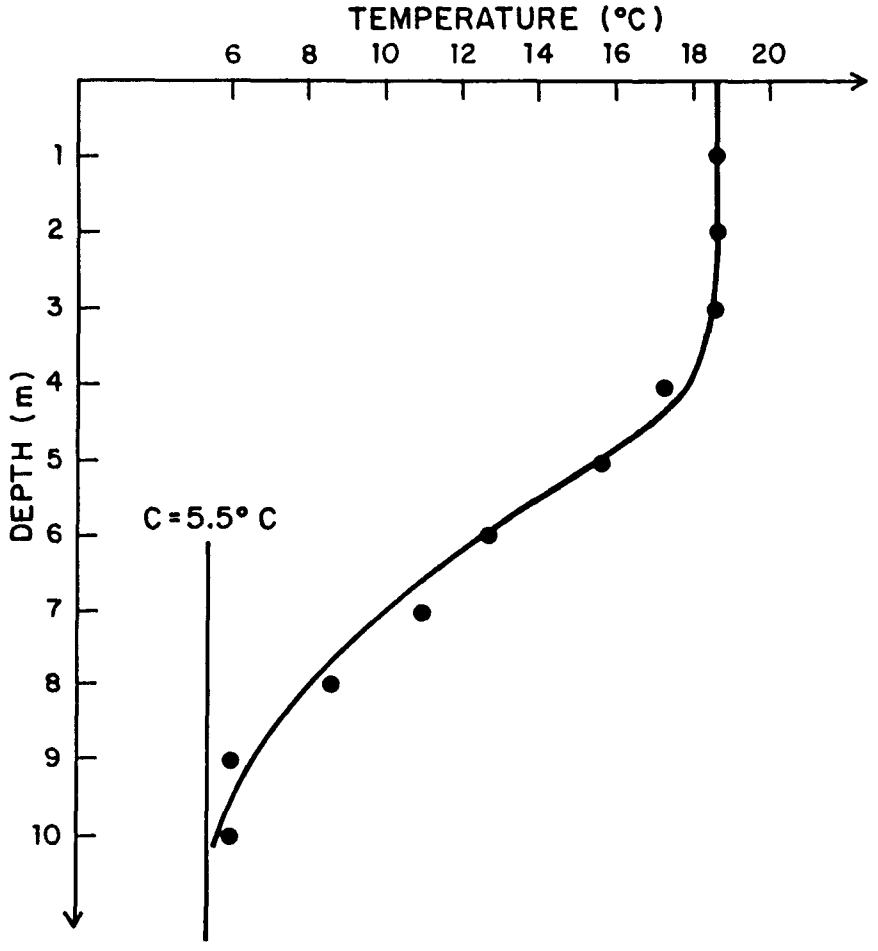

Figure 2.06.Lake Clara average summer temperature profile - 1982.

TABLE 2.07 LINSLEY POND TABULATIONS TO FIND C AND b

z (m)	$\bar{\theta}$ (°C)	$\Delta\theta$ (°C)
4	17.68	4.51
5	13.17	2.49
6	10.67	1.70
7	8.98	0.88
8	8.10	0.59
9	7.50	0.22

C = 6.82, b = 2.42

$$\bar{\theta}_z = C + b\Delta\theta$$

where $\Delta\theta = \bar{\theta}_{z-1} - \bar{\theta}_z$ (see Table 2.07)

Step 5: Compute a and C_1

a (graphical): plot $(\bar{\theta} - C)$ vs. z and $\Delta\theta/\Delta t$ vs. z on semi-log paper (see Figures 2.07 and 2.08). In the thermocline region, the two curves should be parallel. The line tangent to the $(\bar{\theta} - C)$ curve at the thermocline will have slope a and y-intercept C_1. (Note: to find base e slope on semi-log paper, find the change in z over one complete log cycle, i.e., z_1 at y = 10 and z_2 at y = 1).

$$a = 2.303/(z_2 - z_1)$$

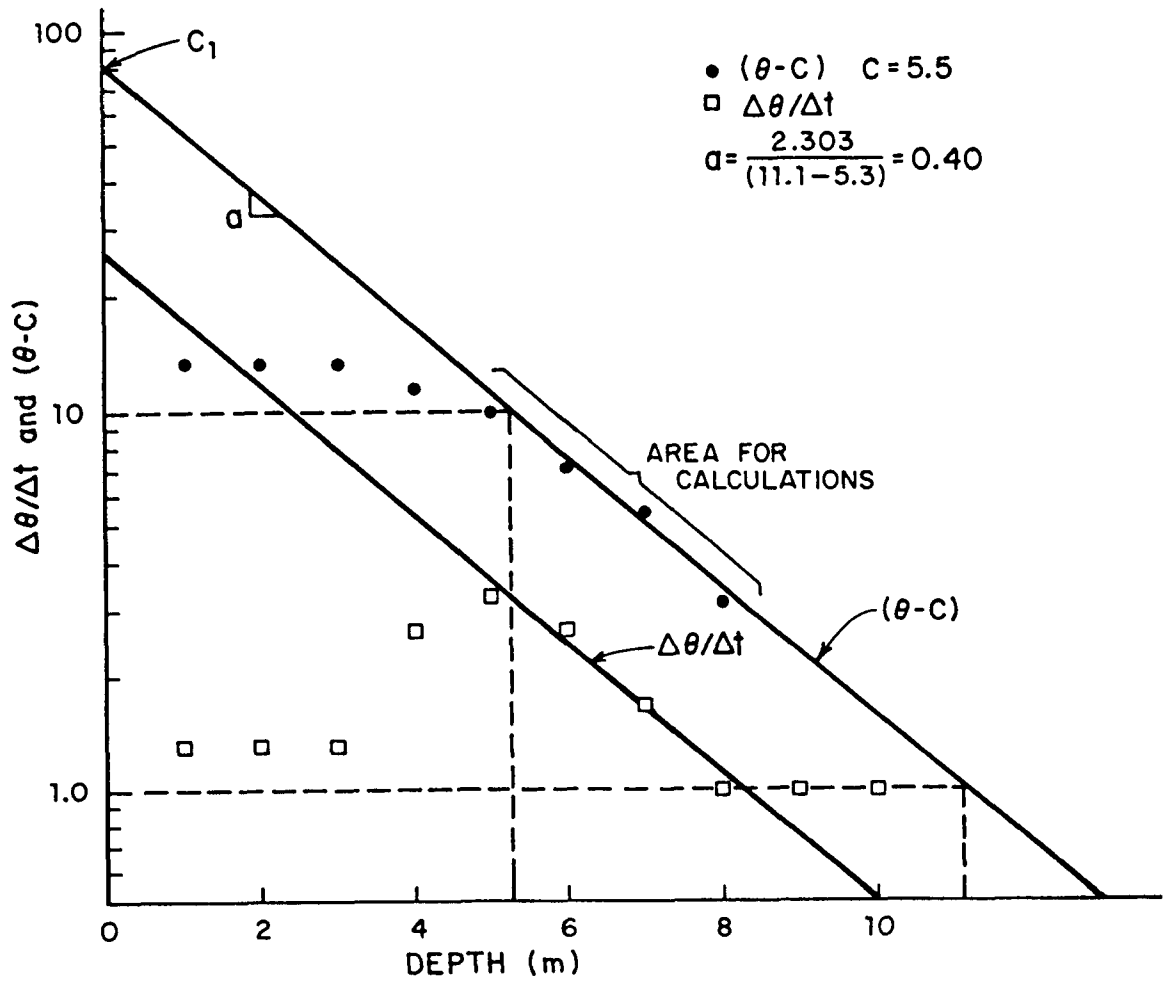

Figure 2.07. Graphical method to find a and C_1 (Lake Clara).

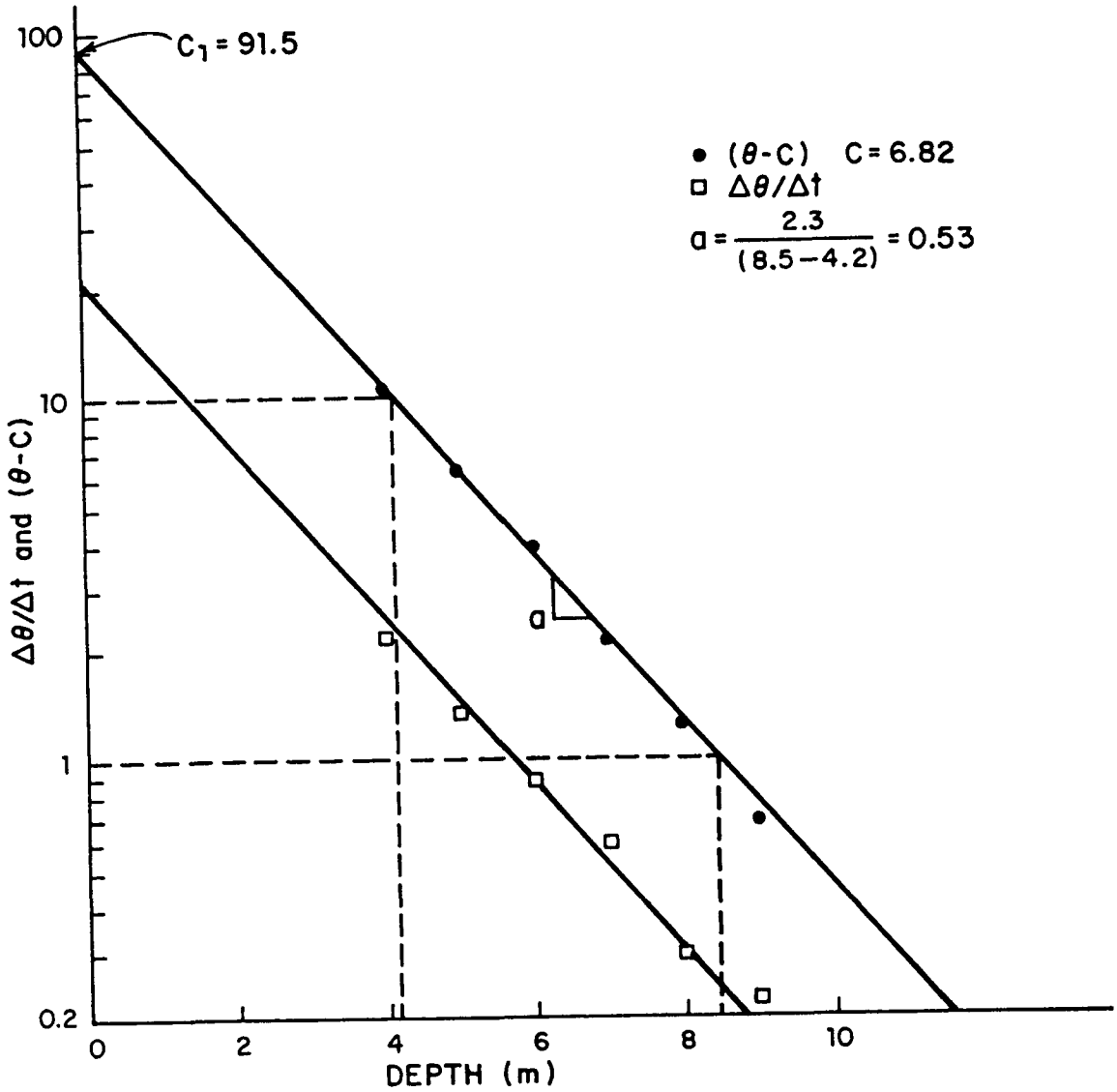

Figure 2.08. Graphical method to find a and C_1 (Lindley Pond).

b (computational):

$$a = -\ln (1 - 1/b)$$

$$C_1 = \frac{\Sigma (\bar{\theta} - C)}{\Sigma e^{-az}}$$ in the thermocline region.

Parallelism tests two parameters: (i) whether E is constant, and (ii) whether C_1 and "a" reasonably describe the temperature curve. If these curves are not parallel, one or both of the assumptions does not hold for the data set, and McEwen's method should not be used.

Step 6: Compute dispersion coefficient E (see Tables 2.08 and 2.09).

TABLE 2.08 LAKE CLARA DISPERSION COEFFICIENT

z	$\Delta\theta/\Delta t$	$C_1 a^2 e^{-az}$	$E = \frac{\Delta\theta/\Delta t}{C_1 a^2 e^{-az}}$
5	5.00	1.73	2.89
6	4.00	1.16	3.45
7	2.50	0.78	3.21
8	1.50	0.52	2.88

C_1 = 80°C E = 3.11 m^2/month

a = 0.4/m = 0.0118 cm^2/sec

TABLE 2.09 LINSLEY POND DISPERSION COEFFICIENT

z	$\Delta\theta/\Delta t$	$C_1 a^2 e^{-az}$	$E = \frac{\Delta\theta/\Delta t}{C_1 a^2 e^{-az}}$
4	2.21	3.08	0.72
5	1.37	1.82	0.76
6	0.88	1.06	0.83
7	0.60	0.63	0.95
8	0.30	0.37	0.81
9	0.22	0.22	1.02

C_1 = 91.5°C E = 0.85 m^2/month

a = 0.53/m = 0.0032 cm^2/sec

2.5.2 Second Derivative Method

Make a table of the following format

z	$\bar{\theta}$	$\Delta\bar{\theta}/\Delta z$	$\Delta(\Delta\bar{\theta}/\Delta z)/\Delta z$	$\Delta\theta/\Delta t$	E
(1)	(2)	(3)	(4)	(5)	(6)

(see Tables 2.10 and 2.11) where column (2) is the average summer temperature at each depth, column (3) is equal to $\bar{\theta}_{z-1} - \bar{\theta}_z$ (as z is measured from the water surface down), and column (4) is similar to (3); one calculates the difference between $(\Delta\bar{\theta}/\Delta z)_{z-1}$ and $(\Delta\bar{\theta}/\Delta z)_z$. Column (5) is

the change in temperature over the summer period at each depth. The method assumes that heat is transferred by vertical eddy conductivity (dispersion) and that there are no sources or sinks of heat within the vertical distance (z), only dispersive transport.

TABLE 2.10 LAKE CLARA SECOND DERIVATIVE METHOD

z (m)	$\bar{\theta}$ (°C)	$\Delta\bar{\theta}/\Delta z$ (°C/m)	$\Delta(\Delta\bar{\theta}/\Delta z)/\Delta z$ (°C/m^2)	$\Delta\theta/\Delta t$ (°C/month)	E (m^2/month)
1	18.67			2.00	
		0.00			
2	18.67			2.00	
		0.00			
3	18.67			2.00	
		1.34			
4	17.33		-0.32	4.00	-12.50
		1.66			
5	15.67		-1.34	5.00	-3.73
		3.00			
6	12.67		1.33	4.0	3.01
		1.67			
7	11.00		-0.66	2.50	-3.79
		2.33			
8	8.67		2.00	1.50	0.75
		0.34			
9	8.33			1.50	
		0.00			
10	8.33			1.50	
					E = -3.25 m^2/month
					= 0.0122 cm^2/sec

TABLE 2.11 LINSLEY POND SECOND DERIVATIVE METHOD

z (m)	$\bar{\theta}$ (°C)	$\Delta\bar{\theta}/\Delta z$ (°C/m)	$\Delta(\Delta\bar{\theta}/\Delta z)/\Delta z$ (°C/m^2)	$\Delta\theta/\Delta t$ (°C/month)	E (m^2/month)
4	17.68			2.21	
		4.51			
5	13.17		2.00	1.37	0.68
		2.51			
6	10.67		0.82	0.88	1.08
		1.69			
7	8.98		0.81	0.60	0.73
		0.88			
8	8.10		0.28	0.30	1.06
		0.60			
9	7.40			0.22	
					E = 0.88 m^2/month
					= 0.0034 cm^2/sec

The dispersion coefficient is calculated from

$$E = \frac{\Delta\theta/\Delta t}{\dfrac{\Delta(\Delta\bar{\theta}/\Delta z)}{\Delta z}} \tag{2.27}$$

One notes that the dispersion coefficient for Lake Clara is negative, which is meaningless and indicates that this method should be discarded and McEwen's method used for this particular lake. Hutchinson (1941) points out that "any errors in the original data are apt to produce inflection points in the temperature curve. Such inflection points cause ... changes of sign in the second [derivative]." There was good agreement in the calculated dispersion coefficient between both methods for Linsley Pond.

2.5.3 Heat Budget Method

The vertical thermal dispersivity also can be estimated from the total heat entering and leaving the lake. A number of field measurements are necessary (pyroheliometer data, air temperature) as well as temperature profiles throughout the lake. A heat budget method results in vertical dispersion coefficients that are both a function of depth and time, E = f(z,t). The reader is referred to G.G. Park and P.S. Schmidt, 1973, "Heat dissipation in a power plant cooling bay," ASME Winter Annual Meeting, New York, New York for further details on the heat budget method.

The basic equation is based on heat transfer and is formulated similar to a mass balance:

$$\frac{d(V_j\theta_j)}{dt} = (Q_{ij}\theta_{ij} - Q_{oj}\theta_{oj}) + (Q_{vj}\theta_{j-1} - Q_{vj+1}\theta_j) - (E_j a_j/\Delta z)(\theta_j - \theta_{j-1}) + (E_{j+1}a_{j+1}/\Delta z)(\theta_{j+1} - \theta_j) + V_j h_{net}/(\rho)c\Delta z \quad (2.28)$$

where V_j is the volume of the jth slice (m^3), θ_j is the mean temperature in the jth slice (°C), Q_i and Q_o are inflows and outflows to slice j, respectively, as θ_o and θ_i are the temperatures associated with those flows (Q in m^3/sec and θ in °C), Q_{vj} is the vertical flow rate at the bottom of the jth element, where upward flow is positive (m^3/sec), E_j is the dispersion across the bottom of slice j (cm^2/sec), a_j is the bottom surface area of slice j (m^2), t is time (sec), h_{net} is the net heat flux(cal/sec-cm^3), (ρ) is density (g/cm^3), c is specific heat (cal/g-°C), and Δz is the thickness of a slice, which must be the same for all slices (m).

The heat flux at the surface, h', equals $h_{net}/\Delta z$, and

$$h_{net} = \beta h_s + h_a - h_b - h_e + j_c \quad (2.29)$$

where β is the fraction of short-wave radiation absorbed at the surface, h_s is short-wave radiative flux, h_a is long-wave or atmospheric radiative flux, h_b is back radiation, h_e is evaporative energyflux, and h_c is convective energyflux.

The net heat flux to the jth slice is

$$h_{net} = h_j' \Delta z \quad (2.30)$$

Below the surface, only short-wave radiation is absorbed. In deeper slices, h_j' is an exponential function of depth. The quantity of solar radiation absorbed by the jth element, is expressed as

$$h_j' = \frac{\Phi_{j+1}\, a_{j+1} - \Phi_j\, a_j}{(a_j + a_{j+1})/2\Delta z} \quad (2.31)$$

where

$$\Phi(z) = (1 - \beta)\, h_s \exp\,[-(h)\,(z_n - z)]$$

and β and h_s are defined above. The short-wave radiative flux can be estimated from pyroheliometer data (where the field data are given in cal/cm^2--sec), and β is 0.4. (h) is the exponential decay constant for the absorption of solar raidation with depth, z_n is the elevation of the bottom of the surface element, and z is the elevation of interest.

The long-wave radiative flux is

$$h_a = 1.17 \times 10^{-18}\,(\theta_a + 273)^6 C_L \quad (2.32)$$

where θ_a is the air temperature 2m above the water surface (°C), C_L is 1 + 0.17 (fraction cloudy)^2.

The back radiation is

$$h_b = 1.192 \times 10^{-14} (\theta_s + 273)^4 \tag{2.33}$$

where θ_s is the surface water temperature (°C).

The evaporative heat flux, h_e, at the surface is

$$h_e = 2.23 \times 10^{-5} w (e_s - e_a) \tag{2.34}$$

where w is the wind speed (kph), e_s is the saturation vapor pressure at the water surface (mm Hg), and e_a is the water vapor pressure (mm Hg).

The convective heat flux, h_c, at the surface is

$$h_c = 1.89 \times 10^{-4} h_e (\theta_a - \theta_s) P_a/(e_s - e_a) \tag{2.35}$$

where h_e, θ_a, θ_s, e_s and e_a are defined above, and P_a is teh atmospheric pressure (mm Hg).

2.5.4 Steps in Calculation

1. Calculate βh_s, h_a, h_b, h_e and h_c.

2. Find h_{net} at the surface and each subsurface slice.

3. Compile the available temperature data by date and slice.

4. Calculate $\Delta\theta_j/\Delta t$ at each depth for temperature data taken in the lake over time.

5. Find the outflow and inflow of heat to the lake, $Q_{oj}\theta_{oj}$ and $Q_{ij}\theta_{ij}$, respectively.

6. Find the vertical flow, Q_{vj}, for each slice.

7. Find the horizontal area of the bottom of each slice, a_j.

8. Write the basic heat transfer equation for each slice. The E_j term drops out for the top slice (at the air-water interface) and a term drops out for the bottom slice (at the sediment interface). The E_{j+1} term for the bottom slice can either be set equal to zero, i.e., there is no heat exchange at the bottom, or the sediment temperature can be set equal to a fixed temperature (which assumes an infinite source/sink of heat) which eliminates θ_{j+1} as a variable for the bottom slice.

One now has n equations (one for each slice) and n unknowns (E_j). The equations can be set up as a set of simultaneous equations and solved using standard matrix techniques.

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SECTION 3

ORGANIC REACTION KINETICS AND RATE CONSTANTS

3.1 INTRODUCTION

Reaction rates for fate processes are presented for the organic priority pollutants. These organic chemicals fall into nine groups and a few chemicals were selected from each group to build summary tables for each fate process. The individual chemicals are intended only for comparisons.

Group	Chemical
Pesticides	Carbofuran (carbamate) DDT (chlorinated) Parathion (organo-phosphate)
PCBs	Aroclor 1248
Halogenated aliphatic hydrocarbons	Chloroform
Halogenated ethers	2-Chloroethyl vinyl ether
Monocyclic aromatics	2,4-Dimethylphenol Pentachlorophenol
Phthalate esters	Bis(2-ethylhexyl)phthalate
Polycyclic Aromatic hydrocarbons	Anthracene Benzo[a]pyrene
Nitrosamines & Miscellaneous	Benzidine Dimethyl nitrosamine

Specific information on 221 chemicals is presented in tables in the appendix and is indexed by chemical name at the end of this chapter for the reader's convenience. These data were compiled from references found by a computer literature search. The following data bases were used:

AQUALINE
CA Search
ENVIROLINE
Environmental Bibliography

Pollution Abstracts
Water Resources Abstracts

The period of literature reviewed, generally, is 1979-1985 to update the data presented in Callahan (1979).

The fate processes addressed include the major kinetics observed in surface fresh waters. These processes are: biotransformation, hydrolysis, oxidation, photolysis, volatilization, partitioning, and bioconcentration. Discussions include a brief overview of the kinetics development, a summary of types of experiments used to generate kinetics data, and synopses of the journal articles from which these data were gathered.

3.2 BIOLOGICAL TRANSFORMATIONS

Biological transformations refer to the microbially mediated transformation of organic chemicals, often the predominant decay pathway in natural waters. It may occur under aerobic or anaerobic conditions, by bacteria, algae or fungi, and by an array of mechanisms (dealkylation, ring cleavage, dehalogenation, etc.). It can be an intra-cellular or extra-cellular enzyme transformation.

The term "biodegradation" is used synonomously with "biotransformation," but some researchers reserve "biodegradation" only for oxidation reactions that eventually lead to CO_2 and H_2O as products. Reactions that go all the way to CO_2 and H_2O are referred to as "mineralization." In the broadest sense, biotransformation refers to any microbially mediated reaction that changes the organic chemical. It does not have to be an oxidation reaction, nor does it have to yield carbon or energy for microbial growth or maintenance. The term "secondary substrate utilization" refers to the utilization of organic chemicals at low concentrations (less than the concentration required for growth) in the presence of one or more primary substrates that are used as carbon and energy sources. "Co-metabolism" refers to the transformation of a substrate that cannot be used as a sole carbon or energy source but can be degraded in the presence of other substrates, e.g., DDT.

The biodegradation tables in the Appendix contain half-life and kinetics data, along with specific characteristics of the experiments. Table 3.01 contains a summary of biodegradation rate constants.

Biological reactions generally follow Michaelis-Menton kinetics, where

$$dc/dt = - k_b \, c \tag{3.1}$$

and k_b is defined as

$$k_b = \frac{\hat{\mu} \, X}{Y \, (K_M + c)} \tag{3.2}$$

In equation (3.2), $\hat{\mu}$ is the maximum growth rate of the culture, X is the biomass concentration, Y is the yield coefficient (cells produced/toxicant

TABLE 3.01 SUMMARY TABLE OF BIOTRANSFORMATION RATE CONSTANTS

	Rate Constant Range (day^{-1})
Pesticides	
Carbofuran	0.03
DDT	0.0 - 0.10
Parathion	0.0 - 0.12
PCBs	
Aroclor 1248	0.0 - 0.007
Halogenated aliphatic hydrocarbons	
Chloroform	0.09 - 0.10
Halogenated ethers	
2-Chloroethyl vinyl ether	0.0 - 0.20
Monocyclic aromatics	
2,4-Dimethylphenol	0.24 - 0.66
Pentachlorophenol	0.00 - 33.6
Phthalate esters	
Bis(2-ethylhexyl)phthalate	0.00 - 0.14
Polycyclic aromatic hydrocarbons	
Anthracene	0.007 - 14.69
Benzo[a]pyrene	0.0 - 0.075
"	0.48 - 3.12*
Nitrosamines & Miscellaneous	
Benzidine	0.0
Dimethyl nitrosamine	0.0

* Zero-order rate constant, μM/day

removed), and K_M is the half-saturation constant (the value of c at which $k_b = 1/2\ \hat{\mu}$). Figure 3.01 shows Michaelis-Menton kinetics in graphical form.

When the toxicant concentration, c, is $\ll K_M$, equation (3.2) reduces to

$$k_b = \frac{\hat{\mu}\ X}{Y\ K_M} = k_{b2}\ X \qquad (3.3)$$

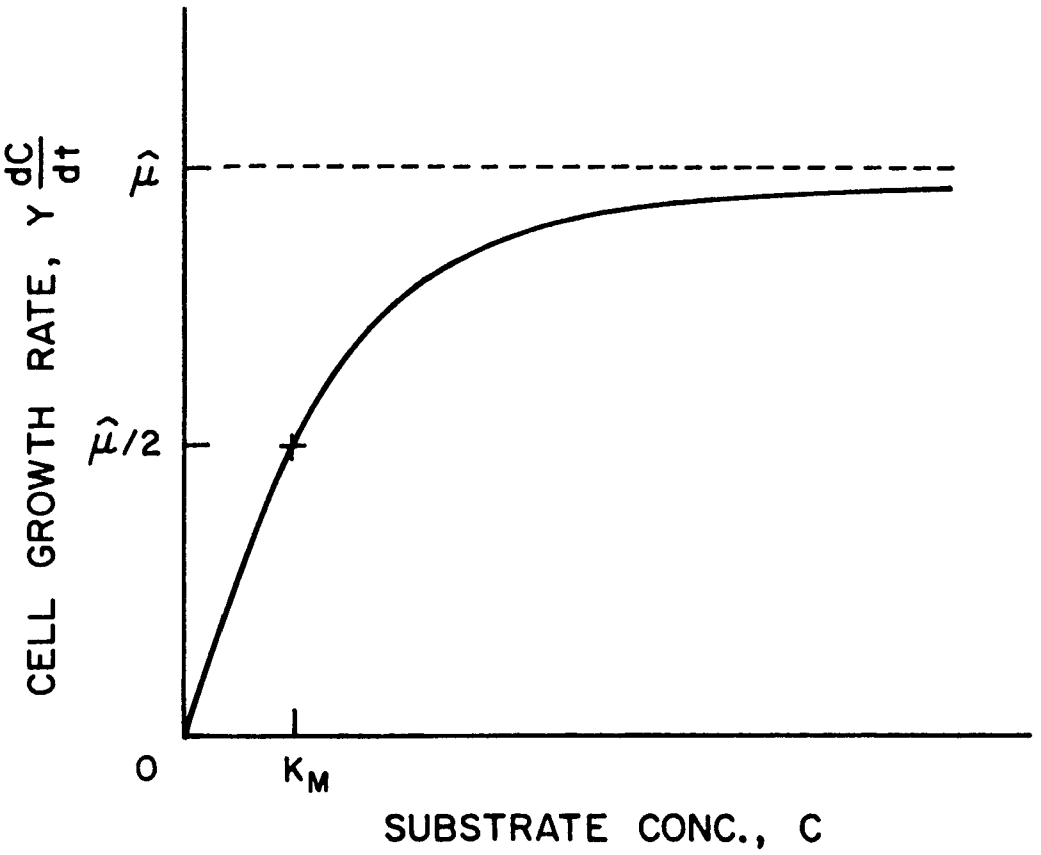

Figure 3.01. Michaelis-Menton kinetics for microbial growth or substrate utilization rate as a function of substrate concentration.

which converts equation (3.1) to

$$dc/dt = - k_{b2} X c$$

so that equation (3.1) becomes first-order in c and X, and is second-order overall (see Fig. 3.02). The second-order rate constant k_{b2}, has units of 1/(cell concentration-time). For constant values of X, the rate may be expressed as a pseudo-first-order reaction rate (1/time), where the investigator would observe an exponential decay of toxicant in the presence of a fixed population (see Fig. 3.03).

If the toxicant concentration is $\gg K_M$, equation (3.2) reduces to

$$k_b = \frac{\hat{\mu} X}{Y c} = k_{b\emptyset} \frac{X}{c} \tag{3.4}$$

which converts equation (3.1) to

$$dc/dt = - k_{b\emptyset} X \tag{3.5}$$

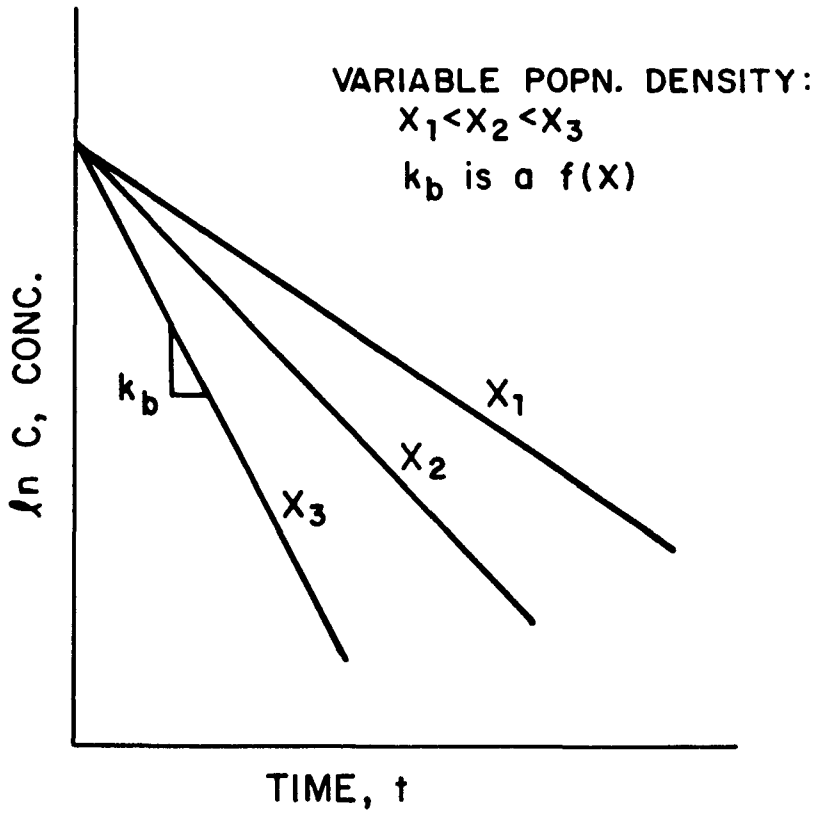

Figure 3.02. Semi-log plot of a second-order biodegration reaction illustrating the increase in chemical degradation (substrate utilization) as a function of the bacteria biomass concentration, X.

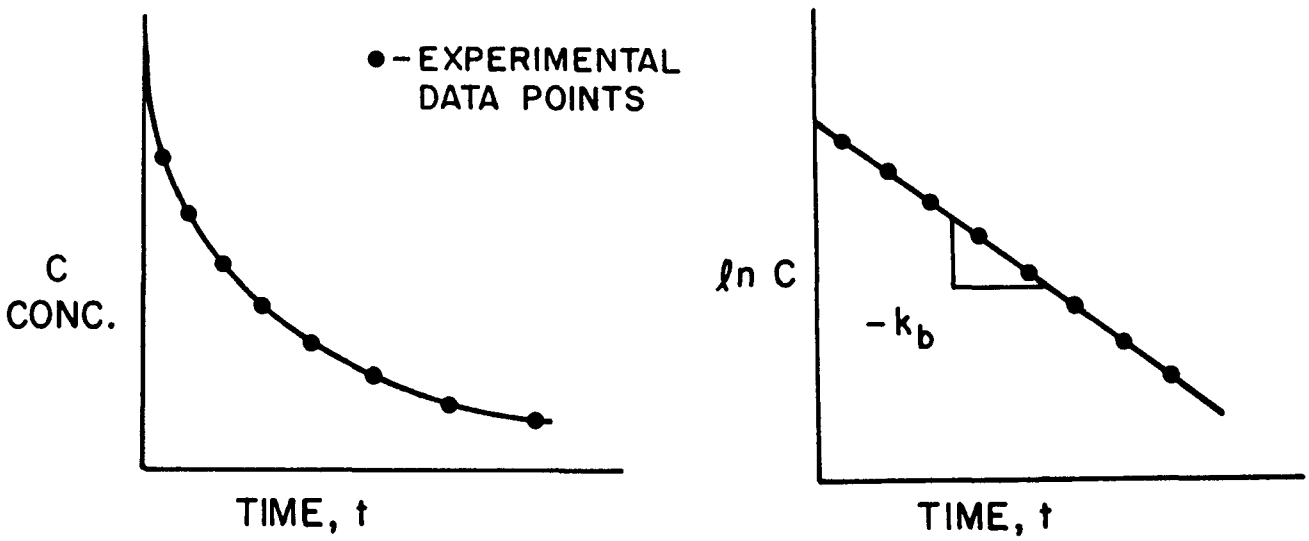

Figure 3.03. First-order Biodegradation Plots. The linear semi-log plot (right) allows estimation of the pseudo-first order rate constant, k_b.

which is zero-order in c and first-order in X. The zero-order rate constant, $k_{b\emptyset}$, has units of toxicant concentration/cell concentration-time.

Biotransformation experiments are conducted by batch and chemostat experimental methods. Other fate pathways (photolysis, hydrolysis, volatilization) must be accounted for in order to correctly evaluate the effects of biodegradation.

There are several basic types of biodegradation experiments. Natural water samples from lakes or rivers can have organic toxicant added to them in batch experiments. Disappearance of toxicant is monitored. Toxicant can be added to a water-sediment sample to simulate in-situ conditions, or a contaminated sediment sample alone may be used without a spiked addition. Primary sewage, activated sludge, or digester sludge may purposefully be contaminated to test degradability and measure toxicant disappearance. Degradation by periphytic and epilithic organisms can also be examined. Radio-labeled organic chemicals can be used to estimate metabolic degradation (mineralization) by measuring $^{14}CO_2$ off-gas, and anabolic incorporation into biomass. These experiments are called heterotrophic uptake experiments. The organic chemical may be added in minute concentrations to simulate exposure in natural conditions, or it may be the sole carbon source to the culture.

Biodegradation is affected by numerous factors that influence biological growth:

1. Temperature. Temperature effects on biodegradation of toxics are similar to those on biochemical oxygen demand (BOD) or ammonia removal.

2. Nutrients. Nutrients are necessary for growth.

3. Acclimation. Adaptation is necessary for expressing repressed (induced) enzymes or fostering those organisms that can degrade the toxicant through gradual exposure to the toxicant over time. A shock load of toxicant may kill a culture that would otherwise adapt if properly exposed.

4. Population Density or Biomass Concentration. Organisms must be present in large enough numbers to significantly degrade the toxicant (a lag often occurs if the organisms are too few).

Some recent results of biotransformation experiments are discussed in the next few pages. Ward and Matsumura (1978) found that evaporation was the major fate process for dioxin in lake water and sediment and that biodegradation was only a minor fate process. Saeger (1979) studied the fate processes of 11 trialkyl, alkyl aryl and triaryl phosphate esters. Solubility in distilled water and octanol-water partition coefficients (K_{ow}) were measured. Biodegradation studies using Mississippi River water and activated sludge showed that phosphate esters are rapidly degraded biologically.

Boyle (1980) tested the degradation of pentachlorophenol in a lentic microcosm containing filamentous algae. The aquaria were operated at a combination of conditions -- aerobic or anaerobic, with or without sediment, and dark or lighted. Boyle found persistance was aided by the absence of light and sediment, low dissolved oxygen concentrations, and pH < 4.8. Cartwright (1980) found that zero-order kinetics best described the biodegradation of alachlor. Gledhill (1980) studied butyl benzyl phthalate in order to assess its environmental safety. Photolysis was measured in natural sunlight over a period of 28 days. Solubility in distilled water, the octanol-water partition coefficient, biodegradation using lake water, bioconcentration, and aquatic toxicity were measured as part of the experiment. The authors found that biodegradation was the most important removal mechanism.

Monnig (1980) investigated the biological treatability of carbaryl, toluene, and α-naphthol using municipal wastewater. A 90% or greater reduction in the toxicants was noted without a decrease in performance of COD removal, but ammonia increased through the treatment units causing the effluent to be more toxic than the influent. Nesbitt and Watson (1980) studied the Avon River (Australia) for degradation of 2,4-D over one winter. Laboratory experiments of field-collected samples with 2,4-D added measured biodegradation half-lives. Sharom (1980) measured the persistence of 12 pesticides in sterile and natural water. DDT, parathion, and lindane degraded only in unsterilized water. Dieldrin, endrin, ethion, and leptophos were the most stable in natural water. Parathion, p,p'-DDT, carbaryl and carbofuran were most easily degraded in natural water.

Fochtman (1981) measured biodegradation of eight organic pollutants after a 7-day period. The study focused on activated carbon adsorption and biodegradation as a treatment scheme for water and wastewater. Liu (1981a) tested fenitrothion and 2,4-D for biodegradability under sole carbon source and cometabolism (mixed substrate) conditions and under aerobic and anaerobic conditions. Liu (1981b) measured the biodegradability of pentachlorophenol by bacterial cultures under aerobic and anaerobic conditions, as sole carbon source and co-metabolism with monochlorophenol. Degradation was enhanced in aerobic conditions. Paris (1981) observed second-order kinetics in the biodegradation of malathion, 2,4-D butoxyethyl ester, and chlorpropham in natural water samples. Sharom and Miles (1981) investigated the degradation of parathion and DDT in the presence of ethanol, glucose and acetone. The maximum degradation rates were observed for DDT and ethanol, and parathion and glucose. Tabak (1981) collected data on the biodegradability of 96 organic compounds. Cultures were kept in the dark, at 25°C, for 7 days, and analyzed for the test compound. Primary sewage was used as the innoculum, and the solution was recultured for a total of 28 days to allow acclimation.

Furukawa (1982) measured the biodegradability of 31 mono- and polychlorinated biphenyls (pure isomers) by cultures of Alcaligenes sp. and Acinetobacter sp. after 1 to 2 hours of incubation. Kilbane (1982) used Pseudomonas cepacia to degrade 2,4,5-T as a sole carbon source, in which 97% disappeared after 6 days. Muir and Yarechewski (1982) studied the degradation of terbutryn under varying redox conditions. Terbutryn degraded

slowly under aerobic conditions in natural water samples and sediments. Papanastasiou (1982) used Monod kinetics to describe a 2,4-D acclimated activated sludge culture that utilized 2,4-D and glucose. A 20-day lag was observed. Scow (1982) developed biodegradation summary data for aquatic systems of 40 organic compounds.

Bailey (1983) used Tittabawassee River (Michigan) water to measure the biodegradation of radio-labeled biphenyl and three chlorinated biphenyls. Biphenyl and the monochlorinated biphenyls degraded in less than 3 days, but the tetrachlorinated biphenyl did not degrade in 98 days. Hallas and Alexander (1983) measured the degradation of nine nitroaromatics in sewage effluent under aerobic and anaerobic conditions. Knowlton and Huckins (1983) conducted a littoral microcosm study using radio-labeled pentachlorophenol. Mineralization and incorporation into macrophyton biomass was observed. Petrasek (1983) reported K_{OW} and Henry's constant as part of a study of toxicants in an activated sludge plant. The influent was spiked with 22 organics, and process flows and sludges were monitored. Pignatello (1983) monitored the photolytic and biological degradation of pentachlorophenol in artificial freshwater stream ecosystems using Mississippi River water. They found: "(1) photolysis of PCP in the near surface waters initially was the primary mechanism of PCP removal, (2) after a period of weeks the aquatic microflora became adapted to PCP mineralization and supplanted photolysis as the major PCP removal process, (3) attached microorganisms were primarily responsible for PCP biodegradation, and (4) total bacterial numbers were not significantly affected by PCP concentrations of micrograms per liter."

Guthrie (1984) examined the fate of pentachlorophenol on anaerobic digestion of sewage sludge. The digesters were acclimated to the chemical, and the digesters were run at three different sludge ages. Methanogenesis was inhibited in unacclimated cultures at concentrations exceeding 200 μg/ℓ. Soluble pentachlorophenol was removed to levels below 5 μg/ℓ. Johnson (1984) investigated the biodegradation of four phthalate esters in freshwater lake sediments. Experiments were conducted under aerobic and anaerobic conditions, and at low, medium, and high chemical concentrations. Johnson found that phthalate esters with complex alkyl groups degraded only very slowly, and degradation was favored by nutrient-rich systems with temperatures above 22°C. Walker (1984) developed half-lives for nine pesticides and dibutylphthalate in sterile and natural water systems. Bravo , Hoelon , methyl parathion, and Bolero degraded more quickly in natural than sterile samples, whereas endosulfan and dimilin degraded most quickly in sterile conditions.

3.3 CHEMICAL HYDROLYSIS

Chemical hydrolysis is that fate pathway by which a toxicant reacts with water. Particularly, a nucleophile (hydroxyl, water or hydronium ions), N, displaces a leaving group, X, as shown (Neely, 1985):

$$R\text{-}X + N \rightarrow RN + X \qquad (3.6)$$

Hydrolysis does not include acid-base, hydration, addition or elimination

reactions. The hydrolysis reaction consists of the cleaving of a molecular bond and the formation of a new bond with components of the water molecule (H^+, OH^-). It is often a strong function of pH (see Fig. 3.04).

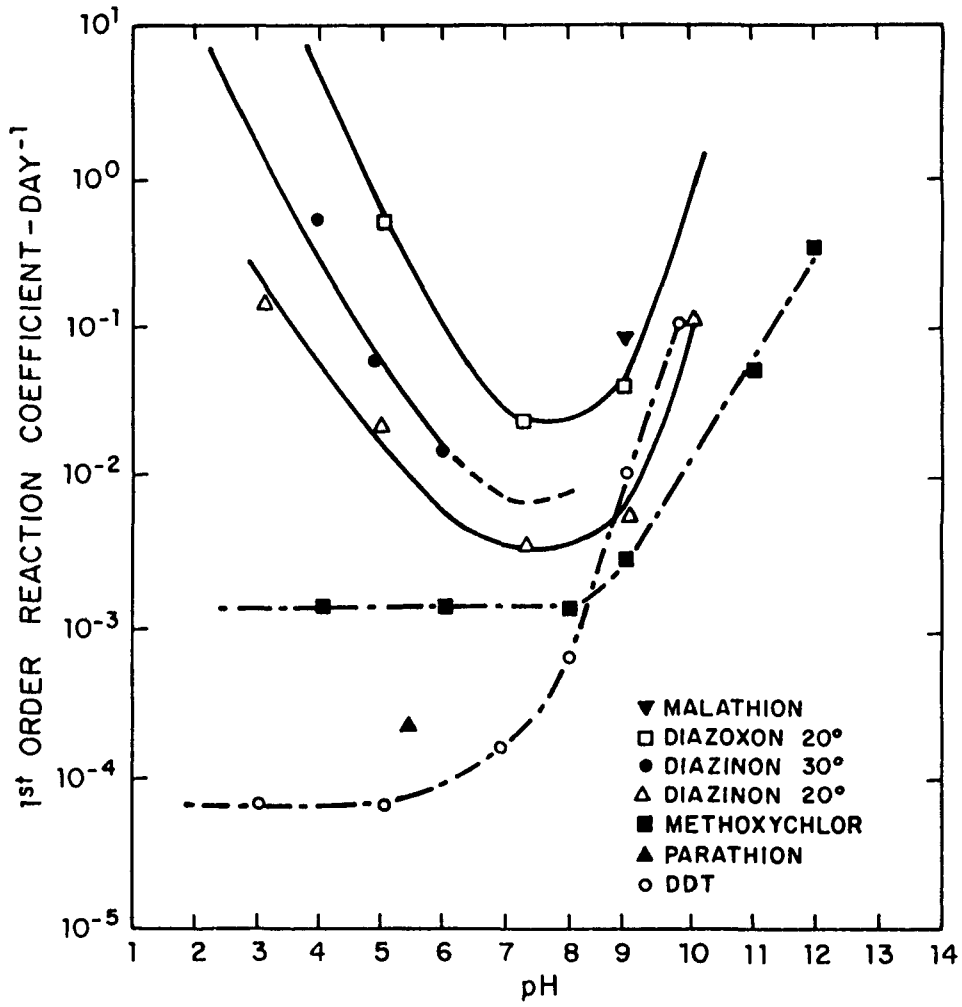

Figure 3.04 Effect of pH on hydrolysis rate constants.

Two examples of a hydrolysis reaction are presented below (Harris, 1982b):

$$CH_3CH_2CH_2\underset{\underset{Br}{|}}{CH}CH_3 \xrightarrow{+H_2O} CH_3CH_2CH_2\underset{\underset{OH}{|}}{CH}\text{-}CH_3 + Br^- + H^+$$

alkyl halide alcohol

$$CH_3O\overset{\overset{O}{||}}{C}NHC_6H_5 \xrightarrow{+H_2O} CH_3OH + CO_2 + NH_2C_6H_5 \qquad (3.7)$$

carbamate alcohol amine

The types of compounds that are generally susceptible to hydrolysis are (Harris, 1982b):

Alkyl halides
Amides
Amines
Carbamates
Carboxylic acid esters
Epoxides
Nitriles
Phosphonic acid esters
Phosphoric acid esters
Sulfonic acid esters
Sulfuric acid esters

The kinetic expression for hydrolysis is

$$dc/dt = - k_a[H^+]c - k_N c - k_b[OH^-]c \qquad (3.8)$$

where c is the concentration of toxicant, k_a, k_N, and k_b are the acid-, neutral- and base-catalyzed hydrolysis reaction rate constants, respectively, and $[H^+]$ and $[OH^-]$ are the molar hydrogen and hydroxyl ion concentrations, respectively.

Hydrolysis data available are presented in tables in the appendix. A summary of these data is presented in Table 3.02.

Hydrolysis experiments usually involve fixing the pH at some target value, eliminating other fate processes, and measuring toxicant disappearance over time. A sterile sample in a glass tube, filled to avoid a gas space, and kept in the dark eliminates the other fate pathways. In order to evaluate k_a and k_b, several non-neutral pH experiments must be conducted.

Wolfe (1977a) measured hydrolysis and photolysis of malathion and found alkaline hydrolysis to be a significant fate process. Wolfe (1977b) also measured hydrolysis of methoxychlor and DDT. At common aquatic environment pH values, methoxychlor was pH-independent and DDT was pH-dependent.

Khan (1978) observed first-order hydrolysis kinetics for atrazine in aqueous fulvic acid solutions. Acid conditions favored the hydrolysis of atrazine. Wolfe (1978) measured hydrolysis of carbaryl, propham, and chlorpropham. At pH 7, the half-lives of photolysis and alkaline hydrolysis for carbaryl varied by a factor of two. The alkaline hydrolysis half-lives for propham and chlorpropham exceeded 10^4 days; biolysis was the most significant degradation process.

Harris (1982b) compiled base, neutral and acid hydrolysis rate constants for 15 pesticides.

Lemley and Zhong (1983) investigated hydrolysis of aldicarb, aldicarb sulfoxide, and aldicarb sulfone. Base hydrolysis was first-order with

TABLE 3.02 SUMMARY TABLE OF HYDROLYSIS DATA

	Hydrolysis Range of Values
Pesticides	
Carbofuran	N/A
DDT	35.6/M-hr (alk)
	6.84 E-6/M-hr (acid)
Parathion	82.8/M-hr (alk)
	0.000162/hr (neut)
PCBs	
Aroclor 1248	0/M-hr (alk)
	0/M-hr (acid)
	0/M-hr (neut)
Halogenated aliphatic hydrocarbons	
Chloroform	0.216/M-hr (alk)
	2.5E-9/M-hr (neut)
Halogenated ethers	
2-Chloroethyl vinyl ether	4E-6/M-hr (neut)
Monocyclic aromatics	
2,4-Dimethylphenol	0/M-hr (alk)
	0/M-hr (acid)
	0/M-hr (neut)
Pentachlorophenol	0/M-hr (alk)
	0/M-hr (acid)
	0/M-hr (neut)
Phthalate esters	
Bis(2-ethylhexyl)phthalate	0.4/M-hr (alk)
	4.0E-5/M-hr (acid)
	0/M-hr (neut)
Polycyclic aromatic hydrocarbons	
Anthracene	0/M-hr (alk)
	0/M-hr (acid)
	0/M-hr (neut)
Benzo[a]pyrene	0/M-hr (alk)
	0/M-hr (acid)
	0/M-hr (neut)
Nitrosamines & Miscellaneous	
Benzidine	0/M-hr (alk)
	0/M-hr (acid)
	0/M-hr (neut)
Dimethyl nitrosamine	0/M-hr (alk)
	0/M-hr (acid)
	0/M-hr (neut)

respect to OH^-, and acid hydrolysis was first-order. Temperatures were varied from 5 to 35°C for base hydrolysis. Wolfe (1982) measured solubility in distilled water, K_{ow}, vapor pressure, and Henry's constant of hexachlorocyclopentadiene as part of an investigation into the fate processes of this chemical. Hydrolysis in water was measured at pH 2.88, 5.08, 6.70, 7.0 and 9.76 at temperatures of 30 to 50°C. Photolysis in natural sunlight was also measured. Wolfe found that photolysis was the most important degradation process, with hydrolysis next in importance.

3.4 CHEMICAL OXIDATION

Chemical oxidation reactions take place in natural waters when oxidants (often formed photochemically) are present in sufficient concentrations to favor the reaction. Chlorine and ozone are commonly reported oxidants. The basic equation for oxidation is

$$\frac{dc}{dt} = -K\ Ox\ C \tag{3.9}$$

where K is the second-order rate constant, Ox is the concentration of oxidant and C is the concentration of toxicant.

In natural waters, the oxidant is generally a free radical at low concentrations. If the free radical formation rate is relatively constant (as expected in natural waters), then the free radical oxidation of the toxicant can be computed as a first-order reaction:

$$\frac{dc}{dt} = -K'\ C \tag{3.10}$$

where K' is the pseudo-first-order rate constant.

Oxidation by ozone is a strong function of pH. At high pH, OH^- radicals catalyze the decomposition of ozone, which is then further decomposed by its own decomposition products (Stumm and Morgan, 1981).

The oxidation rates and oxidants are presented in the appendix; a summary of these data is given in Table 3.03.

Dennis et al. (1979) oxidized diazinon with Clorox, and reported the oxidation half-lives as a function of pH. LC_{50} values also were determined for Lepomis macrochirus (bluegills), Pimephales promelas (fathead minnows), and Daphnia magna.

Koshitani et al. (1982) studied the oxidation of anthracene by oxygen, copper(II) acetate, and sodium chloride. The rate of anthracene degradation was found to be first-order in regard to anthracene and sodium chloride, and 1/2-order in regard to copper(II) acetate.

Kuo and Soong (1984) studied the oxidation of benzene by ozone. The degradation of benzene was found to be zero-order with respect to benzene and first-order with respect to ozone at neutral pH.

TABLE 3.03 SUMMARY TABLE OF OXIDATION DATA

	Oxidation Range of Values
Pesticides	
Carbofuran	N/A
DDT	< 3600/M-hr (D_2) 3600/M-hr (RO_2)
Parathion	N/A
PCBs	
Aroclor 1248	<360/M-hr (O_2) <1/M-hr (RO_2)
Halogenated aliphatic hydrocarbons	
Chloroform	<360/M-hr (O_2) 0.7/M-hr (RO_2)
Halogenated ethers	
2-Chloroethyl vinyl ether	1E10/M-hr (O_2) 34/M-hr (RO_2)
Monocyclic aromatics	
2,4-Dimethylphenol	< 4E6/M-hr (O_2) 1.1E8/M-hr (RO_2)
Pentachlorophenol	< 7E3/M-hr (O_2) 1E5/M-hr (RO_2)
Phthalate esters	
Bis(2-ethylhexyl)phthalate	<<360/M-hr (O_2) 7.2/M-hr (RO_2)
Polycyclic aromatic hydrocarbons	
Anthracene	5E8/M-hr (O_2) 2.2E5/M-hr (RO_2)
Benzo[a]pyrene	5E8/M-hr (O_2) 2E4/M-hr (RO_2)
Nitrosamines & Miscellaneous	
Benzidine	< 4E7/M-hr (O_2) 1.1E8/M-hr (RO_2)
Dimethyl nitrosamine	no reaction

3.5 PHOTO-TRANSFORMATIONS

Photolysis, the light-initiated degradation reaction, is a function of the incident energy on the molecule and the quantum yield of the chemical. Data for photolysis reactions are compiled in the photolysis table in the appendix and are summarized in Table 3.04. Surface photolysis rates, half-lives, quantum yields and wavelength data are presented.

TABLE 3.04 SUMMARY TABLE OF PHOTOLYSIS DATA

	Photolysis Reaction Rates Range of Values
Pesticides	
Carbofuran	N/A
DDT	< 5E-7/hr
Parathion	0.0024-0.003/hr
PCBs	
Aroclor 1248	N/A
Halogenated aliphatic hydrocarbons	
Chloroform	N/A
Halogenated ethers	
2-Chloroethyl vinyl ether	N/A
Monocyclic aromatics	
2,4-Dimethylphenol	N/A
Pentachlorophenol	0.2295-1.224/hr
Phthalate esters	
Bis(2-ethylhexyl)phthalate	N/A
Polycyclic aromatic hydrocarbons	
Anthracene	0.924-1.188/hr
Benzo[a]pyrene	0.348-1.386/hr
Nitrosamines & Miscellaneous	
Benzidine	11.09/hr
Dimethyl nitrosamine	N/A

When light strikes the pollutant molecule, the energy content of the molecule is increased and the molecule reaches an excited electron state. This excited state is unstable and the molecule reaches a normal (lower)

energy level by one of two paths: (1) it loses its "extra" energy through energy emission, i.e., fluorescence or phosphorescence, or (2) it is converted to a different molecule through the new electron distribution that existed in the excited state.

Photolysis may be direct or indirect. Indirect photolysis occurs when an intermediary molecule becomes energized which then energizes the chemical of interest. The basic equation for direct photolysis is of the form:

$$dc/dt = - k_a \phi c \tag{3.11}$$

where c is the concentration of toxicant, k_a is the rate constant for adsorption of light by the toxicant, and ϕ is the quantum yield of the reaction. The quantum yield is defined by

$$\phi = \frac{\text{Number of moles of toxicant reacted}}{\text{Number of einsteins absorbed}} \tag{3.12}$$

An einstein is the unit of light on a molar basis (a quantum or photon is the unit of light on a molecular basis). The quantum yield may be thought of as the efficiency of photo-reaction. Incoming radiation is measured in units of energy per unit area per time (e.g., cal/cm^2-sec). The incident light in units of einsteins/cm^{-2}/sec^{-1}/nm^{-1} can be converted to watts/cm^{-2}/nm^{-1} by multiplying by the wavelength (nm) and 3.03×10^{39}.

The intensity of light varies over the depth of the water column and may be related by

$$I_z = I_o e^{-K_e z} \tag{3.13}$$

where I_z is the intensity at depth z, I_o is the intensity at the surface, and K_e is an extinction coefficient for light disappearance. Light disappearance is caused by the scattering of light by reflection off particulate matter, and absorption by any molecule. Absorbed energy can be converted to heat or cause photolysis. Light disappearance is a function of wavelength and water quality (e.g., color, suspended solids, dissolved organic carbon).

The rate constant k_a is the product of I (at any depth, or an average over the depth) and the absorption of light by the chemical.

Indirect photolysis occurs when a nontarget molecule is transformed directly by light, which in turn, transmits its energy to the pollutant molecule. Changes in the pollutant molecule then occur as a result of the increased energy content. The kinetic equation for indirect photolysis is

$$dc/dt = -k_2 c x = - k_p c \tag{3.14}$$

where k_2 is the indirect photolysis rate constant, x is the concentration of the nontarget intermediary, and k_p is the overall pseudo-first order rate constant. Recently the important role of inducing agents (e.g., algae exudates and nitrate) have been demonstrated by Zepp et al. (1984) and Zepp et al. (1987).

Lu (1977) used radio-labeled vinyl chloride, benzidine, and benzo[a]pyrene for fate analysis in a microcosm ecosystem. Photolytic degradation of benzidine and benzo[a]pyrene was measured, and K_{ow} was reported. Bioconcentration in algae (Oedogonium cardiacum), fish (Gambusia affinis), daphnia (Daphnia magna), mosquito larvae (Culex pipiens quinquefasciatus) and snails (Physa sp.) was measured. Vinyl chloride did not bioaccumulate, whereas benzo[a]pyrene and benzidine bioaccumulation were closely related to their K_{ow}. Zepp (1977) measured the photolysis of DDE and DMDE, which are the photodegradation products of DDT and methoxychlor, respectively.

Hautala (1978) tested the effects of surfactants on the photolysis of 2,4-D, carbaryl and parathion. Quantum yield and half-lives were measured for irradiation by monochromatic light.

Que Hee and Sutherland (1979) measured the photolysis of 2,4-D butyl ester by irradiation of 300 nm light. The half-life was 13 days.

Gledhill (1980) studied butyl benzyl phthalate in order to assess its environmental safety. Photolysis was measured in natural sunlight over a period of 28 days. Solubility in distilled water, K_{ow}, biodegradation using lake water, bioconcentration and aquatic toxicity were measured as part of the experiment. The authors found that biodegradation was the most important removal mechanism.

Harris (1982a) presented quantum yield, half-life and wavelength data for 53 organic compounds (including pesticides and polycyclic aromatics). Wolfe (1982) measured the solubility in distilled water, K_{ow}, vapor pressure, and Henry's constant for hexachlorocyclopentadiene as part of an investigation into the fate processes affecting the chemical. Photolysis in natural sunlight was measured, as was hydrolysis at various pH levels. Wolfe found that photolysis was the most important degradation process, with hydrolysis next in importance.

Pignatello (1983) monitored the photolytic and biological degradation of pentachlorophenol in artificial freshwater stream ecosystems using Mississippi River water. Photolysis of PCP in the near surface waters initially was the primary mechanism of PCP removal.

3.6 VOLATILIZATION

The transfer of pollutants from water to air or from air to water is an important fate process to consider when modeling organic chemicals. Volatilization is a transfer process; it does not result in the breakdown of a substance, only its movement from the liquid to gas phase, or vice versa. Gas transfer of pollutants is analogous to the reaeration of oxygen in surface waters, and will be related to known oxygen transfer rates. The rate of volatilization is related to the size of the molecule (as measured by the molecular weight). The molecular weight is given in the Index to Chemicals at the end of this chapter.

Gas transfer models are often based on the two-film theory (Figure 3.05). Mass transfer is governed by molecular diffusion through a stagnant liquid and gas film. Mass moves from areas of high concentration to areas of low concentration. Transfer can be limited at the gas film or the liquid film. Oxygen, for example, is controlled by the liquid-film resistance. Nitrogen gas, although approximately four times more abundant in the atmosphere than oxygen, has a greater liquid-film resistance than oxygen.

Volatilization, as described by two-film theory, is a function of Henry's constant, the gas-film resistance and the liquid-film resistance. The film resistance depends on diffusion and mixing. Henry's constant, H,

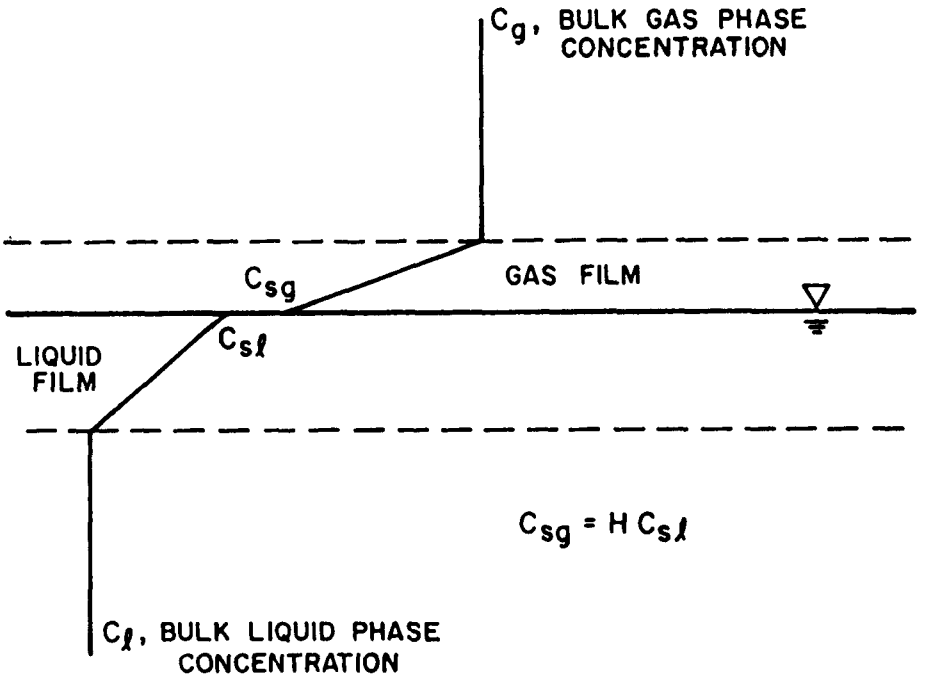

Figure 3.05. Two-film theory of gas-liquid interface.

is a ratio of a chemical's vapor pressure to its solubility. It is a thermodynamic ratio of the fugacity of the chemical (escaping tendency from air and water).

$$H = p/c \tag{3.15}$$

where p is the partial pressure of the chemical of interest, and c is its solubility. Henry's constant can be dimensionless [mg/ℓ (in air)/mg/ℓ (in water)] or can have concentration units, e.g., mm mm Hg/mg/ℓ, atm-m^3/M.

The value of H can be used to develop simplifying assumptions for modeling volatilization. If either the liquid-film or the gas-film controls, i.e., one resistance is much greater than the other, the lesser resistance can be neglected. The threshold of Henry's constant for gas or liquid film control is approximately 0.1 for dimensionless H, or 2.2×10^{-3}

atm-m^3/M. Above this threshold value, the chemical is liquid-film controlled, and below it, it is gas-film controlled.

The diffusion coefficients in water and air have been related to molecular weight (O'Connor, 1980):

$$D_\ell = 22 \times 10^{-5}\ cm^2/sec\ M_W^{-2/3} \tag{3.16}$$

where D_ℓ is the diffusivity of the chemical in water and M_W is the molecular weight, and

$$D_g = 1.9\ cm^2/sec\ M_W^{-2/3} \tag{3.17}$$

where D_g is the diffusivity of the chemical in air. The diffusion can then be related to the oxygen reaeration rate, K_a, by a ratio of the diffusivity of the chemical to that of oxygen:

$$K_{li}/K_a = (D_\ell/D_{O2})^{1/2} \tag{3.18}$$

where D_{O2} is 2.4×10^{-5} cm^2/sec at 20°C. The reaeration rate, K_a, can be calculated from any of the formulae available (e.g., Tsivoglou, O'Connor-Dobbins, Owens, etc.).

The gas film transfer rate may be calculated from

$$K_{gi} = \frac{0.001}{h} (D_g/\nu_g)^{2/3}\ W \tag{3.19}$$

where ν_g is the kinematic viscosity of air (a function of temperature) as presented in Table 3.05, h is the water depth, and W is the wind speed in m/sec. K_g has units of 1/time.

The overall mass transfer rate is K_L, as given by

$$\frac{1}{K_L} = \frac{1}{K_{li}} + \frac{1}{H\ K_{gi}} \tag{3.20}$$

TABLE 3.05 KINEMATIC VISCOSITY OF AIR

Temperature (°F)	ν (cm^2/sec)
0	0.117
20	0.126
40	0.136
60	0.147
80	0.156
100	0.167
120	0.176

Rouse, Hunter (1946). Elementary Mechanics of Fluids. Dover Publications, Inc., New York, New York. p. 363.

where H must be dimensionless, and K_L is in units of length/time. The K_L found from this expression can be incorporated into a mass flux expression such as:

$$\frac{K_L}{d} (C_S - C) = dc/dt \qquad (3.21)$$

where C_S is the saturation value or solubility of the toxicant, d is the mean depth of the water body, and C is the dissolved concentration of toxicant. The overall mass transfer coefficient is sometimes referred to as the "piston velocity", i.e., the velocity that the chemical penetrates the stagnant film.

Solubility, vapor pressure and Henry's constant data are present in the Solubility and Volatilization table at the end of this chapter. (Henry's constant can be converted from atm-m^3/M to a dimensionless number by multiplying by 44.64 = 1000 ℓ-M/22.4ℓ-m^3.) A summary of these data is presented in Table 3.06.

Yalkowsky (1979) measured the solubility of 26 halogenated benzenes at 25°C and developed the following relationship

$$\log Sw = -0.01\ MP - 0.88 \log PC - 0.012 \qquad (3.22)$$

where Sw is solubility (M/ℓ), MP is the melting point (°C) and PC is the calculated partition coefficient.

Gossett and Lincoff (1981) studied the effects of temperature and ionic strength on Henry's constant for six chlorinated organic compounds. Matter-Müller (1981) reported values of Henry's constant for six organic chemicals as part of a study to evaluate the stripping efficiency of several water and wastewater processes. Jaffe and Ferrara (1983) reported partial pressure, solubility, Henry's constant and K_{OW} for ten organic compounds as part of a comparison between a kinetics approach and an equilibrium approach in toxics modeling. Lyman (1982b) compiled solubility data on 78 organic compounds and presented estimation methods based on K_{OW} for different classes of compounds. He also included a method based on the molecular structure. Mackay (1982) measured Henry's constant for 22 organic chemicals as part of a study of volatilization characteristics. Transfer coefficients for the gas and liquid phases were correlated for environmental conditions as:

$$KL = 34.1 \times 10^{-6} (6.1 + 0.6U10)^{0.5} U10\ ScL^{-0.5}$$
$$KG = 46.2 \times 10^{-5} (6.1 + 0.63U10)^{0.5} U10\ ScG^{-0.67} \qquad (3.23)$$

where U10 is the 10-m wind velocity (m/s), ScL and ScG are the dimensionless liquid and gas Schmidt numbers. Thomas (1982) compiled solubility, vapor pressure and Henry's constant data for 43 organic compounds. Wolfe (1982) measured solubility in distilled water, K_{OW}, vapor pressure, and Henry's constant of hexachlorocyclopentadiene as part of an investigation into the fate processes of this chemical. Wolfe found that photolysis was the most important degradation process, with hydrolysis next in importance.

McCall (1983) reported solubility, vapor pressure, Henry's constant and bioconcentration factors for seven organic chemicals as part of a fate model

TABLE 3.06. SUMMARY TABLE OF VOLATILIZATION DATA

	Molecular Weight	Solubility (mg/l)	Vapor Pressure (mm Hg)	*Henry's Constant $\left(\frac{mg/\ell\ air}{mg/\ell\ H_2O}\right)$
Pesticides				
Carbofuran		415-670	N/A	
DDT	354.5	0.0017-0.02	1.9E-7	10^{-3}-10^{-4}
Parathion		24	N/A	
PCBs				
Aroclor 1248	299.5	0.017-0.54	4.9E-4	0.01-0.5
Halogenated aliphatic hydrocarbons				
Chloroform	119.4	8000-9600	150-246	0.15
Halogenated ethers				
2-Chloroethyl vinyl ether	106.6	15,000	26.8	0.012
Monocyclic aromatics				
2,4-Dimethylphenol	122.2	590	0.0621	0.0001
Pentachlorophenol	266.4	14	0.00011-0.00014	0.00013
Phthalate esters				
Bis(2-ethylhexyl)phthalate	391	0.4	2E-7	
Polycyclic aromatic hydrocarbons				
Anthracene	178.2	0.045-0.051	1.7E-5	0.10
Benzo[a]pyrene	252	0.00017-0.0038	5 E-9	10^{-5}-10^{-4}
Nitrosamines & Miscellaneous				
Benzidine	184.2	400-500	5E-4	
Dimethyl nitrosamine	74.1	miscible	8.1	

*H = 16(V.P.) (MW)/(Sol. x T°K) for low solubility substances

for fish in an aquatic system with sediments. Spencer and Cliath (1983) measured the vapor pressure of six pesticides at various tempertures by the gas saturation and Knudsen methods. Smith (1983) measured Henry's constant for five organic chemicals by three different methods. Swann (1983) measured solubilities, K_{oc}, and K_{ow} of 14 organic chemicals using reverse phase high-performance liquid chromatography. Wasik (1983) measured vapor pressure, solubility and K_{ow} of 15 organic chemicals using a generator column and high performance liquid chromatography. Yalkowsky (1983) reported solubility, K_{ow}, and melting points for 162 aromatic compounds, and developed the following relationship

$$\log Sm = -0.994 \log K_{ow} - 0.01\ MP + 0.323 \qquad (3.24)$$

where Sm is the solubility (M/l), and MP is the melting point (°C).

Miller et al. (1985) presented an equation relating K_{ow} and solubility

$$\log K_{ow} = [(Y_1 - Y_2)/Y_1]\log C_s + (X_2 - X_1Y_2/Y_1) \qquad (3.25)$$

where X_1, X_2, Y_1 and Y_2 are functions of molar volume. Miller measured solubilities and K_{ow} for 100 chemicals.

3.7 SORPTION

The sorption of toxicants to suspended particulates and bed sediments is a significant transfer mechanism. Partitioning of a chemical between particulate matter and the dissolved phase is not a transformation pathway; it only relates the concentration of dissolved and sorbed states of the chemical. The partitioning table in the appendix contains octanol-water partion coefficients (K_{ow}) and sediment-water partition coefficient values. The summary of K_{ow} values is given in Table 3.07.

The octanol/water partition coefficient, K_{ow}, is a measure of the solubility of a chemical in water. The less soluble a chemical is in water, the more likely it is to sorb to the surfaces of sediments or microorganisms.

The laboratory procedure for measuring K_{ow} is (Lyman, 1982a):

1. Chemical is added to a mixture of pure octanol (a nonpolar solvent) and pure water (a polar solvent). The volume ratio of octanol and water is set at the estimated K_{ow}.

2. Mixture is agitated until equilibrium is reached.

3. Mixture is centrifuged to separate the two phases. The phases are analyzed for the chemical.

4. K_{ow} is the ratio of the chemical concentration in the octanol phase to chemical concentration in the water phase, and has no units. The logarithm of K_{ow} has been measured from -3 to +7.

The Langmuir isotherm derives from the kinetic equation for sorption-desorption:

TABLE 3.07 SUMMARY TABLE OF PARTITIONING DATA

	log K_{ow}
Pesticides	
Carbofuran	1.60
DDT	4.89-6.9
Parathion	3.81
PCBs	
Aroclor 1248	5.75-6.11
Halogenated aliphatic hydrocarbons	
Chloroform	1.90-1.97
Halogenated ethers	
2-Chloroethyl vinyl ether	1.28
Monocyclic aromatics	
2,4-Dimethylphenol	2.42-2.50
Pentachlorophenol	5.01
Phthalate esters	
Bis(2-ethylhexyl)phthalate	8.73
Polycyclic aromatic hydrocarbons	
Anthracene	4.34-4.63
Benzo[a]pyrene	4.05-6.04
Nitrosamines & Miscellaneous	
Benzidine	1.36-1.81
Dimethyl nitrosamine	0.06

$$dc/dt = -K_1 c\,[c_{pc} - c_p] + K_2 c_p \qquad (3.26)$$

where c is the concentration of dissolved toxicant, c_p is the concentration of particulate toxicant, c_{pc} is the maximum adsorptive concentration of the solids, and K_1 and K_2 are the adsorption and desorption rate constants, respectively. A substitution can be made for c_p and c_{pc}. If m is the concentration of solids, r is the ratio of adsorbed toxicant to solids by mass, and r_c is the maximum adsorptive capacity of the solids, then

$$dc/dt = -K_1 cm\,[r_c - r] + K_2 rm \tag{3.27}$$

At steady-state, equation (3.27) reduces to the famous Langmuir Isotherm in which the amount adsorbed is linear at low dissolved toxicant concentrations but gradually becomes saturated at the maximum value (r_c) at high dissolved concentrations.

$$r = \frac{c\,r_c}{K_2/K_1 + c} \tag{3.28}$$

Generally, the adsorption capacity of sediments is inversely related to particle size: clays > silts > sands. Sorption of organic chemicals is also a function of the organic content of the sediment, as measured by K_{oc}, and silts are most likely to have the highest organic content.

$$K_{oc} = \frac{\text{mass of toxicant sorbed/mass of organic carbon in sediment}}{\text{toxicant concentration in dissolved phase}}$$

At low concentrations, equation (3.15) reduces to

$$r = K_p\,c \tag{3.29}$$

where $K_p = K_1 r_c/K_2$. The partition coefficient is K_p for small concentrations of dissolved toxicant, where the units are ℓ/kg.

Sometimes a Freundlich isotherm is inferred from empirical data. The function is of the form

$$r = K\,c^{1/n} \tag{3.30}$$

where n is usually greater than 1. In dilute solutions, when n approaches 1, the Freundlich coefficient, K, is the partition coefficient, K_p (O'Connor, 1980).

The partition coefficient is derived from

$$\frac{dc}{dt} = -k_1\,c + k_2\,c_p$$

$$\frac{dc_p}{dt} = k_1\,c - k_2\,c_p \tag{3.31}$$

where k_1 is the adsorption rate constant and k_2 is the desorption rate constant.

The total concentration of toxicant, c_T, is

$$c_T = c + c_p = f_d c_T + f_p c_T \tag{3.32}$$

where f_d and f_p are the dissolved and particulate fractions, respectively:

$$f_d = c_\infty/c_T = 1/(1 + K_p m) \tag{3.33}$$

$$f_p = c_{p\infty}/C_T = K_p m/(1 + K_p m) \tag{3.34}$$

and the ratio of the reaction rates is related by

$$\frac{k_2}{k_1} = \frac{c_\infty}{c_{p\infty}} = \frac{1}{K_p m} \tag{3.35}$$

where the ∞ subscripts indicate steady-state.

From kinetics experiments where dissolved and particulate concentrations are monitored over time, the ratio of steady-state concentrations can be read from the graph (Figure 3.06).

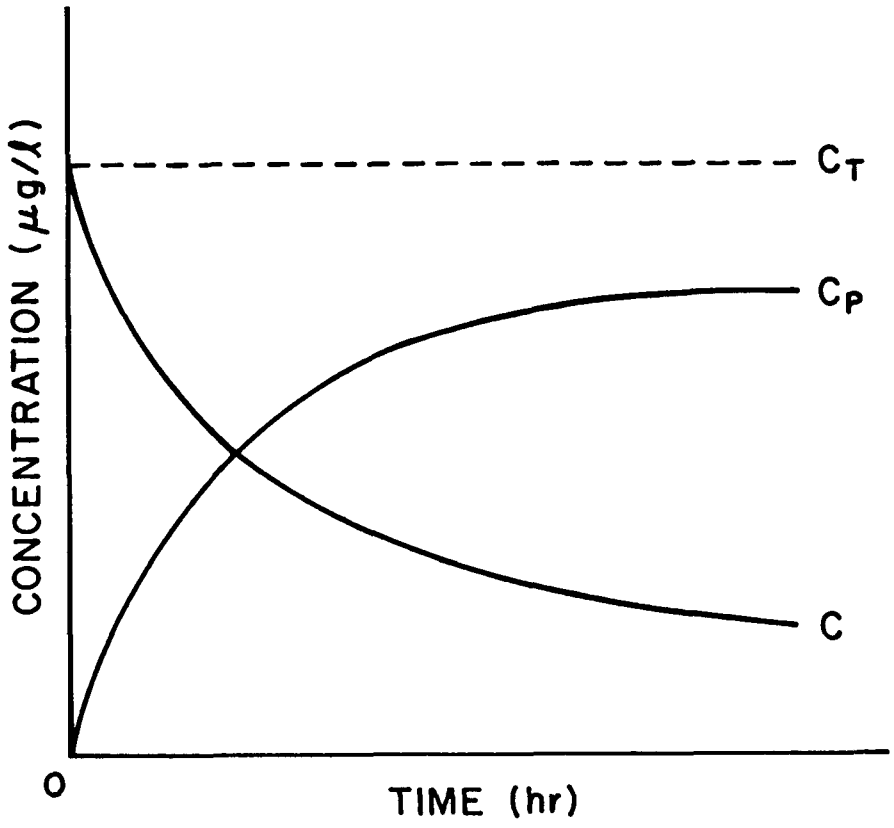

Figure 3.06. Dissolved and particulate toxicant as a function of time.

Sorption reactions usually reach chemical equilibrium quickly, and the kinetic relationships can often be assumed to be at steady-state. This is sometimes referred to as the "local equilibrium" assumption, when the kinetics of adsorption and desorption are rapid relative to other kinetic and transport processes in the system.

Lu (1977) used radio-labeled vinyl chloride, benzidine, and benzo[a]pyrene for fate analysis in a microcosm ecosystem. Photolytic

degradation of benzidine and benzo[a]pyrene was measured, and K_{ow} was reported.

Chiou et al. (1979) reported partition coefficients for 15 compounds, and related them to solubility (uM) by

$$\log K_p = 4.04 - 0.557 \log S \qquad (3.36)$$

Karickoff (1979) investigated the sorption of ten organic chemicals that have varying solubilities. K_{ow} was measured for all chemicals, and partition coefficients were measured for pyrene and methoxychlor. Schwarzenbach and Westall (1981) correlated K_{ow} with the partition coefficient but the slopes and intercepts varied from one sediment sample to another. Karickhoff et al. (1979) were the first investigators to report the dependence of the sediment-water partition coefficient on the fraction of organic carbon in the solid phase, indicating a solubility or solution phenomenon rather than true adsorption. O'Connor and Connolly (1980) investigated the effects of solids concentration on the partition coefficient. Chemicals included were kepone, heptachlor, DDT, dieldrin, PCB, and lindane. Partitioning varied inversely with solids concentration for sediment data.

DiToro et al. (1982) observed that PCB adsorption was a function of sediment solids concentration in Saginaw Bay, Lake Huron, Michigan. Reversibility of adsorption and desorption was investigated, and a resistant-reversible model was developed. DiToro and Horzempa (1982) tested the resistant-reversible model developed for PCB with atrazine, picloram, and 2,4,5-T. The model "provides additional insight into the influence of kinetics, sediment type, and aqueous-phase modifications since it is possible to observe the effects on each of the components individually." Jaffe and Ferrara (1983) reported partial pressure, solubility, Henry's constant, and K_{ow} for ten organic compounds as part of a comparison between a kinetics approach and an equilibrium approach in toxics modeling. Lyman (1982a) presented K_{ow} data on 92 organic chemicals and gave estimation methods based on the fragment method, solubility, and activity coefficients (Figure 3.07).

3.8 BIOCONCENTRATION

Bioconcentration of toxicants is defined as the direct uptake of aqueous toxicant through the gills and epithelial tissues of aquatic organisms. This fate process is of interest because it helps to predict human exposure to the toxicant in food items, particularly fish. Bioconcentration is part of the greater picture of bioaccumulation and biomagnification that includes food chain effects. Bioaccumulation refers to uptake of the toxicant by the fish from a number of different sources including bioconcentration from the water and biouptake from various food items (prey) or sediment ingestion. Biomagnification refers to the process whereby bioaccumulation increases with each step on the trophic level.

Bioconcentration experiments measure the net bioconcentration effect after x days, having reached equilibrium conditions, by measuring the

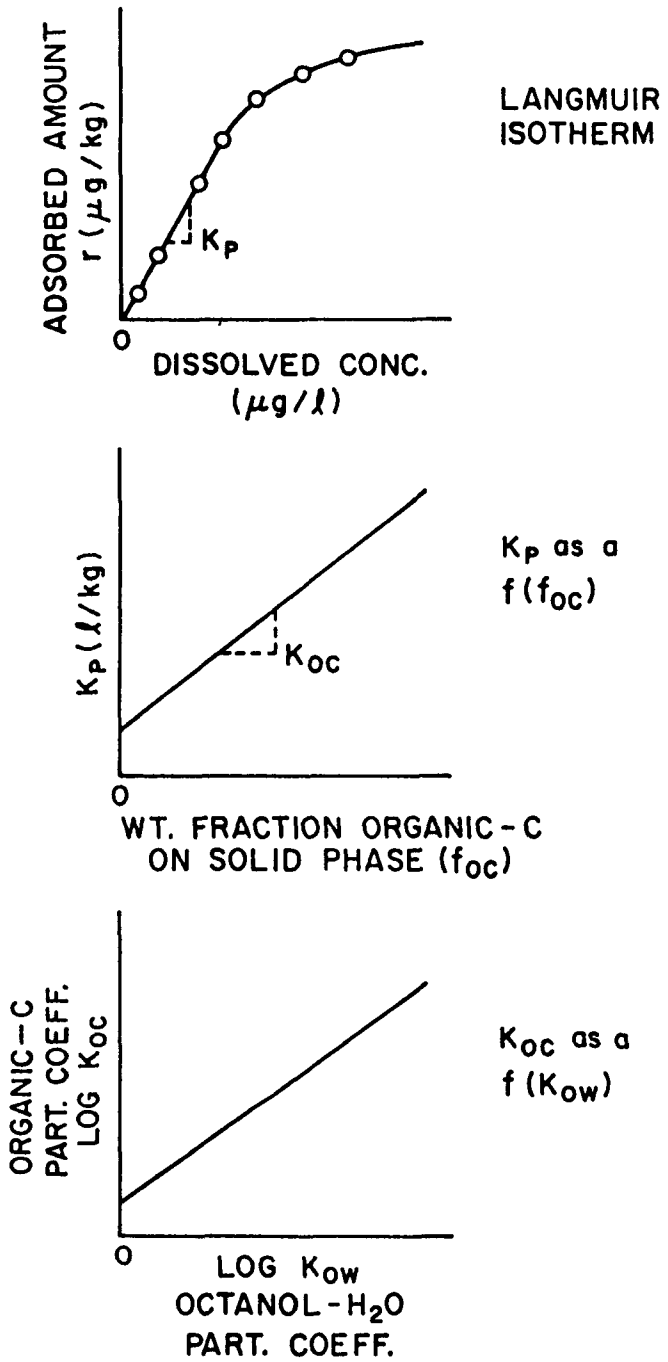

Figure 3.07. Determination of partitioning rate constants.

toxicant concentration in the test organism. The BCF (bioconcentration factor) is the ratio of the concentration in the organism to the concentration in the water.

The BCF derives from a kinetic expression relating the water toxicant concentration and organism mass:

$$dF/dt = ek_1C/B - k_2F \tag{3.37}$$

in which

- e = efficiency of toxic adsorption at the gill
- k_1 = (ℓ filtered/kg organism-day)(kg organism/ℓ)
- k_2 = depuration rate constant including excretion and clearance of metabolites, day^{-1}
- C = dissolved toxicant, μg/ℓ
- B = organism biomass, kg/ℓ, and
- F = organism toxicant residue (whole body), μg/kg.

The steady-state solution is

$$F = ek_1C/k_2B = (BCF)(C) \tag{3.38}$$

where BCF has units of (μg/kg)/(μg/ℓ). Bioconcentration is analagous to sorption, which was discussed previously. Organic chemicals tend to partition into the fatty tissue of fish and other aquatic organisms, and BCF is analagous to the sediment-water partition coefficient, K_p. Bioconcentration also can be measured in algae and higher plants, where uptake occurs by adsorption to the cell surfaces or sorption into the tissues. Several studies have improved and provided more detail on the simple bioconcentration model using pharmacokinetic or bioenergetic approaches (Norstrom et al. 1976; Blau et al. 1975; Jensen et al. 1982; Spacie and Hamelink, 1983; Mackay, 1982; Mackay and Hughes, 1984; Hawker and Connell, 1985; and Suarez et al. 1987).

Many of the chemicals of interest are hydrophobic (lipophilic), which makes them more prone to bioconcentration. Several investigators (Kenaga and Goring, 1980; Veith, 1980; Bysshe, 1982; Oliver and Niimi, 1983) observed strong correlations between the octanol/water partition coefficient and the BCF. (The octanol/water partitioning coefficient data, K_{ow}, are compiled in the Partitioning table in the appendix.) Concentration of lipophilic toxicants in biological tissues is expected because the lipid concentration in cells is much higher than that in the water column. Because the chemical is more easily dissolved in a nonpolar solvent (e.g., lipids), it will seek out biological tissues because it does not dissolve well in polar solvents (e.g., water).

The information presented in the bioconcentration table in the appendix includes <u>only</u> direct uptake of the toxicant from the dissolved phase; a summary of bioconcentration factors is presented in Table 3.08. The tabulation does not include food chain bioaccumulation, where the prey is contaminated and another route of exposure to the test organism is through its food. Biomagnification also includes bioconcentration: biomagnification is that phenomenon in which the toxicant body burden increases as one moves up the food chain from primary producers to top predator.

Bioconcentration experiments, per se, do not measure the metabolism or detoxification of the chemical. Chemicals can be metabolized to more or less toxic products that may have different depuration characteristics. The

TABLE 3.08 SUMMARY TABLE OF BIOCONCENTRATION DATA

Range of Values	Bioconcentration Factor $\left(\frac{\mu g/kg}{\mu g/\ell}\right)$
Pesticides	
Carbofuran	0
DDT	5900-85,000
Parathion	335
PCBs	
Aroclor 1248	72,950
Halogenated aliphatic hydrocarbons	
Chloroform	6
Halogenated ethers	
2-Chloroethyl vinyl ether	N/A
Monocyclic aromatics	
2,4-Dimethylphenol	150
Pentachlorophenol	16-900
Phthalate esters	
Bis(2-ethylhexyl)phthalate	20-13,600
Polycyclic aromatic hydrocarbons	
Anthracene	917
Benzo[a]pyrene	920-134,248
Nitrosamines & Miscellaneous	
Benzidine	55-2617
Dimethyl nitrosamine	N/A

bioconcentration experiment only measures the final body burden at quilibrium (although interim data that were used to determine when equilibrium was reached may be available). The fact that a chemical bioaccumulates at all is an indication that it resists biodegradation and is somewhat "biologically hard" or "non-labile."

Lu (1977) used radio-labeled vinyl chloride, benzidine, and benzo[a]pyrene for fate analysis in a microcosm ecosystem. Photolytic degradation of benzidine and benzo[a]pyrene was measured, and K_{ow} was reported. Bioconcentration in algae (Oedogonium cardiacum), fish (Gambusia affinis), daphnia (Daphnia magna), mosquito larvae (Culex pipiens quinquefasciatus) and snails (Physa sp.) was measured. Vinyl chloride did not bioaccumulate; benzo[a]pyrene and benzidine bioaccumulation were closely related to their K_{ow}.

Glooschenko (1979) measured bioconcentration of chlordane in the alga Scenedesmus quadricauda. Chlordane stimulated respiration and reproduction at 1 to 100 µg/ℓ during the 12-day experiment. Kenaga and Goring (1980) compiled solubility, K_{oc}, K_{ow} and bioconcentration data for 170 organic compounds. They found that bioconcentration data for daphnia were generally within an order of magnitude of bioconcentration data for fish. Bivariate equations were developed relating all the variables. Veith (1980) measured solubility in distilled water and the K_{ow} of 28 organic chemicals as part of a study to estimate the bioconcentration in fish from these physical parameters. Bioconcentration experiments were run using bluegill sunfish (Lepomis macrochirus) for an exposure period of 28 days. The test water was at pH 7.1 with a hardness of 35 mg/ℓ $CaCO_3$. The bioconcentration experiment was followed by a 7 day depuration period. Correlation between the K_{ow} and bioconcentration was observed as:

$$\log BCF = 0.76 \log K_{ow} - 0.23 \qquad (3.39)$$

which has an r of 0.907 for 84 data.

Bysshe (1982) gave many bioconcentration data for organic compounds, and included Veith's equation for estimating bioconcentration from K_{ow}, and Kenaga and Goring's equation for estimating bioconcentration from solubility. Schnoor (1982) calculated bioconcentration factors from field data for six pesticides and PCB from field data for fish. The bioconcentration factors were normalized based on fish oil (or lipid content) and correlated with K_{ow}. Virtanen and Hattula (1982) tested the environmental fate of 2,4,6-trichlorophenol in a microcosm ecosystem. Bioconcentration was measured in waterweed (Elodea sp.), algae (Oedogonium sp.), guppy (Poecilia reticulatus), sowbug (Asellus aquaticus), snail (Lymnea stagnalis), and emergent macrophyte (Echinodorus sp.) after 36 days of exposure.

Ghisalba (1983) compiled bioconcentration data for many organic compounds as part of a project to evaluate the biodegradability of these compounds. McCall (1983) reported solubility, vapor pressure, Henry's constant, and bioconcentration factors for seven organic chemicals as part of a fate model for fish in an aquatic system with sediments. Oliver and Niimi (1983) studied bioconcentration in rainbow trout (Salmo gairdneri) with ten chlorobenzenes. The bioconcentration experiments lasted 119 days and were maintained at 15°C. For equilibrium conditions, the authors developed equations relating bioconcentration and K_{ow}:

$$\log BCF = -0.632 + 1.022 \log K_{ow}$$

for high exposures, and (3.40)

$$\log BCF = -0.869 + 0.997 \log K_{ow}$$

for low exposures. Hexachlorobenzene did not reach equilibrium in the experiments and was not included in the regression equations.

Banerjee, Sugatt and O'Grady (1984) developed a simple method for determining the bioconcentration of stable lipophilic compounds. Bioconcentration for those chemicals tested (pentachlorobenzene, 1,2,3,4-tetrachlorobenzene, 1,2,3,5-tetrachlorobenzene, 1,4-diiodobenzene), and predicted BCF based on K_{ow} were in agreement with the test results. The test organisms were Salmo gairdneri (rainbow trout), Lepomis macrochirus (bluegill sunfish) and Poecilia reticulata (guppy). Call et al. (1984) used ^{14}C to study bioconcentration of five pesticides in Pimephales promelas (fathead minnow). Their study also included LC_{50} testing of 23 compounds (including pesticides and heavy metals] on 8 organisms. Thomann and Connolly (1984) reported bioconcentration values for PCB in phytoplankton, Mysis relicta, Alosa pseudoharenqus (alewife), and Salvelinus namycush (lake trout) calculated from K_{ow} data as part of a food chain model for Lake Michigan. They determined that uptake of PCB from prey items was a more important source of contaminant to the top carnivore (lake trout) than bioconcentration from the dissolved phase through the gill membrane.

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SECTION 4

REACTIONS OF HEAVY METALS

4.1 INTRODUCTION

"Heavy metals" usually refer to those metals between atomic number 21 (scandium) and atomic number 84 (polonium), which occur either naturally or from anthropogenic sources in natural waters. These metals are sometimes toxic to aquatic organisms depending on the concentration and chemical speciation. The lighter metal aluminum (atomic number 13) and the non-metals arsenic and selenium (atomic numbers 33 and 34) also are included in this broad class of pollutants.

Heavy metals differ from toxic organic pollutants in that they frequently have natural background sources from dissolution of geologic strata or volcanic activity. In addition, the total metal concentration is conservative in the environment, so that while the pollutant may change its chemical speciation, the total remains constant. It cannot be "mineralized" to innocuous end-products as is often the case with toxic organic chemicals. Heavy metals are a pollution problem in terms of violations of water quality standards. Thus, waste load allocations are needed to determine the permissable discharges of heavy metals by industries and municipalities.

Heavy metals frequently adsorb or "bind" to solid surfaces. The mechanism of sorption or attachment is different than for organic pollutants. This mechanism has been described as primarily a solution phenomenon of "likes-dissolving-likes", that is, organic pollutants sorbing into the organic matrix of sediments or suspended solids. For heavy metals, the phenomenon is via: 1) physical adsorption to solid surfaces, 2) chemical sorption or binding by ligands at the solid-water interface, or 3) ion exchange with an ion at the solid-water interface. In addition, if the heavy metal is complexed in solution by an organic ligand, it could sorb into the organic solid phase much like an organic pollutant. The mathematical formulation for describing the partitioning of the heavy metal between the solid phase and the aqueous phase is usually called the "distribution coefficient" for heavy metals, although it may be referred to as the partition coefficient or the binding constant in some cases.

$$K_D = \frac{C_p}{CM} \tag{4.1}$$

where K_D = the distribution coefficient, ℓ/kg
C_p = the concentration of the metal in the sorbed phase, μg/ℓ

C = the concentration of the metal in the dissolved phase, μg/ℓ
M = the concentration of solids, kg/ℓ

To calculate the ratio of the concentration of the adsorped particulate phase to the dissolved phase, one needs the solids concentration M to estimate the important dimensionless number K_DM.

$$K_DM = C_p/C \tag{4.2}$$

The calculation of the fraction of the total (whole water) concentration in either the dissolved or the particulate phase is identical to that of organic chemicals, only the distribution coefficient K_D replaces the partition coefficient K_p.

In addition to the distribution between the solid and aqueous phase, one frequently requires knowledge of chemical speciation. Sometimes one chemical species is known to be much more toxic than another for a given heavy metal. This is especially important because some States and EPA have been moving towards "site-specific water quality standards," in which the chemical speciation will be considered on a site-by-site basis. For example, a site that is known to have a great deal of naturally occurring dissolved organics may not require as stringent of a water quality standard because the dissolved organic material may complex the heavy metal and render it non-toxic to biota.

In this Section, we will examine the equilibrium and kinetic reactions that are characteristic of an important subset of heavy metals (Cd, As, Hg, Se, Pb, Ba, Zn, Cu). These elements are frequently cited in the literature as being of concern due to their aquatic toxicity or human carcinogenicity. In addition, they frequently occur in wastewater discharges (Cd, Zn, Cu), from coal and fossil fuel combustion (Hg, Pb, Cd, Zn) and the inter-media transport of atmosphere to water, from leaching of mine-tailings or agricultural return waters (As, Se, Ba), and from natural background sources (As, Se, Ba, Cu).

4.2 EQUILIBRIUM AND KINETIC REACTIONS FOR HEAVY METALS

4.2.1 Cadmium

Divalent cadmium ion, Cd^{2+}, is the predominant species of cadmium found in surface waters, although organic complexes account for a variable (frequently significant) percentage of the dissolved concentration. Other species ($CdSO_4$, $CdCO_3$, $CdOH^+$ and $CdCl^+$) are present in lesser concentrations. Cd^{2+} is usually the dominant (60 - 90%) species in natural water even in the presence of high concentrations of cadmium-complexing ligands. This is significant because free cadmium (Cd^{2+}) is widely accepted as playing an important role in aquatic toxicity (Shepard et al., 1980). Gardiner (1974a) calculated the levels of various species of cadmium in different samples (Table 4.01).

TABLE 4.01 EXTENT OF COMPLEXATION OF CADMIUM IN BOREHOLE WATER, SETTLED SEWAGE, SEWAGE EFFLUENTS, AND RIVER WATER SAMPLES

	Calculated Proportion (%) as							
Sample No.	$CdOH^+$	$CdCO_3$	$CdCl^+$	$CdSO_4$	Cd Humic Complex	Cd^{2+}	E_o-E (mV)	Observed Proportion as Cd^{2+} (%)
1 BH	1.4	3.9	1.8	0.6	0	92	1.5	89
2 SS	1.8	9.0	5.3	3.1	39	41	12.3	38
3 SE	3.2	15	5.2	2.5	38	35	14.4	32
4 SE	3.6	12	6.2	3.0	37	38	12.9	29
5 RW	2.8	6.1	4.6	7.2	24	55	6.0	63
6 RW	6.5	21	2.6	2.6	9.3	59	7.8	54
7 RW	4.9	16	6.0	4.3	24	44	13.8	35
8 RW	5.7	18	3.8	4.1	16	52	8.6	51
9 RW	4.8	12	10	5.1	12	56	5.5	6.5
10 RW	3.6	9.7	9.2	7.7	20	51	8.1	53
11 RW	2.6	3.9	3.5	7.2	24	58	7.9	54

Total added cadmium concentration was 1.0 mg l^{-1} except for Samples 2-4 (10.3 mg l^{-1}) and Sample 5 (2 mg l^{-1})

BH: Borehole water
SS: Filtered Settled Sewage
SE: Filtered Settled Effluent
RW: Filtered River Water

Among the mechanisms by which cadmium is removed from the water column are precipitation and adsorption or chemisorption on the surface of solids. Concentrations of cadmium in freshwater are usually lower than the maximum permitted by the solubility product of the carbonate, which is probably the least soluble salt in most natural waters. Adsorption, therefore, would be the most important factor influencing the partitioning of cadmium between aqueous and solid phases and its transport in a water course.

Adsorption with river mud samples usually occurs fast and a great percentage of the equilibrium concentration of the solid phase is achieved within 2 minutes (Gardiner, 1974a). T.H. Christenson (1984) observed that equilibrium with regard to sorption of Cd to soil samples was achieved in approximately 1 hour. The concentration factor (distribution coefficient)

for river mud samples varied with types of solid, its state of subdivision, time of contact, and the concentration of complexing agent (Gardiner, 1974a). Organic materials such as humic acids were the main component of the mud samples responsible for adsorption of cadmium.

Suzuki et al., (1979) have shown that, in the case of sediments from the Tama River, adsorption capacity of the organic matter was 95 times the adsorption capacity of inorganic matter. Suspended solids, especially organic matter (20mg/l), had seven times more capacity than the aqueous phase for transport of Cd in the flowing water. Binding or complexing agents such as alginic and humic acids increased the uptake of cadmium on kaolinite, whereas EDTA diminished the uptake (Hass and Horowitz, 1986; and Laxen, 1981). The results suggest that the enhancement of uptake is due to the formation of an adsorbed organic layer on the clay serving as a solid phase ligand.

Fristoe and Nelson (1983) applied a chemical speciation model to Cd in activated sludge. They observed that adsorption of cadmium by bacterial solids and cadmium complexation by dissolved organics were both pH dependent. Soluble cadmium speciation was dominated by the free Cd^{2+} ion at pH below 6, by cadmium-organic complex at pH 6 and pH 7 and by inorganic species at pH 8 and pH 9. Cadmium that was adsorbed to bacterial cells increased greatly with pH, from nearly 30% at pH 4 to 90% at pH 9.

Cadmium is extremely toxic to fish even at low concentrations of 5 to 10 ug/ℓ. Sunda et al. (1978), in their study on the effect of speciation on toxicity of cadmium to Grass shrimp (Palaemontes pugia), found that complexation by NTA and chloride greatly reduced cadmium toxicity. An LC_{50} of $4x10^{-7}$ M of Cd^{2+} were reported. The dynamics of Cd and uptake into different organs of Aondonta cygnea L. was studied by Balogh and Solanki (1984). The rate and amount of bioaccumulation of Cd in the kidney was higher than in other organs. Fayed and Abd-EI-Shafy (1985) found that the concentration factor for Cd in plants of the Nile River (Eichhornia crassipes) was approximately 300. The distribution coefficient in sediments was much higher.

The fate of Cd can be described by the generalized schematic given by Fontaine (1984) in Figure 4.01. Fontaine's (1984) model includes a number of ligands or substrates for complexation or binding in both the water column and the active sediment compartment. It also includes transport by advection or groundwater inputs or export.

4.2.2 Arsenic

Arsenic can occur in four stable oxidation states in the environment (+5, +3, 0, -3). It therefore has an unusually complex chemistry. Because extremely low redox potential conditions are required for -3 states, its occurence is rare. A list of arsenic species commonly found in environmental samples is given in Table 4.04.

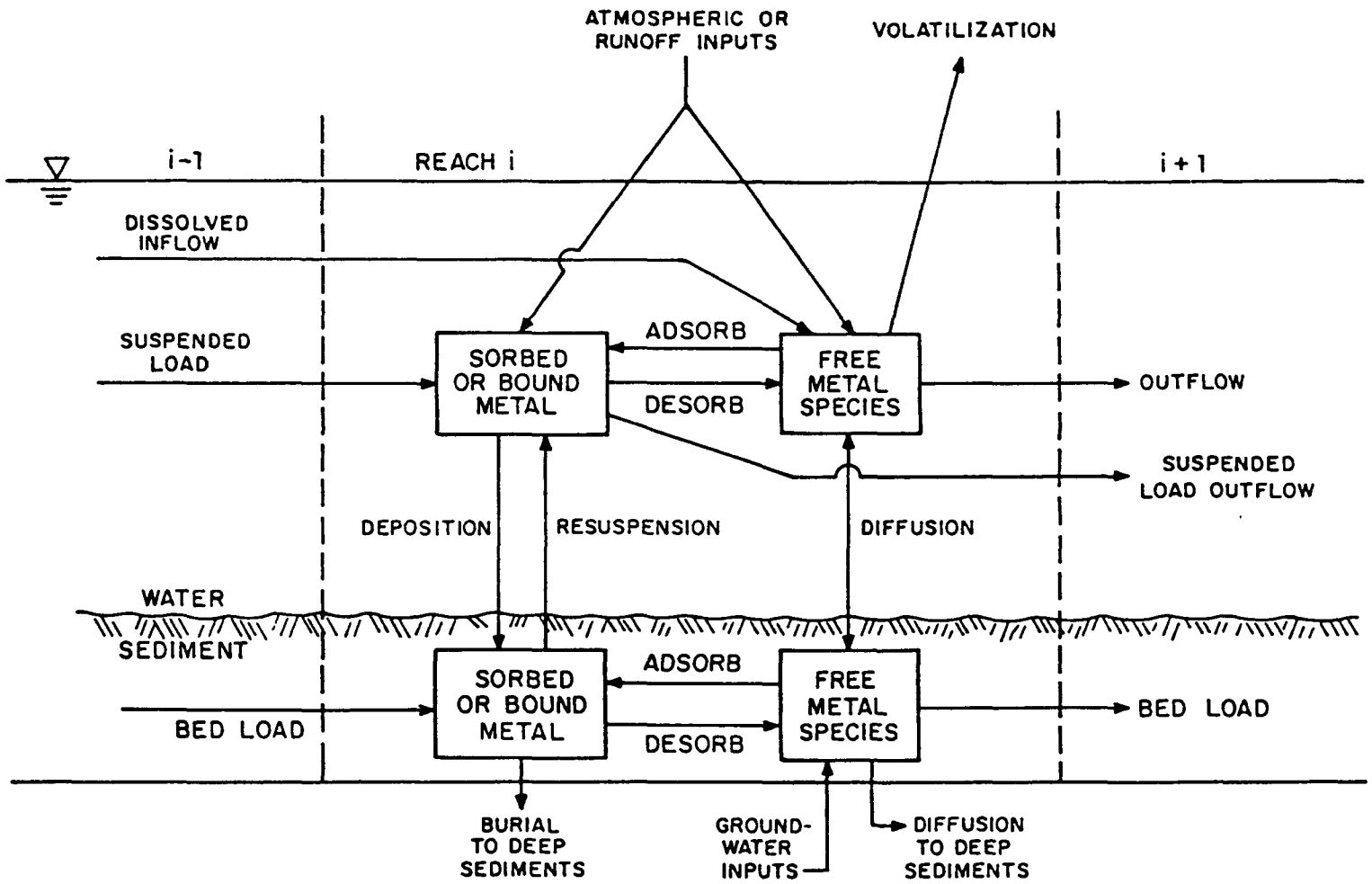

Figure 4.01. General schematic of NONEQUI.

Sergeyeva and Khodakovsky (1969) have used a thermodynamic approach to calculate the stabilities of the arsenic in different oxidation states in an aquatic system and plotted an Eh-pH diagram that illustrates clearly the predominant soluble and solid species. They overlooked the significance of sulfur and its reaction with arsenic in nature, however. Ferguson and Gavis (1972) presented a more detailed Eh-pH diagram that takes into account the influence of sulfur (Figure 4.02). Tables 4.02 and 4.03 show the major equilibrium constants and sorption (binding) constants for cadmium at various pH values and sorbents.

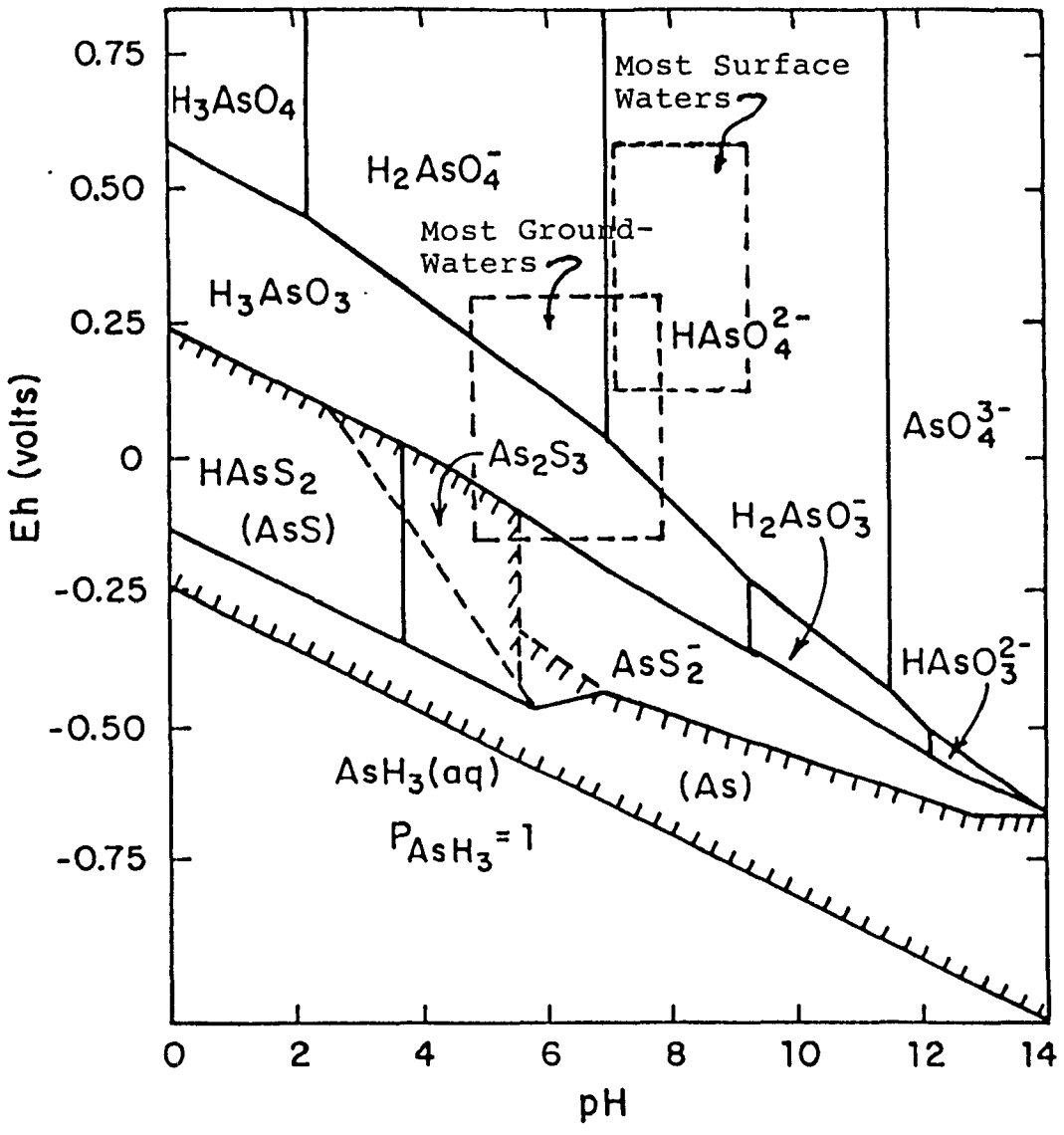

Figure 4.02 The Eh-pH diagram for As at 25°C and one atmosphere with total arsenic 10^{-5} mol L^{-1} and total sulfur 10^{-3} mol L^{-1}. Solid species are enclosed in parentheses in cross-hatched area, which indicates solubility less than $10^{-5.3}$ mol ℓ^{-1}.

TABLE 4.02 EQUILIBRIUM CONSTANTS FOR CADMIUM

Ligand	Log K	Equation and Comments	Reference
OH^-	5.0	$Cd^{2+} + OH^- \rightleftarrows CdOH^+$	Sillen and Martell (1964)
	10.6	$Cd^{2+} + 2)H^- \rightleftarrows Cd(OH)_2$	Sillen and Martell (1964)
	10.0	$Cd^{2+} + 3OH^- \rightleftarrows Cd(OH)_3^-$	Sillen and Martell (1964)
	10.0	$Cd^{2+} + 4OH^- \rightleftarrows Cd(OH)_4^{2-}$	Sillen and Martell (1964)
Cl^-	2.0	$Cd^{2+} + Cl^- \rightleftarrows CdCl^+$	Sillen and Martell (1964)
	2.7	$Cd^{2+} + Cl^- \rightleftarrows CdCl_2$	Sillen and Martell (1964)
	2.1	$Cd^{2+} + 3Cl^- \rightleftarrows CdCl_3^-$	Sillen and Martell (1964)
HCO_3^-	2.1	$Cd^{2+} + HCO_3^- \rightleftarrows CdHCO_3^+$	Zirino and Yamamoto (1972)
CO_3^{2-}	4.1	$Cd^{2+} + CO_3^{2-} \rightleftarrows CdCO_3$	Gardiner (1974)a
F^-	1.1	$Cd^{2+} + F^- \rightleftarrows CdF^+$	Felmy, Grivin, and Jenne (1985)
	1.5	$Cd^{2+} + 2F^- \rightleftarrows CdF_2$	Felmy, Grivin, and Jenne (1985)
Br^-	2.17	$Cd^{2+} + Br^- \rightleftarrows CdBr^+$	Felmy, Grivin, and Jenne (1985)
	2.9	$Cd^{2+} + 2Bf^- \rightleftarrows CdBr_2$	Felmy, Grivin, and Jenne (1985)
I^-	2.15	$Cd^{2+} + IO^- \rightleftarrows CdI^+$	Felmy, Grivin, and Jenne (1985)
	3.6	$Cd^{2+} + 2I^- \rightleftarrows CdI_2$	Felmy, Grivin, and Jenne (1985)
SO_4^{2-}	2.3	$Cd^{2+} + SO_4^{2-} \rightleftarrows CdSO_4$	Sillen and Martell (1964)
	3.5	$Cd^{2+} + 2SO_4^{2-} \rightleftarrows CdSO_4^{2-}$	Sillen and Martell (1964)
S^-	-27	$Cd^{2+} + S^{2-} \rightarrow CdS$	Sillen and Martell (1964)

TABLE 4.02 (continued)

Ligand	Log K	Equation and Comments	Reference
NTA	10.00	$Cd^{2+} + NTA^{3-} \rightleftarrows CdNTA^{-}$	Sillen and Martell (1964)
EDTA	16.4	$Cd^{2+} + EDTA^{4-} \rightleftarrows Cd\text{-}EDTA^{2-}$	Sillen and Martell (1964)
Glycine	4.74	$Cd^{2+} + Gly^{-} \rightleftarrows Cd\text{-}Gly^{+}$	Sillen and Martell (1964)
	3.9	$Cd^{2+} + 2Gl^{-} \rightarrow Cd(Gly)_2$	Sillen and Martell (1964)
FA	4.7	$Cd^{2+} + FA \rightleftarrows CdFA$(pH=6.5)	Sterritt and Lester (1984)
HA	6.9	$Cd^{2+} + 2HA \rightleftarrows Cd(HA)_2$(I=0)	Stevenson (1976)
K. Aerogenes Polymer	5.16	$Cd^{2+} + L \rightarrow Cd\text{-}L$ (pH=6.8)	Rudd et al., (1984)b

TABLE 4.03. CONSTANTS FOR CADIUM ADSORPTION

Adsorbent	Langmuir $b(\frac{m\ mol}{Kg})$	$K(10^5\ \frac{L}{mol})$	Comments	Reference
Humic Acid (HA)	330	5.9	pH=4.4 (Sample A)	Beveridge and Pickering (1980)
	310	2.2	pH=4.4 (Sample B)	
	690	3.8	pH=4.4 (Sample C)	
	575	1.1	pH=4.4 (Sample D)	
Kaolin	17	2.0	25°C, pH=5	Farrah et al., (1980)
Illite	49	5.0	Na^+ form clay	
Montmorillonite	315	8.0		
Bentonite	0.84	13.0		Oakley et al., (1981)
$Fe(OH)_3$	4.4	10.0	Temp=25°C	
MnO_2	13	11.5	pH=8	
Humic	3.5	0.6		
Sandy Loam	0.17	17.6	pH=6	Christenson (1984)
Kaolin	47.7	10.87		Miragaya (1986)
Montmorillonite	31.1	7.85		

Adsorbent	Freundlich K	n	Comments	Reference
Sepiolite	95	0.65	x(ppb), C(ppb)	Rybica
Bentonite	2.25	0.64	X(mg/g), C(mg/ml)	Guy et al., (1975)

Adsorbent	Partition Coeff, Kd(L/Kg)	Comments	Reference
Bentonite	1100	pH=8	Oakley (1981)
$Fe(OH)_3$	4400	pH=8	Oakley (1981)
MnO_2	1500	pH=8	Oakley (1981)
Humic	200	pH=8	Oakley (1981)
Montmorillonite	500	I=0.01M pH=5	Egozy
	50	I=0.1M pH=5	
	10	I=1M pH=5	
Sandy Loam	20	pH=4	Christenson (1984)
	40	pH=5	Christenson (1984)
	200	pH=6	Christenson (1984)
	450	pH=7	Christenson (1984)
	2140	pH=7.7	Christenson (1984)

TABLE 4.03 (continued)

Adsorbent	Partition Coeff, Kd(L/Kg)	Comments	Reference
Loamy Sand	20	pH=4	Christenson (1984)
	60	pH=5	Christenson (1984)
	225	pH=6	Christenson (1984)
	8100	pH=7	Christenson (1984)
	3940	pH=7.7	Christenson (1984)
Silica	1000		J. Gardiner (1974b)
Kaolin	380		J. Gardiner (1974b)
Humic Acid	20,000		J. Gardiner (1974b)
Fish Faecal Matter	200-1000		J. Gardiner (1974b)
Plant Material	1000		J. Gardiner (1974b)

Langmuir Isotherm

$$\frac{C}{q} = \frac{1}{Kb} + \frac{C}{b}$$

C = concentration
q = moles solute/unit mass adsorbent
K = bonding constant
b = sorption capacity

Freundlich Isotherm

$$X = K C^n$$

K, n = constants
X = mass solute sorbed/unit mass adsorbent
C = Concentration

HA = Humic Acid
FA = Fulvic Acid

TABLE 4.04 ARSENIC SPECIES COMMONLY FOUND IN ENVIRONMENTAL SAMPLES

Species	Names	Oxidation State
AsO_4^{-3}	Arsenate	+5
AsO_3^{-3}	Arsenite	+3
$CH_3AsO(CH)_2$	Methanearsonic Monomethyl Arsonic Acid	+3
$(CH_3)_2AsOOH$	Hydroxydimethyl Arsine Oxide Dimethyl Arsinic Acid Cacodylic Acid	+1
AsH_3	Arsine	-3
$(CH_3)_2AsH$	Dimethyl Arsine	-3
$(CH_3)_3As$	Trimethyl Arsine	-3

Ferric arsenate (pK_{sp} = 20.2) is stable only at pH < 2.3 and at an Eh of +0.74 V, and therefore is not normally significant. At high Eh values encountered in oxygenated waters, arsenic acid species (H_3AsO_4, H_2AsO_4, $HAsO_4^{2-}$ and AsO_4^{3-}) are stable. At very low Eh values arsine (AsH_3) may be formed and is very toxic. The organic arsenicals are stable at extremely low Eh values. These compounds are unstable with respect to the organic part of the molecule.

Except for a few oxidation-reduction reactions very little information exists about kinetic rates of arsenic reactions in solution. Specific rate constants are unknown. The rate of oxidation of arsenite with O_2, for example, is reported to be very slow at neutral pH, but proceeds measurably in several days in strong alkaline or acidic solution.

Wagemann (1978) has presented a study in which barium arsenate was added to water as a solid phase in addition to oxides and sulfides. Barium ion effectively limited the dissolved arsenate concentration by the common ion effect in the pH range 6-9, and soluble arsenate concentrations were less than 5 ug/ℓ. Cupric ion and ferric ion activity were controlled by ferric hydroxide and cupric oxide in oxygenated, surface waters. Tenorite, a cupric oxide, at pH 6 allowed 3.8 mg/ℓ of Cu to be soluble which complexed arsenate to 1.8 mg/ℓ. Copper-arsenate complexes can be important in some natural waters.

At 5 mg/ℓ of TOC, approximately 40 to 50% of total dissolved metals were present as metal-fulvic acid complex (Reuter and Perdue, 1977). Equilibrium calculations indicated that the formation of metal-organic complexes occurred largely at the expense of inorganic metal complexes, and

the free metal ion concentration changed little unless the concentration was very high. The amount of dissolved organic matter in most freshwater is sufficiently low that metal-organic complexes are not important. Because arsenic exists only as an anion, its complexation with humic and fulvic acid could be formed only via a metal-organic acid complex.

Braman and Foreback (1973) found methylarsenic and dimethylarsenic acid in a wide range of natural waters. In this study, lakes and ponds had a higher methlyarsenic acid content than rivers. A large fraction of arsenic in bird egg shell and sea-shells was found to be methylarsenic acid or dimethylarsenic acid. The reported toxicity of As (III) is approximately 25 times greater than that of dimethylarsenic acid. Dimethylarsenic is the more prevalent form of organo-arsenic compounds in natural water. Methylation may be serving as a means of detoxification in organisms.

Arsenic is removed from solution by adsorption onto clay or coprecipitation into metal ion precipitates. Anderson et al. (1976) studied arsenate adsorption on amorphous aluminum hydroxide as a model system for aqueous anion adsorption on oxide surfaces. The adsorption of arsenite and arsenate on iron hydroxide obeyed a Langmuir isotherm at low concentrations and low ionic strength (Pierce and Moore, 1982). The adsorption on oxide including aluminum and iron was pH dependent. Arsenite adsorbed on manganese oxide was oxidized to arsenate. Arsenate forms an insoluble salt with Mn^{2+}, Ni^{2+} or other alkaline cations. Takamatsu et al. (1985) state that the high concentration of arsenic in a manganese concretion from Lake Biwa is evidence for the accumulation of As into Mn^{2+} - rich sediments.

A cycle for arsenic in a stratified lake (Ferguson and Gavis, 1972) is illustrated in Figure 4.03. Tables 4.05 and 4.06 show the equilibrium constants for arsenate and Langmuir sorption constants on iron and aluminum hydroxides.

4.2.3 Mercury

Mercury occurs in nature in three oxidation states (0, +1, +2). The presence of the predominant species is dependent on the redox potential and pH of the environment, the existence of anions and other ligands that might form complexes with mercury.

Mercury is released into the air by outgassing of soil, by transpiration and decay of vegetation, and by volatilization and combustion processes. Most mercury is adsorbed onto atmospheric particulate matter. This is removed from air by dry fallout and rainout. Humic material forms complexes that are adsorbed onto alluvium, and only a small soluble fraction is taken up by biota. Small clay particles and rainout particles are distributed throughout the oceans because of slow settling velocities. Pelagic organisms agglomerate the mercury bearing clay particles, thus promoting sedimentation and affecting the fate of mercury in mid-oceanic chain. Another fate process is the uptake of dissolved mercury by phytoplankton and algae.

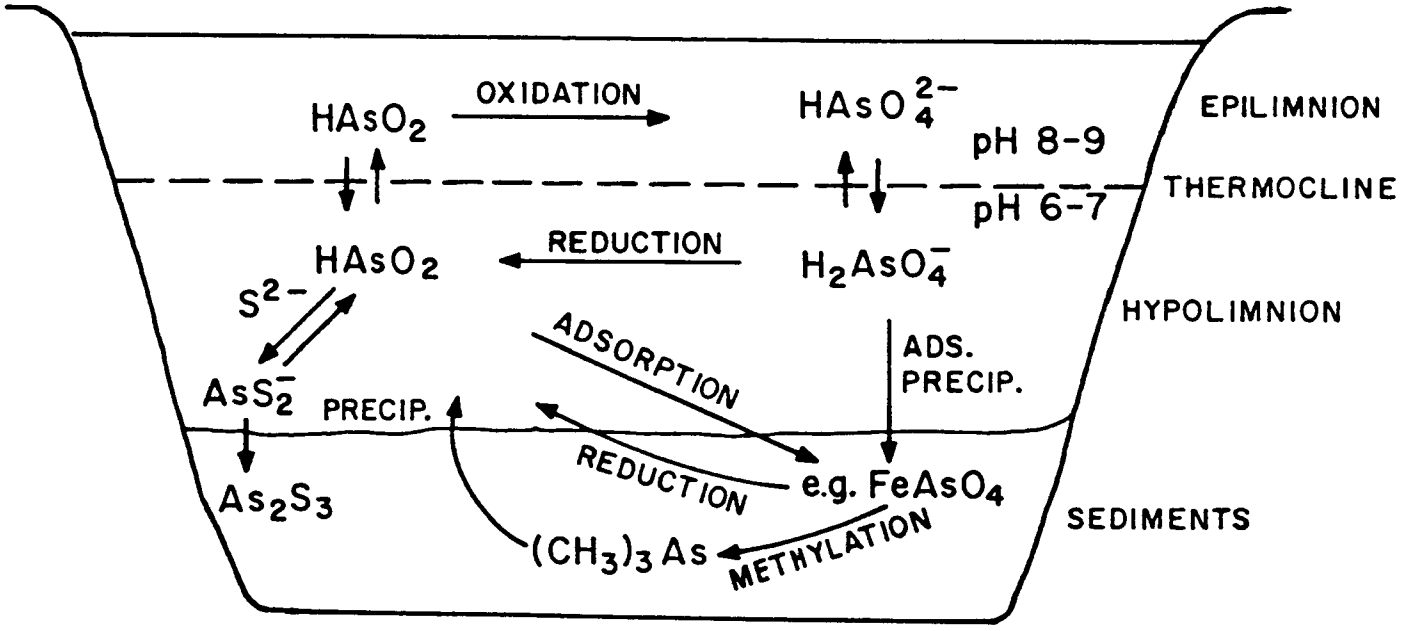

Figure 4.03. Cycle of arsenic in a stratified lake.

TABLE 4.05. EQUILIBRIUM CONSTANTS FOR ARSENIC

Ligand	Log K	Equation and Comments	Reference
H^+	20.5	$AsO_4^{3-} + 3H^+ \rightleftarrows H_3AsO_4$	Servgeyera & Khodakovsky (1969)
	18.5	$AsO_4^{3-} + 2H^+ \rightleftarrows H_2AsO_4^-$	Servgeyera & Khodakovsky (1969)
	11.0	$AsO_4^{3-} + H^+ \rightleftarrows H\ AsO_4^{2-}$	Servgeyera & Khodakovsky (1969)
	34.6	$AsO_3^{3-} + 3H^+ \rightleftarrows H_3AsO_3$	Servgeyera & Khodakovsky (1969)
	25.4	$AsO_3^{3-} + 2H^+ \rightleftarrows H_2AsO_3^-$	Servgeyera & Khodakovsky (1969)
	13.4	$AsO_3^{3-} + H^+ \rightleftarrows H\ AsO_3^{2-}$	Felmy et al (1985)

Solids in Equilibrium	Solubility Product Log K_{SP}	Comment	Reference
AlA_sO_4	-15.8		Frankenthal (1963)
$Ba_3(A_sO_4)_2$	-50.11		Frankenthal (1963)
$Ca_3(_sO_4)_2)$	-18.16		Frankenthal (1963)
$Cd_3(A_sO_4)_2$	-32.6		Frankenthal (1963)
$CO_3(A_sO_4)_2$	-28.1		Frankenthal (1963)
$Cu_3(A_sO_4)_2$	-35.1		Frankenthal (1963)
$Cr\ A_sO_4$	-20.1		Frankenthal (1963)
$Fe\ A_sO_4$	-20.2		Frankenthal (1963)
$Mg_3(A_sO_4)_2$	-19.6		Frankenthal (1963)
$Ni_3(A_sO_4)_2$	-25.5		Frankenthal (1963)
$Pb(A_sO_4)_2$	-34.4		Frankenthal (1963)
$Sr_3(A_sO_4)_2$	-18.1		Frankenthal (1963)
$Zn(A_sO_4)_2$	-27.4		Frankenthal (1963)
$Mn_3(A_sO_4)_2$	-28.7		Frankenthal (1963)

TABLE 4.06. CONSTANTS FOR ARSENATE ADSORPTION

Adsorbent	Langmuir $b(\frac{m\ mol}{Kg})$	$K(10^5 \frac{L}{mol})$	Comments	Reference
$Al(OH)_3$	1600	1.23	pH=5	Anderson et al., (1976)
Suspension	1178	1.49	pH=6	Anderson et al., (1976)
	1179	1.78	pH=7	Anderson et al., (1976)
	838	1.34	pH=8	Anderson et al., (1976)
	680	0.72	pH-8.5	Anderson et al., (1976)
	501	0.41	pH=9	Anderson et al., (1976)
$Fe(OH)_3$	1530	14.6	pH=4	Pierce & Moore (1982)
	1100	25.2	pH=5	Pierce & Moore (1982)
	850	32.3	pH=6	Pierce & Moore (1982)
	454	11.4	pH=7	Pierce & Moore (1982)
	344	11.9	pH=7.5	Pierce & Moore (1982)
	226	14.0	pH=8	Pierce & Moore (1982)
	136	11.5	pH=9	Pierce & Moore (1982)
	482	6.6	pH=9.9	Pierce & Moore (1982)
		Arsenite - Adsorption		
$Fe(OH)_3$	457	9.7	pH=4	Pierce & Moore (1982)
	463	15.2	pH=5	Pierce & Moore (1982)
	490	18.3	pH=5.7	Pierce & Moore (1982)
	503	22	pH=6.1	Pierce & Moore (1982)
	513	23.2	pH=7.0	Pierce & Moore (1982)
	488	20.2	pH=8.0	Pierce & Moore (1982)
	417	15.4	pH=8.8	Pierce & Moore (1982)
	417	5.5	pH=9.0	Pierce & Moore (1982)

A typical Eh-pH diagram for the predominance of mercury species is presented in the paper by Gavis and Ferguson (1972) in which only the inorganic system is considered. In natural water systems, where pH is likely to fall between 6 and 9 and the measured electrode potential (Eh) values seldom are higher than 0.5v, metallic mercury Hg° and HgS are the species most likely to enter into equilibrium with mercury species in solution. The Eh-pH diagram for the soluble species in equilibrium with the solids phase shows that $Hg(OH)_2$ and $HgCl_2$ are the predominant species in most surface waters. At low redox potentials observed in reducing sediments, mercury is effectively immobilized by sulfide ion. At extremely low redox potential and pH greater than 9, the solubility increases markedly by the formation of HgS_2^{2-} ions. The stability field for aqueous mercury constructed by Stolzenburg et al. (1986) is shown in Figure 4.04. Bartlett and Craig (1981) have summarized mercury chemistry over a wide range of redox conditions within the sediment. Fagerstrom and Jernelov (1972) and others have reported that the rate or extent of mercury methylation is increased when sediments are exposed to air, e.g., on dredging or during ebb tide.

Methylmercury is produced in sediments by bacteria through the methylation of inorganic mercury (Hg^{2+}) (Spangler et al., 1973). Two types of methylation are possible: microbial (enzymatic) and chemical (non-enzymatic by methylcobalamine). They have noted the presence of bacteria capable of degrading methylmercury to methane and Hg^0 which volatilizes and escapes into the atmosphere. The rate of methylation increases with temperature. The rate is higher with suspended material and in the surficial sediment rather than deep sediment (Jernelov, 1970). The rate is also higher at low oxygen concentrations. Formation of dimethylmercury is not favored in acidic environments (Gavis and Ferguson, 1972), and the amount of dimethylmercury formed is usually several orders of magnitude less than that of monomethylmercury ion, CH_3Hg^+. Fagerstrom and Jernelov (1972) reported the formation of both species in organic sediments at various pH, with a maximum of dimethylmercury production at pH 9 and a maximum of methylmercury at pH 6.

Lee et al. (1985) studied the catalytic effect of various metal ions on the methylation of mercury in the presence of humic acids (HA). Methylmercury production (in dark reactions during 2-4 day incubations at 30°C) increased with the concentration of Hg ions and fulvic acid as well as with the addition of metal ions. Metal ions competitively reduced the Hg bonding with HA, thus freeing it for methylation. The observed catalytic activity of metal ions followed the order: Fe^{3+} (Fe^{2+}) > Cu^{2+} Mn^{2+} > Al^{3+}. The production of methylmercury had a pH optimum of 4 to 4.5.

Bartlett and Craig (1981), from their study of the Mersey Estaury, drew correlations between total mercury, methylmercury, silt and organic carbon contents of the sediments. The computer-generated, least-square fitted lines were:

Total Hg (ng/g) = -148 + 217 methyl Hg (ng/g)
Methyl Hg (ng/g) = - 10.24 + 5.29 organic C (%)
Total Hg (ng/g) = -749 + 623 organic C (%)

Total Hg (ng/g) = -388 + 46 silt (%)
Methyl Hg (ng/g) = - 4.34 + 0.33 silt (%)

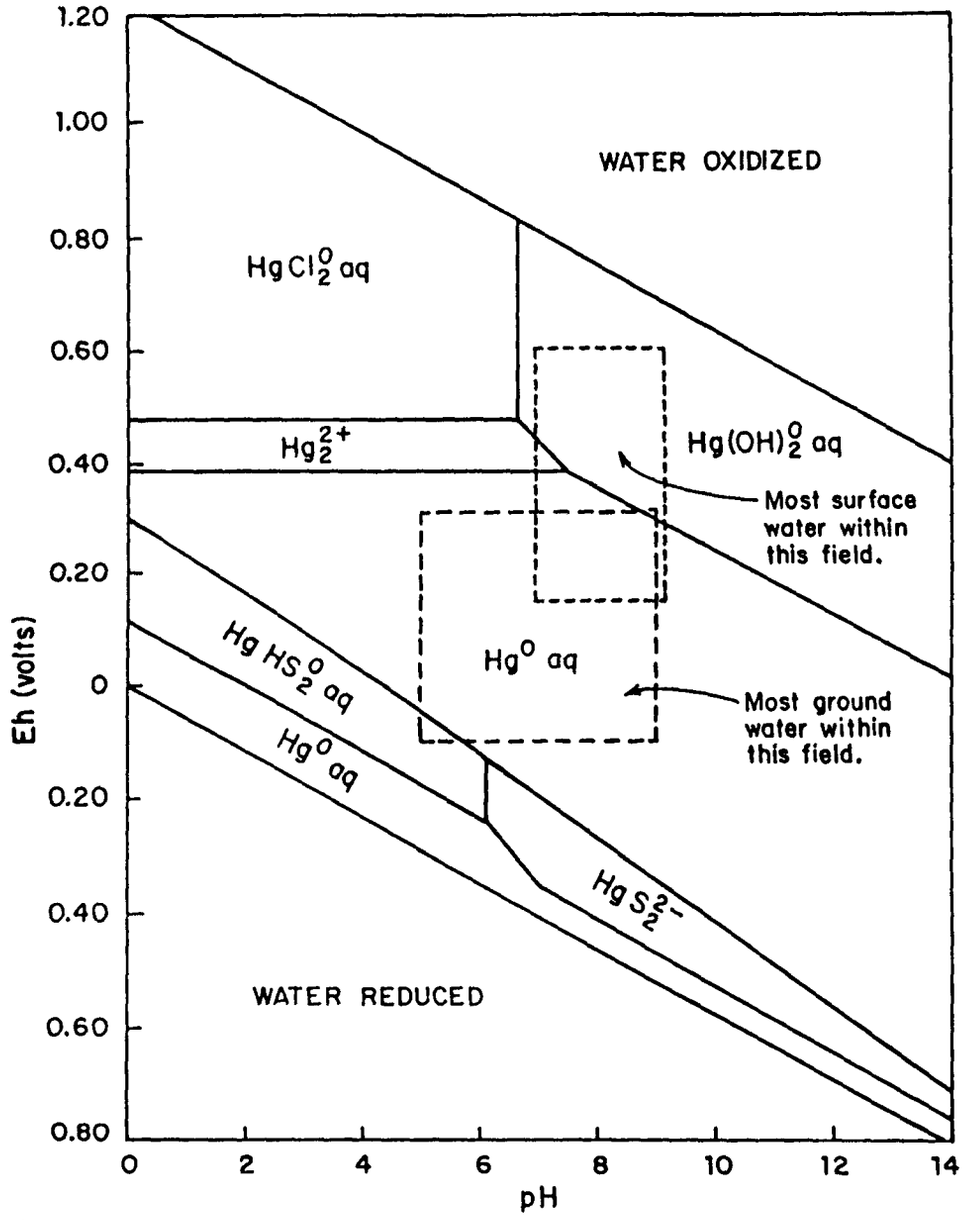

Figure 4.04 Stability fields for aqueous mercury species at various Eh and pH values (chloride and sulfur concentrations of 1 mM each were used in the calculation; common Eh-pH ranges for groundwater are also shown).

The correlation coefficient of the above relations were 0.76, 0.55, 0.77, 0.94 and 0.76, respectively. The greater was the organic or silt content of the sediment, the higher was the mercury concentration in nanogram per gram of dry sediment.

The proportion of methylmercury to the total amount of mercury in waters is significant at approximately 30%. The concentration of Hg^{2+} was ~50% and the remaining 20% were other species (Kudo, 1982). Modeling of mercury dynamics indicated that mercury in well water is highly unlikely to be methylated to the toxic methylmercury form (Stolzenburg et al., 1986).

The stability constants for Hg-fulvic acid complexes (Hg-FA) at pH 3 and pH 5 were reported as log K_{Hg-FA} of 4.9 and 5.1, respectively (Cheam and Gamble, 1974). A strong complexation between Hg^{2+} and FA is well documented (log K = 10-19.7) at pH = 8 (Montoura et al., 1978).

$$Hg^{+2} + FA^{-2} \rightleftarrows Hg\text{-}FA_{(aq)} \qquad K_{Hg-FA} = \frac{\{Hg\text{-}FA\}}{\{Hg^{+2}\}\{FA^{-2}\}} \tag{4.3}$$

Inoue and Munemori (1979) examined the coprecipitation of Hg (II) with Iron (III) hydroxide. Mercury is coprecipitated over the whole pH range of 4 to 12. Flouride does not affect the coprecipitation whereas Cl^- and Br^- suppress it at low pH depending on the stability of Hg (II)-halogen complexes and the halogen ligand concentrations. The Hg(II) species that coprecipitated was inferred to be $Hg(OH)_2$ based on chemical equilibrium considerations.

Adsorption of both Aretan (2-methoxymethylmercury) and $HgCl_2$ correlated well with the distribution of organic carbon and with the cation exchange capacity (CEC) of soils (Semu et al., 1986). The lack of such correlation in the other soils studied suggests other reactions like precipitation may also be involved in Hg retention by soils in addition to purely adsorptive process. The affinity of mercury for the sulfhydryl group can bind it to suspended organic matter, both living (e.g., plankton) and non-living (e.g., peat and humus). In aquatic environments, as organic and inorganic suspended matter settles, mercury is delivered to the sediment.

The bioconcentration factor (BCF) in fish ranges from 10^3 to 10^5 (D. Gardiner, 1978).

$$BCF = \frac{\text{residue in fish tissue}}{\text{dissolved conc. in water}} = \frac{mg/kg}{mg/\ell} = \ell/kg \tag{4.4}$$

A greater methylation rate would result in higher mercury levels in fish. Nishimura and Kumagai (1983) reported, based on their survey of Hg pollution in and around Minamata Bay, that there was a good correlation between Hg levels of croaker and that of the sediments. A better correlation was observed between Hg content of croaker and that of zooplankton. A very close relationship was found between Hg content of zooplankton and suspended particulate matter. A pathway of Hg from sediment to fish via suspended matter ingestion was suggested. Wren et al. (1983) examined the concentration of 20 elements in sediments, clams, fish, birds, and mammals. Mercury was the only element to exhibit biomagnification in both aquatic and terrestrial food chains. Mercury was the only metal that accumulated in the muscle tissue with increased age and size of all fish tested. Wren and MacCrimmon (1983) in their study at Tadenca Bay and Tadenca Lake have found clear evidence of bioaccumulation of mercury.

Mercury levels in biota in adjacent waters can differ due to different sediment mercury levels and ambient water quality characteristics.

By using the REDEQL II chemical equlibrium program, Vuceta and Morgan (1978) studied a hypothetical toxic freshwater system (pE = 12, P_{CO_2} = $10^{-3.5}$ atm), which contained four major cations (Ca, Mg, K, Na), nine trace metals (Pb, Cu, Ni, Zn, Cd, Co, Hg, Mn, and Fe), eight inorganic ligands (CO_3^{2-}, SO_4^{2-}, Cl^-, F^-, Br^-, NH_3, PO_4^{3-} and OH^-), and a solid surface with adsorption characteristics of $SiO_2(s)$. They found that Hg(II) was present mainly either as chloro-complexes (pH < 7.1) or as hydroxo-complexes (pH > 7.1). They also modeled the conditions at pH of 7 with the presence of organic ligands (EDTA, citrate, histine, aspartic acid, and cystine).

From the viewpoint of quantitative ecology of mercury, Fagerstrom and Jernelov (1972) presented a detailed description about the conversion among the mercury compounds that included: HgS, Hg^0, Hg^{2+}-organic material, Hg^{2+}-inorganic material of silica type, Hg^{2+}-inorganic material of ferro-magnetic type, CH_3HgX and $(CH_3)_2Hg$.

Huckabee and Goldstein (1976) developed a linear, eight-compartment model to describe the dynamic redistribution of methylmercury in a pond ecosystem following a pulse input. The eight compartments were water, sediment, seston, benthic invertebrates, mosquitofish, bluegill, largemouth bass, and carp. Using radioactive ^{203}Hg-tagged CH_3Hg^+ as tracers, they found that seston, especially plankton-organic detritus, is the major reservoir of CH_3Hg^+ in the system.

Fontaine (1984) has proposed a mercury submodel (Figure 4.05), incorporating the special features of mercury, along with the generalized model NONEQUI. Elemental mercury can volatalize under commonly encountered environmental conditions. The submodel includes as state variables the species Hg^{2+} (ionic form), CH_3Hg^+ (monomethylmercury), and Hg^0 (elemental mercury). The Hg^+ formed by the disproportion of Hg^0 and Hg^{2+} was not included. Dimethylmercury also was not included in the model as a state variable because its formation was not favored in acidic conditions and the amount formed was usually very small. For the purpose of this model, these reactions were set at equilibrium until better information becomes available on their kinetics.

A schematic diagram on the cycling of Hg in the environment by Stolzenburg et al. (1986) is given by Figure 4.06. Equilibrium constants for mercury are summarized in Table 4.07 with sediment/water partition coefficients (distribution coefficients) in Table 4.08.

4.2.4 Selenium

Selenium is one of the most widely distributed minerals in the earth's crust, usually associated with sulfide minerals. Selenium enters aquatic environments by natural weathering processes; combustion of fossil fuels; metal mining, melting and refining; and other industrial activities. Nriagu and Wong (1983) reported that the Se concentrations within a 30 km radius of

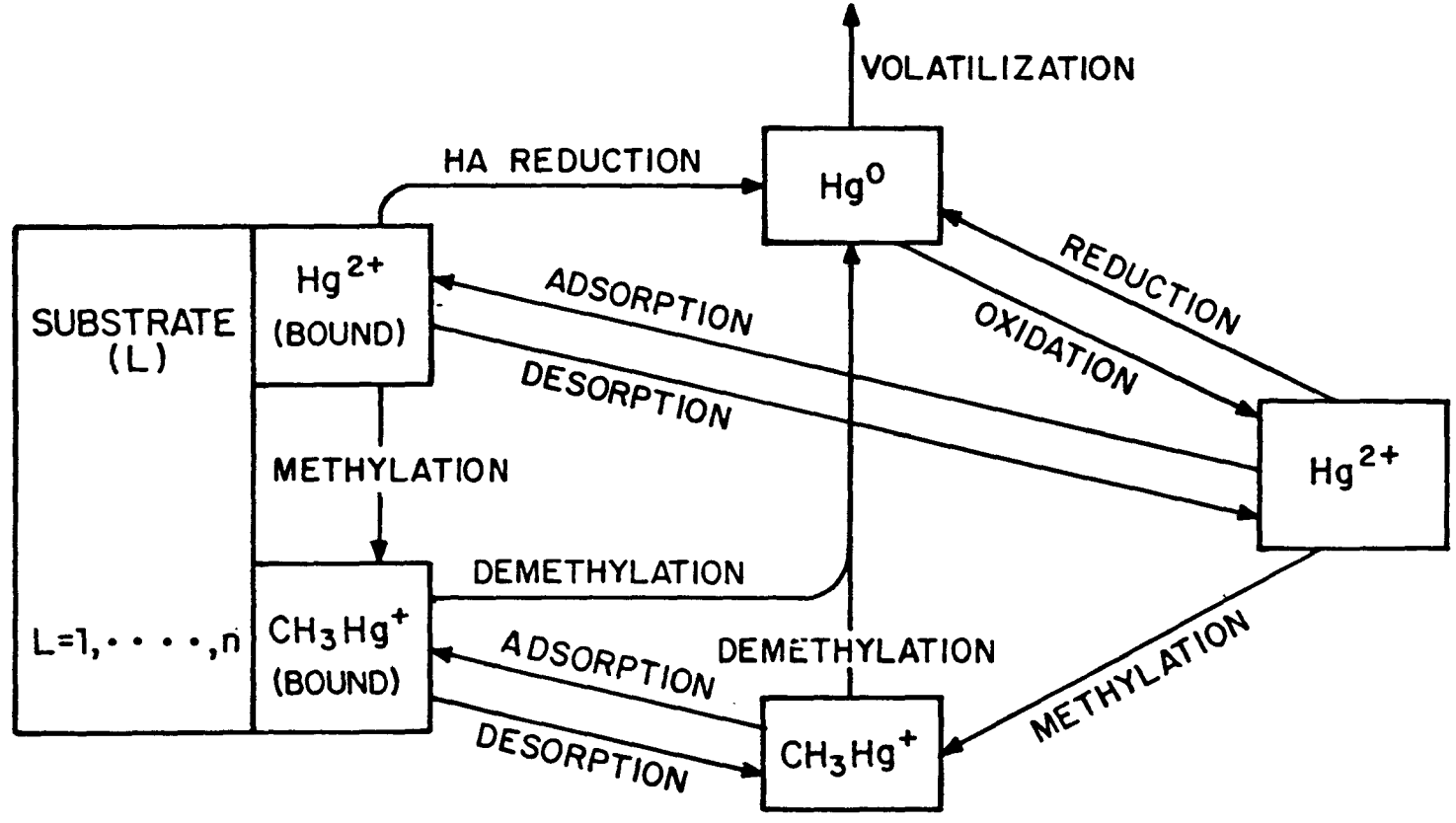

Figure 4.05. Model of mercury dynamics of NONEQUI.

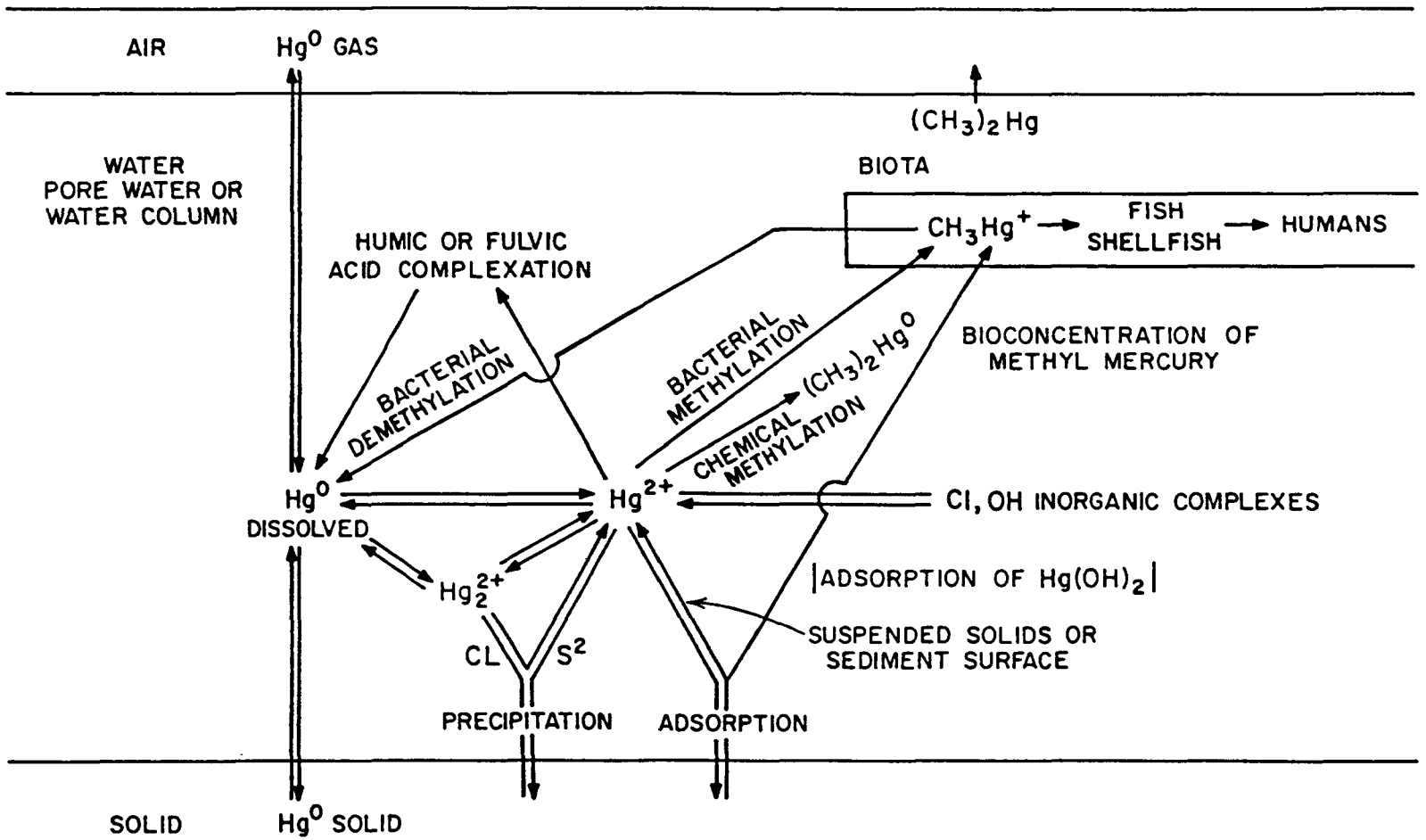

Figure 4.06. Schematic diagram of the cycling of mercury in the environment.

TABLE 4.07. EQUILIBRIUM CONSTANTS FOR MERCURY

Ligand	Log K	Equation and Comments	Reference
OH^-	10.4	$Hg^{2+} + OH^- \rightleftharpoons Hg(OH)^+$ (I=0)	Sillen & Martell (1971)
	21.8	$Hg^{2+} + 2OH^- \rightleftharpoons Hg(OH)_2$ (I=0)	Sillen & Martell (1971)
	21.3	$Hg^{2+} + 3OH^- \rightleftharpoons Hg(OH)_3^-$	Rubin (1974)
	-3.7	$HgO_{(S)} + H_2O \rightleftharpoons Hg(OH)_2$	Rubin (1974)
Cl^-	6.7	$Hg^{2+} + Cl^- \rightleftharpoons HgCl^+$	Sillen & Martell (1971)
	13.2	$Hg^{2+} + 2Cl^- \rightleftharpoons HgCl_2$	Sillen & Martell (1971)
	14.2	$Hg^{2+} + 3Cl^- \rightleftharpoons HgCl_3^-$	Sillen & Martell (1971)
	15.2	$Hg^{2+} + 4Cl^- \rightleftharpoons HgCl_4^{2-}$	Sillen & Martell (1971)
F^-	1.01	$Hg^{2+} + F^- \rightleftharpoons HgF^+$	Sillen & Martell (1971)
	1.03	$Hg^{2+} + 2F^- \rightleftharpoons HgF_2$	Sillen & Martell (1971)
	1.05	$Hg^{2+} + 3F^- \rightleftharpoons HgF_3^-$	Sillen & Martell (1971)
Br^-	9.1	$Hg^{2+} + Br^- \rightleftharpoons HgBr^+$	Sillen & Martell (1971)
	17.4	$Hg^{2+} + 2Br^- \rightleftharpoons HgBr_2$	Sillen & Martell (1971)
	19.8	$Hg^{2+} + 3Br^- \rightleftharpoons HgBr_3^-$	Sillen & Martell (1971)
	21.1	$Hg^{2+} + 4Br^- \rightleftharpoons HgBr_4^{2-}$	Sillen & Martell (1971)
I^-	12.9	$Hg^{2+} + I^- \rightleftharpoons HgI^+$	Sillen & Martell (1971)
	23.9	$Hg^{2+} + 2I^- \rightleftharpoons HgI_2$	Sillen & Martell (1971)
	27.7	$Hg^{2+} + 3I^- \rightleftharpoons HgI_3^-$	Sillen & Martell (1971)
	29.9	$Hg^{2+} + 4I^- \rightleftharpoons HgI_4^{2-}$	Sillen & Martell (1971)
CO_3^{2-}	16.05	$Hg^{2+} + CO_3^{2-} \rightleftharpoons HgCO_3$	Sillen & Martell (1971)
S^{2-}	-53	$Hg^{2+} + S^{2-} \rightleftharpoons HgS$	Sillen & Martell (1971)
SO_4^{2-}	1.34	$Hg^{2+} + SO_4^{2-} \rightleftharpoons HgSO_4$	Sillen & Martell (1971)

TABLE 4.07 (continued)

Ligand	Log K	Equation and Comments	Reference
	2.4	$Hg^{2+} + 2SO_4^{2-} \rightleftharpoons Hg(SO_4)_2^{2-}$	Sillen & Martell (1971)
CN^-	17.00	$Hg^{2+} + CN^- \rightleftharpoons HgCN^+$	Sillen & Martell (1971)
	15.75	$Hg^{2+} + 2CN^- \rightleftharpoons Hg(CN)_2$	Sillen & Martell (1971)
	3.56	$Hg^{2+} + 3CN^- \rightleftharpoons Hg(CN)_3^-$	Sillen & Martell (1971)
	2.66	$Hg^{2+} + 4CN^- \rightleftharpoons Hg(CN)_4^{2-}$	Sillen & Martell (1971)
NTA	14.6	$Hg^{2+} + NTA \rightleftharpoons Hg\text{-}NTA$	Sillen & Martell (1971)
EDTA	21.8	$Hg^{2+} + EDTA^{4-} \rightleftharpoons Hg\text{-}EDTA^{2-}$	Sillen & Martell (1971)
Glycine	10.3	$Hg^{2+} + Gly^- \rightleftharpoons Hg\text{-}Gly^+$	Sillen & Martell (1971)
	8.9	$Hg^{2+} + 2Gly^- \rightleftharpoons Hg\text{-}Gly$	Sillen & Martell (1971)

TABLE 4.08. CONSTANTS FOR MERCURY ADSORPTION

Adsorbent	Partition Coeff. $Kd(\frac{L}{Kg})$	Comments	Reference
Bentonite	408	pH=6.7 0.01M $Ca(NO_3)_2$	Newton et al., (1976)
	214	pH=7.3 0.01M $Ca(NO_3)_2$	Newton et al., (1976)
	179	pH=7.9 0.01M $Ca(NO_3)_2$	Newton et al., (1976)
	119	pH=8.9 0.01M $Ca(NO_3)_2$	Newton et al., (1976)
	140	pH=10.2 0.01M $Ca(NO_3)_2$	Newton et al., (1976)
	156	pH=10.7 0.01M $Ca(NO_3)_2$	Newton et al., (1976)
	164	pH=11.0 0.01M $Ca(NO_3)_2$	Newton et al., (1976)
Bentonite	30.0	pH=6.6 0.01M $CaCl_2$	Newton et al., (1976)
	29	pH=6.4 0.01M $CaCl_2$	Newton et al., (1976)
	29.2	pH=7.2 0.01M $CaCl_2$	Newton et al., (1976)
	58	pH=8.1 0.01M $CaCl_2$	Newton et al., (1976)
	141	pH=8.9 0.01M $CaCl_2$	Newton et al., (1976)
	164	pH=10.5 0.01M $CaCl_2$	Newton et al., (1976)
	224	pH=10.9 0.01M $CaCl_2$	Newton et al., (1976)

Sudbury (Ontario), where Cu-Ni ore is mined and smelted, ranged from 0.1 to 0.4 ug/ℓ. The selenium content of the suspended particles ranged from 2 to 6 ug/ℓ. The Se profiles in the lake paralleled the history of Cu-Ni production in the Sudbury district. The present day selenium accumulation rate in the sediment is 0.3 - 12 mg/m^2-yr.

Typical river concentrations average 0.2 ug/ℓ, although in some surface waters concentrations exceeding 200 ug/ℓ have been reported. The selenium content of sea water has an average value of 0.1 ug/ℓ. Selenium exists in two common oxidation states as either Se(VI) or Se(IV).

Very few data are available for selenium speciation in natural waters. Seawater has a significant concentration of selenium(IV) concentrations, but it is less than 8% of the total selenium in river water (Florence and Batley, 1980). Measure and Burton (1978) suggested that the remainder was most probably Se(VI) as the selenate ion, but the presence of organically associated species, or more importantly, selenium-collodial matter could contribute significantly. Frost (1983) has presented a probable selenium cycle in the environment.

According to a study by van Dorst and Peterson (1984), the concentrations of both selenite and selenate were much greater at pH 7 than at pH 4.5. The occurrence of selenoglutathione also was noted. Selenite (SeO_3^{2-}) was stable in alkaline to mildly acidic conditions and should be present in nature. The presence of low levels of selenite measured by Shamberger (1981) in soil indicated that most of the active selenite had sorbed on mineral surfaces.

Adsorption of Se from seawater and river water onto colloidal ferric hydroxide and a range of clays has been demonstrated by Kharkar et al. (1968). The presence of sediments in the water or on the bottom of enclosures reduced selenium bioaccumulation (Rudd and Turner, 1983). This suggests the binding of Se by fine sediment particles.

The water quality criterion for Se by U.S.EPA is 10 ug/ℓ for domestic water supplies. Klaverkamp et al. (1983) determined that the selenium concentration required to produce 50% mortality in fish was approximately 11 mg/ℓ for northern Pike (Esox Lucius), 29 mg/ℓ for white sucker (Catostomes commersoni), and 5 mg/ℓ for yellow perch (Perca flovescens) after 75, 96, and 240 hours of exposure, respectively. Turner and Rudd (1983) summarized the literature on toxicity of Se to aquatic biota.

Wehr et al. (1985) demonstrated an absolute physiological requirement of the planktonic alga Chrysochromulina breviturrita for Se in axenic culture. This alga is capable of utilizing dimethylselenide (DMSe) and this is believed to be the first demonstration of the utilization of DMSe as a Se source by any organism.

Elevated selenium appeared to retard the rate of heavy metal bioaccumulation by fish, Crayfish, and haptobenthos (Rudd et al., 1980). Turner and Swick (1983) observed that waterborne selenium did not alter the

amount of Hg accumulated from water or its subsequent partitioning among pike tissues sampled. When elevated in food, however, selenium decreased both the body burden of Hg in pike and the proportion in muscle.

Certain plants, fungi, bacteria, and rats have the ability to synthesize volatile Se compounds. The volatile compounds were predominantly dimethylselenide, although dimethyldiselenide (DMDSe) and dimethyselenone are also volatile. Zeive and Peterson (1981) in a laboratory study showed that volatilization was dependent upon microbial activity, temperature, moisture, time, concentration of water-soluble Se, and season of the year. Jiang et al. (1983) identified DMSe and DMDSe compounds in air in concentrations up to 2.4 ng m^{-3} near different aquatic system. Using model simulations, Medinsky et al. (1985) predicted that most of the selenium in human tissue is likely to come from diet; selenium in urban atmosphere contributed a very small fraction of the total body selenium.

Frost (1983) reported that bioavailability of Se is on the decline, and this could trigger a Se-responsive disease. Selenium is thought to be an anti-cancer agent at low concentrations. The use of sulfated fertilizers favors the uptake of S over Se by plants. The modeling of selenium poses considerable difficulty because of a lack of knowledge of its partitioning and chemical speciation.

4.2.5 Lead

Lead in soil may be derived from natural or anthropogenic sources. The natural sources include weathering of rocks and ore deposits, volcanoes (mantle degassing), fires, and wind-blown dust. Anthropogenic contributions of lead in soils is a relatively recent event (100 years or so), but it has increased to such an extent that the build-up of lead concentrations in many soils has significant biological effects.

The movement of lead over long distances invariably involves transport in particulate or sorbed form. Close to ore deposits, lead may be mobilized at a relatively high rate due to the production of acidic components as a consequence of the weathering of sulfides:

$$\begin{aligned} PbS + 4H_2O &\longleftrightarrow Pb^{2+} + SO_4^{2-} + 8H^+ + 8e^- \\ 2PbS + 4H_2O &\longleftrightarrow 2Pb^{2+} + S^0 + SO_4^{2-} + 8H^+ + 8e^- \end{aligned} \qquad (4.5)$$

The lead ion so derived may be sorbed onto other soil components or converted into secondary materials such as anglesite ($PbSO_4$), currusite ($PbCO_3$), hydrocerrusite ($Pb(OH)_2 \cdot 2PbCO_3$), pyromorphite, etc. Because of the low solubilities of those secondary minerals and the strong binding capacities of the soil components for lead, the metal has a low geochemical mobility (as measured by distance of penetration from the ore bed into the host rock).

Zirino and Yamamoto (1972) constructed a pH dependent model for the chemical speciation of lead in seawater. Between pH 7 and pH 9, lead in seawater is mainly complexed with carbonate ions and to some extent chloride

ions. At pH values near 7, $PbCO_3$ and $PbC\ell^+$ are present in nearly equal amounts and there is an appreciable amount of $PbC\ell O^-$. As the pH increases, however, $PbCO_3^0$ becomes the predominant species. Lead exists in aqueous solution almost entirely as Pb(II) species. The equilibrium: reaction $Pb^{4+} + 2e \longleftrightarrow Pb^{2+}$, has a pE value of over +21, and thus Pb(IV) species exist only under extremely oxidizing conditions. Pb(II) forms a number of hydroxide complexes. These include $Pb(OH)^0$, $Pb(OH)_2^-$, and $Pb(OH)_3^-$. Lead is predominantly $Pb(OH)^+$ at pH > 6.3 and lead activities less than 0.001 M. $Pb(OH)_3^-$ dominates above pH 10.9, and polynuclear species dominate when total Pb(II) ≥ 0.001 M.

Lead forms organic complexes with various ligands: amino acids, proteins, polysaccharides and fulvic and humic acids. The stability constants of Pb-FA were determined by Schnitzer and Skinner (1967) to be: log K of 3.09 and 6.13 at pH 3.5 and 5.0, respectively. Stevenson (1976) reported a value of log K of 8 for Pb-humic acid complex. Schecher and Driscoll (1985) observed that the presence of sulfate enhance the adsorption removal of lead by cells of Nostoe muscorum.

Tetra-alkyl lead compounds apparently can be formed in natural aquatic sediments. This can have serious implication for man-made pollution of waterways, because tetralkyl lead is considerably more toxic than inorganic lead. Craig and Rapsomanikis (1985) demonstrated the production of methyl lead derivatives from the reaction of Pb(II) ions with CH_3^+ donor agents. They also suggested some reaction mechanisms. Two static bioassays (on rainbow trout) in hard water resulted in a 96 hr LC_{50} (lethal concentration with 50% survival) of 1.32 and 1.47 mg/ℓ dissolved lead with a total lead LC_{50} of 542 and 471 mg/ℓ, respectively (Davis et al., 1976). The experiment demonstrated that the dissolved fraction is directly toxic to fish in aquatic environments.

Chau and Lum-Shue-Chan (1974) found that in 16 out of 17 Canadian lakes studied, lead was readily adsorbed on inorganic adsorbents. Gonzalves et al., (1985) measured the particulate and dissolved Pb^{2+} in the presence of hydrous MnO_2 and silica using voltammetric methods. This was accompanied without separation or filtration of the solid phase.

In addition to precipitation and complexation, adsorption represents another important process in the environmental cycling of lead. Based on statistical thermodynamic considerations, the exchange equilibrium constant (log K_{ex}) for the reaction was calculated to be 1.4 for Utah bentonite and Wyoming montmorillonite clays.

$$Pb^{2+}_{(aq)} + \text{Ca-clay} \longleftrightarrow Ca^{2+} + \text{Pb-clay} \qquad K_{ex} = 10^{1.4} \tag{4.6}$$

Regarding ion exchange, it has been found that the K_{ex} for the Pb^{2+}-K^+ exchange was about an order of magnitude greater than the value for Pb^{2+}-Ca^{2+} exchange. They also observed that vermiculite was an excellent exchanger for lead ions; the vermiculite virtually removed all the lead in the solution.

Lead is transported from source areas either in ionic solution and/or as more stable organo-metallic complexes. Reservoirs or lakes interrupt transportation in a fluvial system, and because of the long water residence times, the metal ions are adsorbed onto clay minerals and are deposited. The sediment therefore acts as a sink for this heavy metal (Pita, 1975).

Seasonal variations of lead concentrations in an oligotrophic lake (Crystal Lake, Wisconsin) were studied by Talbot and Andren (1984). They observed that during the transient periods of high biological productivity, a large net flux of radio-labeled lead nuclides was deposited to the sediment. It was during these short periods that most of the annual net removal of lead occurred. Pb sources to the water column appeared to occur mainly from atmospheric inputs. A conceptual model is depicted qualitatively in Figure 4.07. Although considerable information would be required to model the system, the Figure serves to illustrate the interdependence between the chemical and biological processes. Tables 4.09 and 4.10 give the equilibrium constants for lead complexation and sorption.

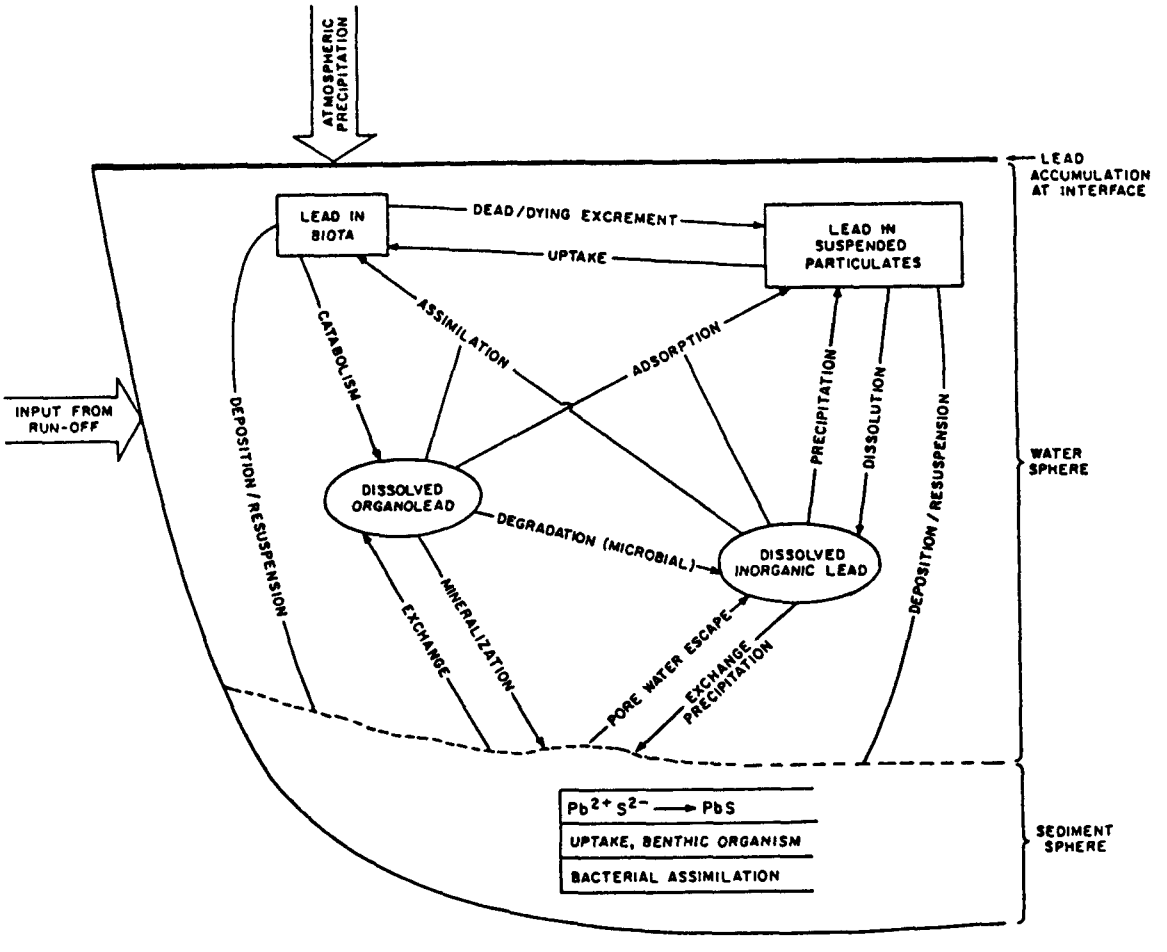

Figure 4.07 Cycling of lead in an aquatic ecosystem.

TABLE 4.09. EQUILIBRIUM CONSTANTS FOR LEAD

Ligand	Log K	Equation and Comments	Reference
OH^-	6.2	$Pb^{2+} + OH^- \rightleftharpoons PbOH^+$	Sillen & Martell (1964)
	7.0	$Pb^{2+} + OH^- \rightleftharpoons PbOH^+$	Billinski et al., (1976)
	11.5	$Pb^{2+} + 2OH^- \rightleftharpoons Pb(OH)_2$	Billinski et al., (1976)
	10.9	$Pb^{2+} + 2OH^- \rightleftharpoons Pb(OH)_2$	Sillen & Martell (1964)
	13.9	$Pb^{2+} + 3OH^- \rightleftharpoons Pb(OH)_3^-$	Sillen & Martell (1964)
	16.3	$Pb^{2+} + 4(OH)^- \rightleftharpoons Pb(OH)_4^{2-}$	Sillen & Martell (1964)
	7.64	$Pb^{2+} + (OH)^- \rightleftharpoons Pb_2(OH)^{3+}$	Felmy et al., (1985)
Cl^-	1.6	$Pb^{2+} + Cl^- \rightleftharpoons PbCl^+$	Hegelson (1969)
	1.73	$Pb^{2+} + Cl^- \rightleftharpoons PbCl^+$	Sillen & Martell (1971)
	1.78	$Pb^{2+} + 2Cl^- \rightleftharpoons PbCl_2$	Hegelson (1969)
	1.68	$Pb^{2+} + 3Cl^- \rightleftharpoons PbCl_3^-$	Hegelson (1969)
	1.38	$Pb^{2+} + 4Cl^- \rightleftharpoons PbCl_4^{2-}$	Hegelson (1969)
F^-	1.25	$Pb^{2+} + F^- \rightleftharpoons PbF^+$	Felmy et al., (1985)
	2.56	$Pb^{2+} + 2F^- \rightleftharpoons PbF_2$	Felmy et al., (1985)
	3.42	$Pb^{2+} + 3F^- \rightleftharpoons PbF_3^-$	Felmy et al., (1985)
	3.10	$Pb^{2+} + 4F^- \rightleftharpoons PbF_4^{2-}$	Felmy et al., (1985)
Br^-	1.77	$Pb^{2+} + Br^- \rightleftharpoons PbBr^+$	Felmy et al., (1985)
	1.44	$Pb^{2+} + 2Br^- \rightleftharpoons PbBr$	Felmy et al., (1985)
I^-	1.94	$Pb^{2+} + I^- \rightleftharpoons PbI_2$	Felmy et al., (1985)
	3.19	$Pb^{2+} + 2I^- \rightleftharpoons PbI_2$	Felmy et al., (1985)
HCO_3^-	2.9	$Pb^{2+} + HCO_3^- \rightleftharpoons PbHCO_3^+$	Zirino & Yamamoto (1972)
CO_3^{2-}	6.3	$Pb^{2+} + CO_3^{2-} \rightleftharpoons PbCO_3$	Bilinski et al., (1976)
	9.8	$Pb^{2+} + 2CO_3^{2-} \rightleftharpoons Pb(CO_3)_2^{2-}$	Bilinski et al., (1976)
	10.64	$Pb^{2+} + 2CO_3^{2-} \rightleftharpoons Pb(CO_3)_2^{2-}$	Ernst et al., (1975)
S^{2-}	27.5	$Pb^{2+} + S^{2-} \rightleftharpoons PbS$	Sillen & Martell (1964)
SO_4^{2-}	2.7	$Pb^{2+} + SO_4^{2-} \rightleftharpoons PbSO_4$	Sillen & Martell (1964)
	3.47	$Pb^{2+} + 2SO_4^{2-} \rightleftharpoons Pb(SO_4)_2^{2-}$	Sillen & Martell (1964)
HS^-	15.27	$Pb^{2+} + 2HS^- \rightleftharpoons Pb(HS)_2(aq)$	Felmy et al., (1985)
	16.57	$Pb^{2+} + 3HS^- \rightleftharpoons Pb(HS)_3^-$	Felmy et al., (1985)

TABLE 4.09 (continued)

Ligand	Log K	Equation and Comments	Reference
NO_3^-	1.17	$Pb^{2+} + NO_3^- \rightleftarrows PbNO_3^+$	Felmy et al., (1985)
NTA	11.47	$Pb^{2+} + NTA \rightleftarrows Pb\text{-}NTA$	Sillen & Martell (1976)
EDTA	17.9	$Pb^{2+} + EDTA^{4-} \rightleftarrows PbEDTA^{2-}$	Sillen & Martell (1976)
	17.7	$Pb^{2+} + EDTA^{4-} \rightleftarrows Pb\text{-}EDTA^{2-}$	J. Gardiner (1976)
Glycine	5.47	$Pb^{2+} + Gly \rightleftarrows PbGly$	Sillen & Martell (1976)
		$Pb^{2+} + 2Gly \rightleftarrows Pb(Gly)_2$	Sillen & Martell (1976)
FA	6.3	$Pb^{2+} + FA \rightleftarrows PbFA$ (ISE method) pH = 6.5	Sterritt & Lester (1984)
	3.1	$Pb^{2+} + FA \rightleftarrows PbFA$ pH = 3.5	Schnitzer & Skinner (1967)
	6.14	$Pb^{2+} + FA \rightleftarrows PbFA$ pH = 5.0	Schnitzer & Skinner (1967)
	3.1	$Pb^{2+} + FA \rightleftarrows PbFA$ pH = 3.5)	Schnitzer (1969)
	6.13	$Pb^{2+} + FA \rightleftarrows PbFA$ pH = 5)	Schnitzer (1969)
HA	8.7	$Pb^{2+} + 2HA \rightleftarrows Pb(HA)_2$ (I = 0)	Stevenson (1976)
Sludge Solids	6.3	(ISE method) $Pb^{2+} + L \rightleftarrows PbL$	Sterritt & Lester (1985)
	6.17	(Filtration method) $Pb^{2+} + L \rightleftarrows PbL$	Sterritt & Lester (1985)
<u>Colloids</u>			
Geothite	-1.9	$M\text{-}OH + Pb^{2+} \rightleftarrows MOPb + H^+$	Gonzalves (1985)
MnO_2	1.2	$M\text{-}OH + Pb^{2+} \rightleftarrows MOPb + H^+$	Gonzalves (1985)
Silica	-4.4	$2(MOH) + Pb^{2+} \rightleftarrows (M\text{-}O)_2Pb + 2H^+$	Gonzalves (1985)
		[M = particle surface]	

TABLE 4.10 CONSTANTS FOR LEAD ADSORPTION

Adsorbent	Langmuir $b(\frac{m\ mol}{K_g})$	$K(10^5\ \frac{L}{mol})$	Comments	Reference
HA				
Sample A	990	1.0		Beveridge & Pickering (1980)
B	740	1.2		Beveridge & Pickering (1980)
C	1235	6.8		Beveridge & Pickering (1980)
D	810	12.2		Beveridge & Pickering (1980)
Kaolin	19	2.6	25°C pH=5	Farrah et al., (1980)
Illite	68	3.8	(Na^+ form Clay)	
Montmorillonite	347	9.7		

4.2.6 Barium

Barium occurs in nature chiefly as barite, $BaSO_4$, and witherite, $BaCO_3$, both of which are highly insoluble salts. Many of the salts of Ba are soluble in both water and acid, and soluble barium salts are reported to be poisonous. They can affect the muscular and nervous system. Insoluble barium salts are not toxic. Brennimann (1979) recently suggested that there was a positive correlation between the occurence of cardiovascular diseases and barium concentration in drinking water. The U.S. EPA recommends a 1 mg/ℓ limit for barium in domestic water supplies.

In a study of the behaviour of barium in soil, Lagas et al. (1984) observed that 18 to 39% of barium added leached-out, probably as Ba-complexes. Part of the Ba was adsorbed or precipitated in the sand; part of the Ba remained in the original state as $BaCO_3$. Complexation of Ba-ions is comparable to those for Ca (Smith and Martell, 1976). Barium complexes with fatty acids. In its complexed form, Ba is much more mobile in soil water.

Adsorption of Ba ions will be stronger than that of Ca or Mg ions because the radius of the hydrated Ba-ions is smaller than the radii of the hydrated Ca and Mg ions. Ba-ion forms surface complexes with sand and exchanges with H^+ and Al^{3+} (Lagas et al., 1984). Despite adsorption by sand and waste material, Ba always reaches the ground water to some extent. $BaSO_4$ precipitation is another important path for Ba removal from natural waters.

Sebesta et al. (1981) studied uranium mine waste waters and observed that the main factors regulating the concentrations and the forms of radium and barium in adjacent surface waters were the dilution of waste water with river water and the sedimentation of particulate forms in the river.

The distribution of both elements between the water phase and suspended solids obeyed the homogenous distribution law for isomorphous coprecipitation of radium and barium sulfate. Consequently the predominant particulate form of radium and barium in such waters was $BaRaSO_4$. If certain limiting conditions are fulfilled, the distribution of radium and barium between solutions and barium sulfate crystals can be described by:

$$(C_{Ra}/C_{Ba})_{diss} = K_{RaBaSO_4} \, (C_{Ba}/C_{Ra})_{particles} \qquad (4.7)$$

Here K_{BaRaSO_4} is the so-called homogenous distribution coefficient or separation factor, and C_{Ra} and C_{Ba} are concentration of radium and barium. The values of the separation factors were 1.8, 1.8, 2.2, 2.9, 1.9, and 3.5 at pH 4, 5, 6, 7, 8 and 9, respectively (Sebesta et al., 1981).

The main particulate form of radium and barium in a uranium mine waste water system was $BaRaSO_4$ (Benes et al., 1983). River water upstream of the mine water discharge contained Ba mainly as $BaSO_4$ or detritus.

Knowledge of the physicochemical forms of barium and its interaction with various ligands and particulates in natural waters is scarce. Further information on adsorption, ion exchange, and complexation behavior of Ba would be required to effectively model its fate in the aquatic environment. Because Ba is in many respects similar to Ca, however, we may examine the possibility of using the exchange, complexation, and adsorption behavior of Ca to approximately model Ba. Table 4.11 gives the few equilibrium constants available in the literature for barium.

TABLE 4.11 EQUILIBRIUM CONSTANTS FOR BARIUM

Ligand	Log K	Equation and Comments	Reference
OH^-	0.85	$Ba^{2+} + OH^- \rightleftarrows Ba(OH)^+$	Sillen & Martell (1964)
CO_3^{2-}			
SO_4^{2-}			
EDTA	8.0	$Ba^{2+} + EDTA^{4-} \rightleftarrows BaEDTA^{2-}$	Sillen & Martell (1964)
NTA	4.85	$Ba^{2+} + NTA \rightleftarrows Ba\text{-}NTA$	Sillen & Martell (1964)
Glycine	0.77	$Ba^{2+} + Gly^- \rightleftarrows BaGly^+$	Sillen & Martell (1964)

4.2.7 Zinc

Recent studies have indicated that the toxicity of zinc is due to the presence of the free zinc ion and thus may not be directly related to the total metal concentration. Shephard et al. (1980) measured the concentration and distribution of Zn in Palestine Lake, Indiana. The average dissolved Zn concentrations in the lake were as high as 293 ug/ℓ, but the concentration associated with suspended solids was less than 293 ug/ℓ. Average levels of Zn in the dissolved fraction exceeded those in the suspended fraction. Under anaerobic conditions occurring in lake hypolimnia, a marked decrease in the dissolved fraction and concommitant increase in the suspended fraction was noted.

Mouvet and Bourg (1983) used the computer model ADSORB to calculate the speciation of Zn in Meuse River (France). Adsorption sites were treated as conventional ligands and the adsorbed organic-solids interactions were also considered. The complex formation of zinc with OH^-, HCO_3^- and CO_3^{2-} have been previously determined at high and low pH. Billinski et al. (1976) determined the complexation between Zn(II) and hydroxide and carbonate ions under conditions that approximate those in natural waters, i.e., $[Zn]_t < 10^{-7}$ M. The carbonate complexes of Zn(II) are less stable; hence, the metal is present in natural waters, depending on solution variables, as aquo-, hydroxo-, or chloro- (sea water) complexes. Chemical speciation of Zn and other trace metals in mixed freshwater, seawater, and brine solution have been modeled by Long and Angino (1977). A large fraction of Zn was calculated to be as free ions. In fresh water, bicarbonate and sulfate complexes were predominant below pH 6.5. At pH greater than 6.5, the carbonate and $Zn(OH)_2$ species predominated. Zinc complexes strongly with chloride ion when a small amount of sea water is present.

The sorption of zinc species by clay minerals such as kaolinite, illite, and montmorillonite have been investigated by Farrah and Pickering (1976). The uptake of Zn by clay increased significantly as the pH was increased from 3.5 to 6.5. The stability of bound zinc hydroxide was great at high pH. Sorption is the dominant fate process affecting Zn, and it results in the enrichment of suspended sediments relative to the water column (Nienke and Lee, 1982). Variables affecting the mobility of Zn include the concentration and composition of suspended and bed sediments, the dissolved and particulate iron and manganese concentrations, the pH, the salinity, the concentration of complexing ligands, and the concentration of Zn. Rybicka (1985) presented an isotherm for Zn on sepiolite. Sepiolite has a large adsorption capacity for zinc, which is almost identical to that of montmonillonite and illite. Miragaya et al. (1986) studied Cd and Zn sorption by kaolinite and montmorillonite from low concentration solutions. The metal sorption affinity decreased markedly with increasing concentration for both layer silicates. There is a greater affinity (distribution coefficient) for both Zn and Cd by kaolinite and montmorillonite at low concentrations.

The complexation of Zn with humic acid was quantified by Randhawa and Broadbent (1965): Log K_{Zn-HA} of 6.8 for a humic acid-Zn complex at pH 7.0. Ardhakani and Stevenson (1971) determined log K_{Zn-HA} = 3.1 - 5.1 at pH

6.5 for a soil humic acid - Zn(II) complex. Metal ion formation constants were determined for several sedimentary humic acids from fresh water and coastal marine environments, and conditional log K_{Zn-HA} values between 4.5 and 5.5 at pH 8.0 (I = 0.01 M) were found (Sohn and Hughes, 1981). With so few data available, no conclusion should be made regarding the difference in values of Zn-humic acid stability constants.

Peterson (1982) observed the influence of Zn (and Cu) on the growth of a freshwater alga, Scenedesmus quadricauda. The results suggest that the free metal ion is the chemical specie that is toxic to algae. Harding and Witton (1978) found that submerged plants in the Derwent Reservoir accumulated large amounts of Zn. The Zn concentration in Nitella flexilis ranged from 500 ug/g to 1500 ug/g. The Zn concentration in water was 0.216 ug/L. These plants could increase or decrease the rate of deposition of metals depending upon the rapidity with which the plants get buried and decompose.

Table 4.12 represents the equilibrium contants for zinc in natural waters, and the adsorption constants are presented in Table 4.13.

4.2.8 Copper

In aquatic environments, metals can exist in three phases -- particulate, colloidal, and soluble. Particulate matter includes oxide, sulfide, and malachite ($Cu_2(OH)_2\ CO_3$) precipitates, as well as insoluble inorganic complexes and copper adsorbed on clays and on other mineral solids. Soluble matter includes free cupric ion and soluble complexes; colloidal matter includes polypeptide material and some fine clays ($\leq$ 2μm) and metallic hydroxide precipitates. In unpolluted fresh waters, two types of processes are possible, namely precipitation and complex formation (Stiff, 1971).

Two precipitation reactions are thermodynamically possible -- (a) precipitation of cupric hydroxide followed by conversion of hydroxide to oxide (b) precipitation of malachite.

$$Cu^{2+} + 2H_2O \rightarrow Cu(OH)_2 + 2H^+ \rightarrow CuO_{(s)} + 2H^+ + H_2O$$

$$Cu^{2+} + 2H_2O + HCO_3^- \dashrightarrow Cu_2\ (OH)_2\ CO_{3(s)} + 3H^+ \qquad (4.8)$$

Both reactions are dependent on the pH values and on the bicarbonate (alkalinity) concentration of the solution. Based on equilibrium calculations, malachite will be the only precipitated specie in the pH range of most fresh waters. In the presence of copper precipitates, the free cupric ion can further complex with bicarbonate ions to form soluble $CuCO_3$ species. This explains why the concentration of free cupric ion only represents a small fraction of the total soluble copper (Stiff, 1971). A speciation of Cu(II) diagram is presented by Sylva (1976) as shown in Figure 4.08.

TABLE 4.12. EQUILIBRIUM CONSTANTS FOR ZINC

Ligand	Log K	Equation and Comments	Reference
OH^-	4.4	$Zn^{2+} + OH^- \rightleftharpoons Zn(OH)^+$	Sillen & Martell (1964)
	12.89	$Zn^{2+} + 2OH^- \rightleftharpoons Zn(OH)_2$	Sillen & Martell (1964)
	14.0	$Zn^{2+} + 3OH^- \rightleftharpoons Zn(OH)_3^-$	Sillen & Martell (1964)
	15.0	$Zn^{2+} + 4OH^- \rightleftharpoons Zn(OH)_3^{2-}$	Sillen & Martell (1964)
Cl^-	0.43	$Zn^{2+} + Cl^- \rightleftharpoons ZnCl^+$	Sillen & Martell (1964)
	0.61	$Zn^{2+} + 2Cl^- \rightleftharpoons ZnCl_2$	Sillen & Martell (1964)
	0.53	$Zn^{2+} + 3Cl^- \rightleftharpoons ZnCl_3^-$	Sillen & Martell (1964)
	0.2	$Zn^{2+} + 4Cl^- \rightleftharpoons ZnCl_4^{2-}$	Sillen & Martell (1964)
CO_3^{2-}	5.3	$Zn^{2+} + Co_3^{2-} \rightleftharpoons ZnCO_3^-$	Sillen & Martell (1964)
	9.63	$Zn^{2+} + 2CO_3^{2-} \rightleftharpoons ZnCO_3^{2-}$	Sillen & Martell (1964)
HCO_3^-	2.1	$Zn^{2+} + HCO_3^- \rightleftharpoons ZnHCO_3^+$	Sillen & Martell (1964)
SO_4^{2-}	2.3	$Zn^{2+} + SO_4^{2-} \rightleftharpoons ZnSO_4$	Sillen & Martell (1964)
HS^-	14.9	$Zn^{2+} + 2HS^- \rightleftharpoons Zn(HS)_2$	Sillen & Martell (1964)
	16.1	$Zn^{2+} + 3HS^- \rightleftharpoons Zn(HS)_3^-$	Sillen & Martell (1964)
F^-	1.15	$Zn^{2+} + F^- \rightleftharpoons ZnF^+$	Felmy, et al., (1985)
Br^-	-9.58	$Zn^{2+} + Br^- \rightleftharpoons ZnBR^+$	Felmy, et al., (1985)
	-0.98	$Zn^{2+} + Br^- \rightleftharpoons ZnBR_2$	Felmy, et al., (1985)
I^-	-2.91	$Zn^{2+} + I^- \rightleftharpoons ZnI^+$	Felmy, et al., (1985)
	-1.69	$Zn^{2+} + 2I^- \rightleftharpoons ZnI_2$	Felmy, et al., (1985)
CN^-	17.5	$Zn^{2+} + 3CN^- \rightleftharpoons Zn(CN)_3^-$	Sillen & Martell (1964)
	16	$Zn^{2+} + 4CN^- \rightleftharpoons Zn(CN)_4^{2-}$	Sillen & Martell (1964)
	20.2	$Zn^{2+} + 5CN^- \rightleftharpoons Zn(CN)_5^{3-}$	Sillen & Martell (1964)

TABLE 4.12 (continued)

Ligand	Log K	Equation and Comments	Reference
S^{2-}	24.7	$Zn^{2+} + S^{2-} \rightleftarrows ZnS$	Sillen & Martell (1976)
EDTA	1.64	$Zn^{2+} + EDTA \rightleftarrows Zn\text{-}EDTA$	Sillen & Martell (1976)
NTA	10.5	$Zn^{2+} + NTA \rightleftarrows Zn\text{-}NTA$	Sillen & Martell (1976)
Glycine	5.23	$Zn^{2+} + Gly \rightleftarrows Zn\text{-}Gly$	Sillen & Martell (1976)
	4.3	$Zn^{2+} + 2Gly \rightleftarrows ZnGly$	Sillen & Martell (1976)
FA	6.76	$Zn^{2+} + 2FA \rightleftarrows Zn\text{-}(FA)_2$	Tan et al., (1971)
	1.76	$Zn^{2+} + .54FA \rightleftarrows Zn(FA)_{.54}$	Tan et al., (1971)
	1.73	$Zn^{2+} + FA \rightleftarrows Zn\text{-}FA$ (pH = 3.5)	Schnitzer (1969)
	2.34	$Zn^{2+} + FA \rightleftarrows Zn\text{-}FA$ (pH = 5.0)	Schnitzer (1969)
HA	4.42	$Zn^{2+} + 1.25HA \rightleftarrows Zn(HA)_{1.25}$ (pH = 3.6)	Randhawa & Broadwent (1965)
	6.18	$Zn^{2+} + 1.59HA \rightleftarrows Zn(HA)_{1.59}$ (pH = 5.6)	Randhawa & Broadwent (1965)
	6.80	$Zn^{2+} + 1.70HA \rightleftarrows Zn(HA)_{1.70}$ (pH = 7.0)	Randhawa & Broadwent (1965)

TABLE 4.13. CONSTANTS FOR ZINC ADSORPTION

Adsorbent	Langmuir $b(\frac{m\ mol}{Kg})$	$K(10^5 \frac{L}{mol})$	Comments	Reference
Humic Acids A	360	2.4	pH = 4.4	Beveridge & Pickering (1980)
B	290	1.8	pH = 4.4	Beveridge & Pickering (1980)
C	565	6.1	pH = 4.4	Beveridge & Pickering (1980)
D	420	1.7	pH = 4.4	Beveridge & Pickering (1980)
Kaolin	57.1	6.73		Miragaya (1986)
Montmorillonite	363	1.53		Miragaya (1986)
Fe hydrous oxide	147	5.1	fresh	Shuman (1977)
	13.2	0.2	aged	Shuman (1977)
Al hydrous oxide	392	5.9	fresh	Shuman (1977)
	37	.08	aged	Shuman (1977)
Clays (A Horizon)				
Decatur cl	63	0.53		Shuman (1976)
Cecil sl	55	0.34		Shuman (1976)
Norfolk Is	20	0.40		Shuman (1976)
Leefield Is	55	0.31		Shuman (1976)
(B 2t Horizon)				
Decatur cl	55	0.24		Shuman (1976)
Cecil sl	27	0.34		Shuman (1976)
Norfolk	28	0.44		Shuman (1976)
Leefield Is	71	0.4		Shuman (1976)

Adsorbent	Freundlich K	n	Comments	Reference
Bentonite	1.98	0.6		Guy et al., (1975)
Sepiolite	105	0.65		Rybicka (1985)

Mouvet and Bourg (1983) have used the computer model ADSORB to calculate the speciation of copper in the Meuse River (France). Adsorption sites were treated as inorganic ligands. The conditional stability constants of copper-fulvic acid were: log K of 4.0, 4.9, and 6.0, at pH 4, 5, and 6, respectively. This indicates a strongly bound complex (Buffle et al., 1977). The conditional stability constants of Cu-fulvic acid and Cu-humic acid were also determined by Shuman & Cromer (1979).

Nriagu et al. (1981) determined that, in general, 50 to 80% of the copper in Lake Ontario was bound to suspended particles. Adsorption of Cu onto hydrous ferric oxide was significantly modified in the presence of humic substances (Laxen, 1981). Copper uptake was either enhanced or reduced depending, respectively, on whether the metal-ligand complex formed was strongly bound by oxide surfaces or was a non-adsorbing complex in solution. Blutstein and Shaw (1981) suggested that naturally occurring organic compounds in Albert Park lake effectively reduced the adsorption of copper(II) onto particulate matter by the formation of non-adsorbing complexes. Elliot and Huang (1980) investigated the adsorption of Cu(II) by aluminosilicates with varying Si/Al ratios. The presence of complex-forming organic ligands (NTAm, Glycine) modified Cu adsorption characteristics that can influence its fate. The adsorption of Cu(II) on wollastonite was studied by Pandey et al. (1986). There was a higher adsorption at increased pH, which is explained by the adsorption of hydrolyzed Cu(II) species at the solid surface interface. Fayed et al. (1985) found that the concentration factor of metals including Cu was lower in plants as compared to the sediment.

The most important species of copper causing toxicity (studied for culthroat trout) was Cu^{2+}, $Cu(OH)^{+}$ and $Cu(OH)_2^0$ (Chakoumakos et al., 1979). The concentrations of each of these species varies with pH and alkalinity. Lower alkalinity concentrations favor all these species; $CuHCO_3^+$, $CuCO_3^0$ and $Cu(CO_3)_2^{2-}$ were not toxic. The lethal toxicity of copper to rainbow trout was found to be related to the total concentration of Cu and $CuCO_3$ (in the absence of organic complexes) rather than to the concentration of either of these forms alone (Shaw 1974). Sato et al. (1986a), in their study of the effects of copper on the growth of Nitrosomonas europaea, observed that copper inhibition caused a decrease in the growth rate. In another study, Sato et al. (1986b) determined that the decrease in specific growth rate of N. europaea was linearly correlated with the logarithmic activities of Cu(II)-amine species, regardless of the total Copper(II) activity in the medium.

Geesey et al. (1984) studied the effect of flow rate on the distribution of Cu species and other metals in rivers. Increased flow resulted in a loss of soluble reactive copper from sediments of Still Creek and Fraser River (British Columbia). Decreased flow was accompanied by an increase in the levels of reactive copper. Chemical speciation of copper can be estimated from the MINTEQ model if pH, alkalinity, and complexing ligand concentrations are specified. The fate of copper in natural waters can be modeled by the non-equilibrium model NONEQUI as developed by Fontaine (1984). Information on rate constants is scarce, however. A schematic of

the model is presented in Figs. 4.01 and 4.08. Tables 4.14 and 4.15 are a summary of the many equilibrium constants available for copper.

4.3 TRANSPORT AND TRANSFORMATION MODELS

A number of computer models exist to calculate transport and transformation of toxic organics in the aquatic environment, but few models are currently available for heavy metals. The model developed by Woodard et al. (1981) takes into account dynamic processes of rivers, and relies heavily on the relationship between transport of suspended matter and that of heavy metals. Christophensen and Seip (1982) developed a model for stream water discharge and chemical composition, incorporating a two-reservoir hydrology model (Lundquist, 1976 and 1977) with sulfate and cation submodels. The cation submodel includes H^+, Al^{3+}, Ca^{2+}, and Mg^{2+}, and is based on the mobil anion concept. Chemical processes include cation exchange, weathering, dissolution/precipitation of gibbsite, and adsorption/desorption and mineralization of sulfate. The model was developed for application to acidification of streams by acid deposition.

A model developed by Chapman (1982) includes the effects due to processes such as precipitation, sedimentation, and adsorption, and it adopts the program MINEQL as a basis for the chemical equilibrium model. The Metal EXposure Analysis Modeling System (MEXAMS), developed by Felmy et al. (1984), has a capability for assessing the impact of priority pollutant metals on aquatic systems. The program allows the user to consider the complex chemistry affecting the behavior of metals in conjunction with the transport processes that affect their migration and fate. The modeling system is accomplished by linking a geochemical model, MINTEQ, with an aquatic exposure assessment model, EXAMS. The NONEQUI model, developed by Fontaine (1984a and 1984b), can simulate sorption and ion exchange kinetics among a variety of heavy metals and organic ligands interactions (Figure 4.01). MINTEQ, developed by Felmy et al. (1983) is the most recent computer program to calculate speciation at chemical equilibrium. The program computes aqueous speciation, adsorption, and precipitation/dissolution of solids. It requires thermodynamic data and water quality data as input.

A summary of the heavy metal models is given in Table 4.16. The first three models are stream models, and the distribution of heavy metals is controlled by advective-dispersive flow and metal-adsorbed sediment transport (settling and scouring) processes. NONEQUI and MEXAMS can be applied for both a stream and a lake where physical, chemical and biological reactions (e.g., volatilization, speciation, and biouptake) are more important. MEXAMS calculates equilibrium concentrations of chemical species using MINTEQ. NONEQUI uses a non-equilibrium approach considering the kinetics of sediment-water exchange, metal-organic complexation reactions, cation exchange, methylation/demethylation, and humic acid mediated reduction reactions.

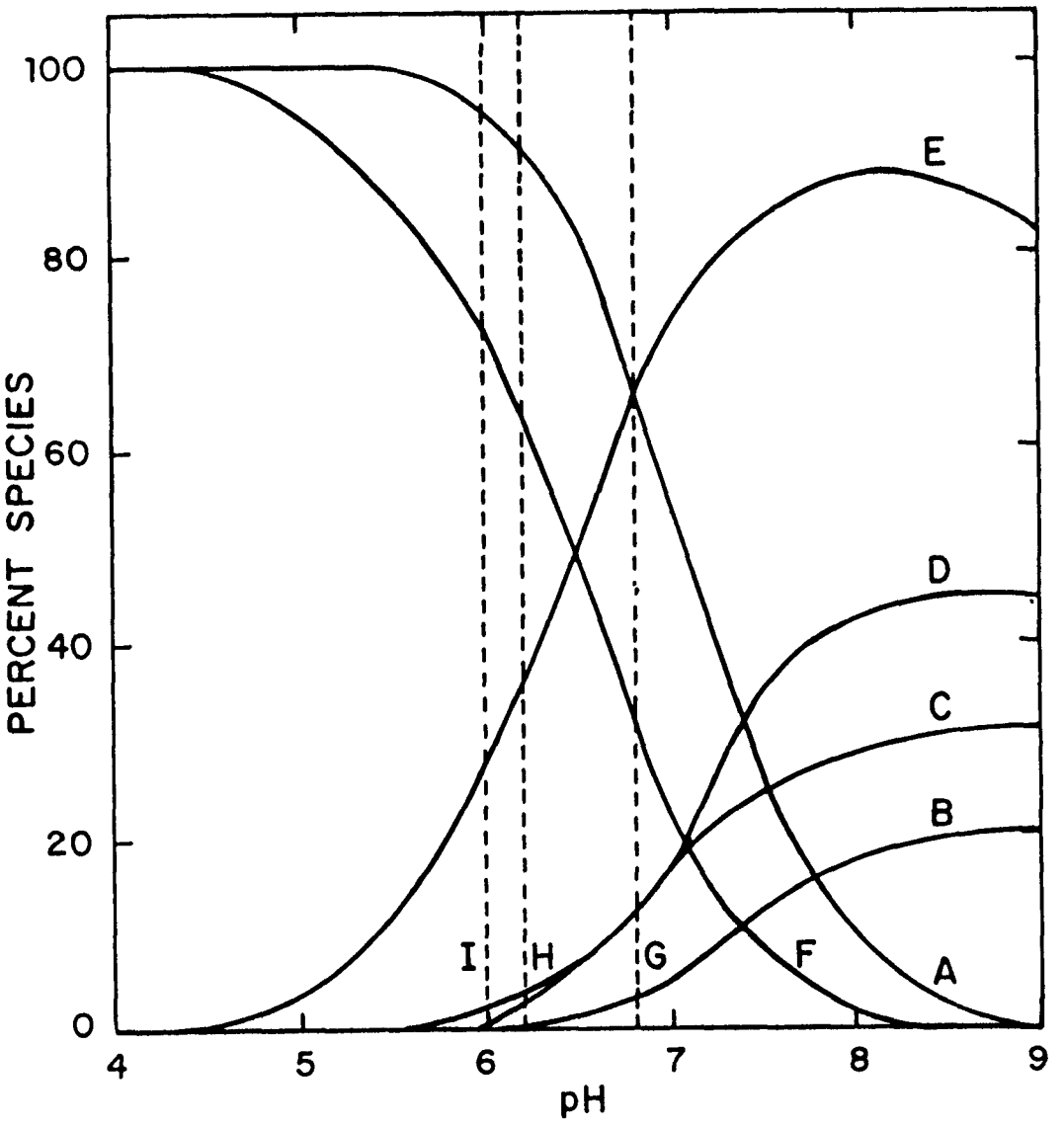

Figure 4.08. Speciation of copper(II) (total concentration 2 ppm) and carbonate as a function of pH. (A) Cu^{2}, (b) $Cu_2(OH)_2^2$ (C) $CuOH^+$, (D) $CuCO_3$, (E) HCO_3, (F) H_2CO_3, (G) pH at which $Cu(OH)_2$ will precipitate, (HO pH at which $Cu_3(OH)_2(CO_3)_2$ will precipate, (I) pH at which $Cu_2(OH)_2CO_3$ will precipitate.

TABLE 4.14. EQUILIBRIUM CONSTANT FOR COPPER

Ligand	Log K	Equation and Comments	Reference
OH^-	6.37	$Cu^{2+} + OH^- \rightleftarrows CuOH^+$	Sillen and Martell (1971)
	6.21	$Cu^{2+} + OH^- \rightleftarrows CuOH^+$ (pH=8.4)	Borgman and Ralph (1983)
	11.7	$Cu^{2+} + 2OH^- \rightleftarrows Cu(OH)_2$ (pH=8.4)	Borgman and Ralph (1983)
	14.3	$Cu^{2+} + 2OH^- \rightleftarrows Cu(OH)_2$	Sillen and Martell (1971)
	15.0	$Cu^{2+} + 3O^- \rightleftarrows Cu(OH)_3^-$	Sillen and Martell (1971)
	16.0	$Cu^{2+} + 4OH^- \rightleftarrows Cu(OH)_4^{2-}$	Sillen and Martell (1971)
	17.7	$2Cu^{2+} + 2OH^- \rightleftarrows Cu_2(OH)_2^{2+}$	Felmy et al. (1985)
Cl^-	0.02	$Cu^{2+} + Cl^- \rightleftarrows CuCl^+$	Hegelson (1969)
	2.05	$Cu^{2+} + Cl^- \rightleftarrows CuCl^+$	Sillen and Martell (1971)
	-0.71	$Cu^{2+} + 2Cl^- \rightleftarrows CuCl_2$	Hegelson (1969)
	-2.3	$Cu^{2+} + 3Cl^- \rightleftarrows CuCl_3^-$	Hegelson (1969)
	-4.6	$Cu^{2+} + 4Cl^- \rightleftarrows CuCl_4^{2-}$	Sillen and Martell (1971)
F^-	1.26	$Cu^{2+} + F^- \rightarrow CuF^+$	Felmy et al (1985)
CO_3^{2-}	5.97	$Cu^{2+} + CO_3^{2-} \rightleftarrows CuCO_3$ (aq)	Ernst et al., (1975)
	6.0	$Cu^{2+} + CO_3^{2-} \rightleftarrows CuCO_3$ (aq)	Bilinsk et al., (1976)
	6.34	$Cu^{2+} + CO_3^{2-} \rightleftarrows CuCO_3$ (aq)	Scaife (1957)
	6.8	$Cu^{2+} + CO_3^{2-} \rightleftarrows CuCO_3$ (aq)	Stiff (1971)
	6.2	$Cu^{2+} + CO_3^{2-} \rightleftarrows CuCO_3$ (aq) (pH=8.4)	Borgman and Ralph (1983)
	10.3	$Cu^{2+} + 2CO_3^{2-} \rightleftarrows Cu(CO_3)_2^{2-}$	Borgman and Ralph (1983)
	9.83	$Cu^{2+} + 2CO_3^{2-} \rightleftarrows CU(CO_3)_2^{2-}$	Mesmer and Baes (1975)
S^{2-}	40	$Cu^{2+} + S^{2-} \rightarrow CuS$	Sillen & Martell (1971)
SO_4^{2-}	2.25	$Cu^{2+} + SO_4^{2-} \rightleftarrows CuSO_4$ (aq)	Sillen and Martell (1971)
HS^-	26	$Cu^{2+} + 3HS^- \rightleftarrows Cu(HS)_3^-$	Sillen and Martell (1971)

TABLE 4.14 (continued)

Ligand	Log K	Equation and Comments	Reference
CN^-	28.6	$Cu^+ + 3CN^- \rightleftarrows Cu(CN)_3^{2-}$	Sillen and Martell (1971)
	30.3	$Cu^+ + 4CN^- \rightleftarrows Cu(CN)_4^{3-}$	Sillen and Martell (1971)
	25	$Cu^{2+} + 4CN^- \rightleftarrows Cu(CN)_4^{2-}$	Sillen and Martell (1971)
NTA	13.05		Sillen & Martell (1971)
EDTA	18.8	$Cu^{2+} + EDTA^{4-} \rightleftarrows Cu\text{-}EDTA^{2-}$	Sillen and Martell (1971)
HA^-	8.9	$Cu^{2+} + 2HA^- \rightleftarrows Cu\text{-}(HA)_2$	Stevenson (1976)
	6.23	$Cu^{2+} + HA \rightleftarrows Cu\text{-}HA$ Site: GL (freshwater sediment) pH=8, I=0.01M	Sohn and Huges (1981)
	6.5	$Cu^{2+} + HA \rightleftarrows Cu\text{-}HA$ Site: SH, pH=8, I=0.01M	Sohn and Huges (1981)
	6.55	$Cu^{2+} + HA \rightleftarrows Cu\text{-}HA$ Site: BV, pH=8, I=0.01M	Sohn and Huges (1981)
	6.56	$Cu^{2+} + HA \rightleftarrows Cu\text{-}HA$ Site: SR, pH=8. O=0.01M	Sohn and Huges (1981)
FA	6.0	$Cu^{2+} + FA \rightleftarrows Cu\text{-}FA$ (pH=6.0) (Shawsheen River)	McKnight et al., (1983)
	6.1	(Ogeechee River)	McKnight et al., (1983)
	6.6	(Ohio River)	McKnight et al., (1983)
	5.7	(Missouri River)	McKnight et al., (1983)
	6.1	(South Platte River)	McKnight et al., (1983)
	6.0	$Cu^{2+} + FA \rightleftarrows Cu\text{-}FA$ (Bear River) (pH=6.2	McKnight et al., (1983)
	5.9	(Como River) (pH=6.2)	McKnight et al., (1983)
	5.9	Deer Creek	McKnight et al., (1983)
	5.6	Hawaian River	McKnight et al., (1983)
	6.3	Black Lake	McKnight et al., (1983)
	6.4	Island Lake	McKnight et al., (1983)
	5.4	Brainard Lake	McKnight et al., (1983)
	5.8	Merril Lake	McKnight et al., (1983)
	5.9	Suvannee Lake	McKnight et al., (1983)

TABLE 4.14 (continued)

Ligand	Log K	Equation and Comments	Reference
	6.0	Hawain Marsh	McKnight et al., (1983)
	6.0	Yuma Canal	McKnight et al., (1983)
	5.7	Yuma Canal (chlorinated)	McKnight et al., (1983)
	5.6		
	6.1	Cu^{2+} + FA → Cu(FA) (pH=6.9)	Breshnan et al., (1978)
	5.7	Cu^{2+} + FA → Cu(FA) (pH=7.0)	Shuman and Cromer (1979)
	5.4 - 6.6	Cu^{2+} + FA → Cu(FA) (pH=6.2)	McKnight et al., (1983)
	3.3	Cu^{2+} + FA → Cu(FA) (pH=3)	Y.H. Lee (1984)
	4.0	Cu^{2+} + FA → Cu(FA) (pH=5	Y.H. Lee (1984)
	9.1	Cu^{2+} + FA → Cu(FA) (pH=8)	Mantoura et al., (1978)
FA	6.5	Cu_{2+} + FA ⇄ CuFA (pH=6.5)	Sterritt and Lester (1984)
<u>Amino Acids</u>			
Glycine	8.51	Cu^{2+} + L ⇄ Cu-L	Sillen and Martell (1971)
	15.5	Cu^{2+} + 2L ⇄ Cu-L_2	Sillen and Martell (1971)
Alanine	8.27	Cu^{2+} + L ⇄ Cu-L	Sillen and Martell (1971)
	15.1	Cu^{2+} + 2L ⇄ Cu-L_2	Sillen and Martell (1971)
Valine	8.1	Cu^{2+} + L ⇄ Cu-L	Sillen and Martell (1971)
	14.7	Cu^{2+} + 2L ⇄ Cu-L_2	Sillen and Martell (1971)
Leucine	8.1	Cu^{2+} + L ⇄ Cu-L	Sillen and Martell (1971)
	14.6	Cu^{2+} + 2L ⇄ Cu-L_2	Sillen and Martell (1971)
Phenylalamine	7.87	Cu^{2+} + L ⇄ Cu-L	Sillen and Martell (1971)
	14.77	Cu^{2+} + 2L → Cu-L_2	Sillen and Martell (1971)
B-Alanine	7.4	Cu^{2+} + L ⇄ Cu-L (pH=8.4)	Borgman and Ralph (1983)
	13	Cu^{2+} + 2L ⇄ Cu-L_2 (pH=8.4)	Borgman and Ralph (1983)
Glycine	9.3	Cu^{2+} + L ⇄ Cu-L (pH-8.4)	Borgman and Ralph (1983)
	15.1	Cu^{2+} + 2L ⇄ Cu-L_2 (pH=8.4)	Borgman and Ralph (1983)

TABLE 4.14 (continued)

Ligand	Log K	Equation and Comments	Reference
Glutamate	9.71	$Cu^{2+} + L \rightleftarrows Cu\text{-}L$ (pH=8.4)	Borgman and Ralph (1983)
	15.4	$Cu^{2+} + 2L \rightleftarrows Cu\text{-}L_2$ (pH=8.4)	Borgman and Ralph (1983)
K. Aerogenous Polymer	7.69	$Cu^{2+} + L \rightleftarrows Cu\text{-}L$ (pH=6.8)	Rudd et al., (1986)
Sludge Solids	6.75	ISE-method	Sterrit and Lester (1985)
	5.93	Filtration-method	Sterrit and Lester (1985)
Sludge Extract	7.3		Rudd et al., (1984)
Polymer	5.9	Extracted Extracellular Polymer	Rudd et al., (1984)
Soil FA	5.6	pH=4	Bresnahan et al., (1978)
	6.0	pH=5	Bresnahan et al., (1978)
	6.3	pH=6	Bresnahan et al., (1978)
Water-FA	5.47	pH=4	Bresnahan et al., (1978)
	6.0	pH=4.7	Bresnahan et al., (1978)
	5.95	pH=5.0	Bresnahan et al., (1978)
	6.1	pH=6.0	Bresnahan et al., (1978)
FA	5.67	Correction for Kinetics	Shuman and Cromer (1979)
HA	5.96	Correction for Kinetics	Shuman and Cromer (1979)
FA	5.78	pH=3.5	M. Schnitzer (1969)
	8.69	pH=5	M. Schnitzer (1969)
<u>Ligand in Natural Waters</u>			
Gloucester	9.3	$Cu^{2+}+L \rightarrow Cu\text{-}L$ (pH=8.4)	van de Berg (1979)
Lake Huron	9.2	(pH=8.3)	van de Berg (1979)
White Water Lake	8.6	(pH=8.6)	van de Berg (1979)
Onaping Lake	8.6	(pH-7.8)	van de Berg (1979)
Windy Lake	7.2	(pH=6.6)	van de Berg (1979)
Lake Ontario	9.5	(pH=8.4)	van de Berg (1979)
	8.6	(pH=7.4)	van de Berg (1979)

TABLE 4.14 (continued)

Ligand	Log K	Equation and Comments	Reference
Dickie No. 5	8.5	(pH=8.4)	van de Berg (1979)
	7.75	(pH=7.6)	van de Berg (1979)
Dickie No. 6	7.8	(pH=7.6)	van de Berg (1979)
Fulvic Acid	7.8	(pH=7.6)	van de Berg (1979)
Fresh Water Organic Ligands			
Swains Mill	5.7	pH=6.5	Shuman and Woodard (1977)
Chapel Mill	4.87	pH=5.7	Shuman and Woodard (1977)
	5.0	pH=6.0	Shuman and Woodard (1977)
	5.15	pH=6.5	Shuman and Woodard (1977)
	5.2	pH=7.0	Shuman and Woodard (1977)
L. Waccaman	4.5	pH=6.5	Shuman and Woodard (1977)
Black Lake	4.8	pH=6.5	Shuman and Woodard (1977)

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TABLE 4.15. CONSTANTS FOR COPPER ADSORPTION

Adsorbent	Langmuir $b(\frac{m\ mol}{Kg})$	$K(10^5\ \frac{L}{mol})$	Comments	Reference
Ottawa River Sediments				
Sample 75-15	0.009		% Org. matter = 0.6	Ramamoorthy (1978)
75-35	0.107	28.5	% Org. matter = 3.2	Ramamoorthy (1978)
75-6	0.055	4.8	% Org. matter = 35.7	Ramamoorthy (1978)
75-16	0.01	1.4	% Org. matter = 0.6	Ramamoorthy (1978)
75-22	0.01	0.8	% Org. Matter = 2.4	Ramamoorthy (1978)
Humic Acid	605	3.6	Sample A pH=4.4	Beveridge & Pickering (1980)
	450	8.5	Sample B pH=4.4	Beveridge & Pickering (1980)
	970	5.1	Sample C pH=4.4	Beveridge & Pickering (1980)
	250	4.0	Sample D pH=4.4	Beveridge & Pickering (1980)
Kaolin	22	0.1	pH = 5, Temp. 25°C	Farah et al., (1980)
Illite	40	2.2	(Na^+ form clays)	Farah et al., (1980)
Montmorillonite	367	6.1		Farah et al., (1980)
Bentonite Clay	83	5.1	pH = 8	Oakley (1981)
$Fe(OH)_3$	830	2.46	pH = 8	Oakley (1981)
MnO_2	11000	6.67	pH = 8	Oakley (1981)
Humic	492	7.4	pH = 8	Oakley (1981)
Wollastonite	12.4	0.12	Temp. = 20°C	Panday et al., (1986)
	14.7	0.15	Temp. = 30°C	Panday et al., (1986)
	17.3	0.227	Temp. = 40°C	Panday et al., (1986)

Adsorbent	Freundlich K	n	Comments	Reference
Bentonite	2.96	0.65	C = mg/mℓ, X = mg/g	Guy et al., (1975)

Adsorbent	Partition Coeff. Kd $(\frac{L}{Kg})$	Comments	Reference
Bentonite	43000		Oakley et al., (1981)
$Fe(OH)_3$	205000		Oakley et al., (1981)
MnO_2	7340000		Oakley et al., (1981)
Humic	366000		Oakley et al., (1981)

TABLE 4.16. SUMMARY OF THE HEAVY METALS MODELS

	Woodard et al. (1981)	Christophersen & Seip (1982)	Chapman (1982)	Felmy et al. (1984) MEXAMS	Fontaine, III (1984 a,b) NONEQUI
Base Model	stream sediment transport model, steady state	Compartmentalized Hydrologic model, nonsteady state	stream, 1-D, time-variable model	EXAMS base model, completely mixed, compartmentalized mass balance model, steady state	completely mixed, compartmentalized mass balance model, nonsteady state
Physical Process	Sorption of metal, sedimentation, particle size	Sorption of sulfate	Advection, dispersion sorption of metal	Advection, dispersion sorption of metal	sorption kinetics diffusion kinetics
Chemical Process	No chemical reaction; considers Hg, Cd, Pb, and As total metal conc.	Cation exchange weathering, Dissolut. precipitation of gibbsite, mineraliz. of sulfate; Considers Hg^{+}, Al^{3+}, Ca^{2+}, Mg^{2+}, and SO_4^{2-}	Equilibrium speciation w/MINEQL Considers over 80 components, 150 species and equlibrium with solids	Equilibrium speciation w/MINTEQ	Kinetics of: cation exchange Methylation, demethylation, humic acid-mediated reduction, volatilization, metal-organics, complexation
Source	point	non-point	point	point, non-point	point, non-point (Atmospheric, runoff & bed loads)
Application	Stream waste-water discharge effect	stream, acid rain effects	stream, metal pollution	stream, lake	stream, lake

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SECTION 5

ANALYTICAL SOLUTIONS

5.1 INTRODUCTION

Modeling the transport and transformation of toxic chemicals is performed by development of a mass balance around a clearly defined control volume or ecosystem. If toxic substances are discharged into receiving waters, they will be transported by advection and dispersion, and they may be subject to chemical, physical, and biological reactions and phase-transfer.

For reservoirs and lakes, far enough away from discharge sites, one can generally assume that the substances are well mixed and uniformly dispersed, mainly by turbulence and differential advection caused by wind and bed shear over the time of scale of interest (days to years). A completely mixed model (CSTR, continuously stirred tank reactor) is appropriate for those lakes where dispersive transport is predominant. For streams and rivers, one can assume that advection is the primary transport mechanism and that there is negligible mixing due to diffusion or dispersion in the direction of flow. The plug-flow (PF) model may be applicable for those rivers and streams where diffusive transport is minimal and advection by the current velocity is predominant. A third type of model, the advective-dispersive (plug-flow with dispersion) model, is appropriate for estuaries and reservoirs where toxic chemicals advect and diffuse simultaneously as they move through the system.

As was discussed in Section 2, a key feature in determining the appropriate model is the magnitude of the mixing, which approaches infinity in the completly mixed system and approaches zero in the plug-flow system. The plug-flow-with-dispersion (PFD) model lies in between the idealization of completely mixing and of plug-flow. For many applications in water quality analysis, the completely mixed model or plug-flow model are appropriate when a first approximation of water quality is required.

Once the mixing characteristics of the surface water are determined, then an effort should be made to express the dynamics in mathematical form as a mass balance equation around a control volume (bay, lake, or compartment). The model formulation may incorporate transport and reactions based on the principle of conservation of mass. A mass balance around a control volume may be expressed as

Accumulation = Inputs - Outputs ± Reactions
of mass

In this Section, analytical solution techniques are described for idealized systems. It should be recognized, however, that the models described here represent only the simplest, most ideal mixing conditions. In spite of this fact, they may be quite useful in checking more complicated numerical results and in gaining insight to the dynamics of toxic chemical movement in the environment.

5.2 COMPLETELY MIXED SYSTEMS

An ideal completely mixed system is illustrated, using a lake as an example, in Figure 5.01. The major assumptions involved in this model are

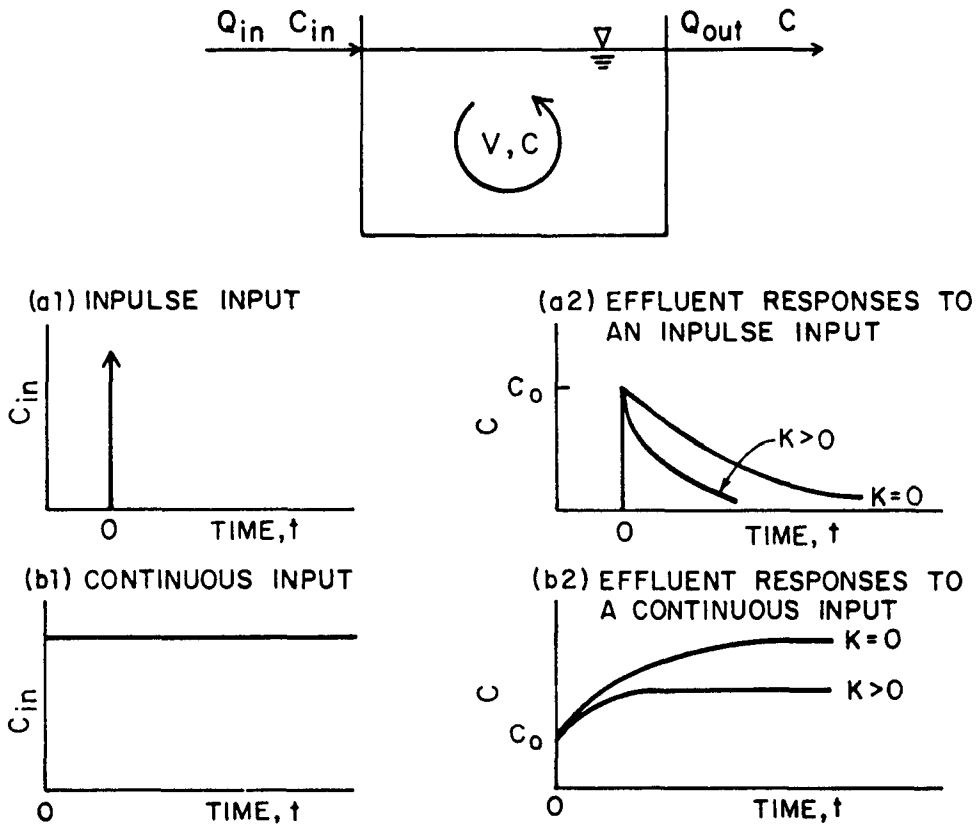

Figure 5.01. Schematic of a completely mixed lake, with inputs and effluent responses.

that the concentration of chemicals in the lake is uniform (completely-mixed) and the lake outlet has a concentration, C, and the concentration is the same everywhere within the lake. The mass balance yields

Change in Mass in the lake	=	Mass in Inflow	-	Mass in Outflow	±	Mass reacting in the lake

This can be expressed mathematically as

$$\frac{\Delta(VC)}{\Delta t} = Q_{in}\, C_{in} - Q_{out}\, C \pm rV$$

where C_{in} = chemical concentration in inflow (ML^{-3}),

C = chemical concentration in the lake and in outflow (ML^{-3}),

Q_{in} = volumetric inflow rate (L^3T^{-1}),

Q_{out} = volumetric outflow rate (L^3T^{-1}),

V = volume of the lake (L^3),

r = reaction rate ($ML^{-3}T^{-1}$); positive and negative signs indicate formation and decay reactions, respectively,

and

t = time (T).

The limit as Δt approaches zero gives the ordinary differential equation below.

$$\frac{d(VC)}{dt} = Q_{in}C_{in} - Q_{out}\, C \pm rV \tag{5.1}$$

The volume of the lake V, flows Q_{in} and Q_{out}, and inflow concentration C_{in} can be time-dependent variables. In addition to the completely mixed assumption, assumptions also may be made to simplify the equation:

(1) The inflow concentration C_{in} is constant,

(2) The volumetric flow rate into and out of the lake is constant ($Q_{in} = Q_{out} = Q$ = constant), and the volume of the lake V is constant ($dV/dt = 0$).

(3) The rate of change in the concentration C that is occurring within the lake is governed by a first-order reaction ($r = -KC$; note that the negative sign refers to a decay reaction).

Incorporating these assumptions, equation (5.1) can be written as

$$V\frac{dC}{dt} = QC_{in} - QC - KCV \tag{5.2}$$

Equation (5.2) is the general first-order decay equation for a completely mixed system.

A response to an accidental spill of chemical to a lake, for example, can be formulated using the impulse (or delta) function if the discharge of chemical occurred for a relatively short time period. For a simple case, that conservative tracer is instantaneously injected into the lake as in impulse input, equation (5.2) may be reduced to

$$V\frac{dC}{dt} = -QC \tag{5.3}$$

Dividing by V yields

$$\frac{dC}{dt} = -\frac{Q}{V} C = -\frac{C}{t_d} \tag{5.4}$$

where $t_d = V/Q$ = mean hydraulic detention time (T). With an initial condition of $C = C_0$ at $t = 0$, equation (5.4) can be integrated as

$$\int_{C_o}^{C} \frac{1}{C} dC = -\frac{1}{t_d} \int_{0}^{t} dt \tag{5.5}$$

Integrating equation (5.5) for the time-interval zero to t yields

$$C = C_0 \exp(-t/t_d) \tag{5.6}$$

Equation (5.6) is the analytical solution to an impulse input for a conservative tracer.

In the event that a reactive chemical was spilled to the lake, equation (5.2) may be reduced to

$$V \frac{dC}{dt} = -QC - KCV \tag{5.7}$$

which can be solved similarly:

$$C = C_0 \exp -(K + 1/t_d)t \tag{5.8}$$

Equation (5.8) is the analytical solution to an impulse input for reactive substances. A graphical sketch of the responses to an impulse input for reactive (K>0) and non-reactive (K=0) chemicals is shown in Figure 5.01.

Response to a continuous load, such as a waste discharge from a municipality or an industry to a lake, is also represented by equation (5.2), which can be rewritten as:

$$\frac{dC}{dt} + \left(\frac{1}{t_d} + K\right) C = \frac{C_{in}}{t_d} \tag{5.9}$$

Equation (5.9) has the form of a first-order, nonhomogeneous linear differential equation. If only the steady-state concentration is desired, then solution of equaiton (5.9) can be obtained noting that the change in concentration is zero ($dC/dt = 0$). The steady-state solution of equation (5.9) is given as:

$$C_{ss} = \frac{QC_{in}}{Q + KV} = \frac{C_{in}}{1 + Kt_d} \tag{5.10}$$

where C_{ss} = steady-state concentration (ML^{-3}). Note that there is no change in concentration with respect time, t.

If one desires to see the change in concentration with time, the non-steady-state solution can be obtained for equation (5.9), a first-order linear differential equation that has a general form:

$$y' + p(x)y = q(x) \tag{5.11}$$

with the general solution

$$y = y_0 \exp(-P(t)) + \exp(-P(t)) \int_0^t \exp(P(t))\, q(t)dt \tag{5.12}$$

where $P(t) = \int p(t)\, dt$

This solution technique is known as the integrating factor method. The solution of equation (5.9) can be obtained as the integral equation:

$$C = C_0 e^{-(K + \frac{1}{t_d})t} + e^{-(K + \frac{1}{t_d})t} \int_0^t e^{(K + \frac{1}{t_d})t} \frac{C_{in}}{t_d} dt \tag{5.13}$$

Integrating this equation over the interval 0 to t yields

$$C = C_0 e^{-(K + \frac{1}{t_d})t} + \frac{C_{in}}{Kt_d + 1} \left(1 - e^{-(K + \frac{1}{t_d})t}\right) \tag{5.14}$$

Note that the solution is composed of two concentration changes; the first term on the right-hand side of the equal sign represents "die-away" of the initial concentration, and the second term represents "build-up" of concentration due to continuous input. When t approaches infinity, equation (5.14) reduces to equation (5.10), the steady-state equation.

If a number of lakes are present in series, these water bodies can be analyzed collectively. Figure 5.02 shows a series of lakes that consists of n equal-volume, completely mixed lakes. As was done above for a single lake, the approach is based on a mass balance around each lake of series. Before deriving time variable solutions, the steady-state solution will be developed.

The mass balance for the 1st lake is given as

$$V \frac{dC_1}{dt} = QC_{in} - QC_1 - KC_1V$$

and solved for

$$C_1 = \frac{C_{in}}{1 + Kt_d} \tag{5.15}$$

For the 2nd lake,

$$V \frac{dC_2}{dt} = QC_1 - QC_2 - KC_2V$$

and solved for

$$C_2 = \frac{C_1}{1 + Kt_d} \tag{5.16}$$

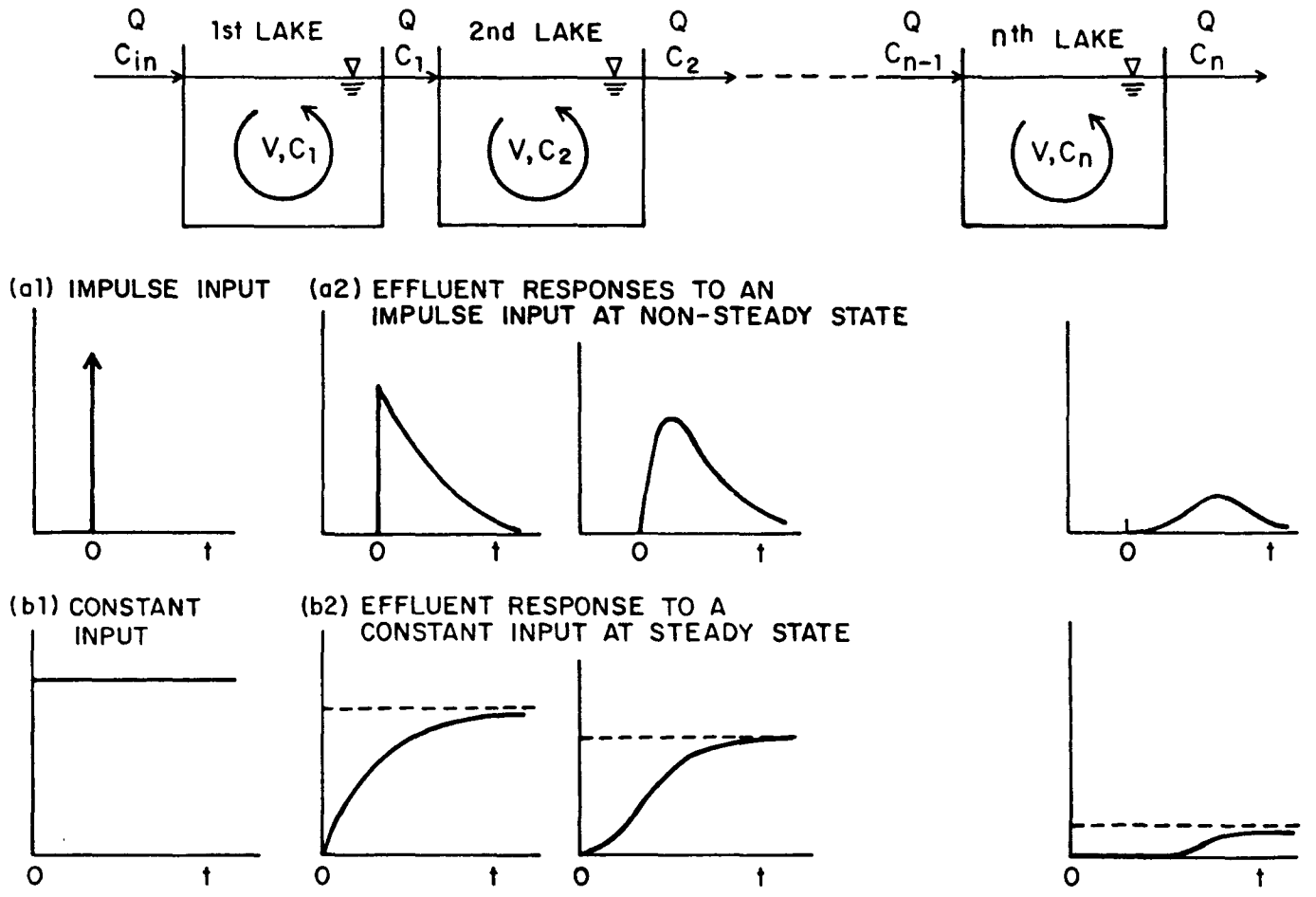

Figure 5.02. Schematic of completely mixed lakes in series, and inputs and effluent responses with reaction decay.

Substitution of equation (5.15) into equation (5.16) yields

$$C_2 = \frac{C_{in}}{(1 + Kt_d)^2} \tag{5.17}$$

where t_d is the detention time of each individual lake, not the overall detention time.

The mass balance for the nth lake is given as

$$V \frac{dC_n}{dt} = QC_{n-1} - QC_n - KC_nV$$

and solved for

$$C_n = \frac{C_{n-1}}{(1 + Kt_d)} \tag{5.18}$$

where n is the number of lakes in question and n-1 designates the upstream lake. Therefore, the analytical solution for the nth lake is given as

$$C_n = \frac{C_{in}}{(1 + Kt_d)^n} \tag{5.19}$$

The time variable solution can be obtained for an impulse input of conservative tracer. The mass balance for the first lake may be given as

$$V \frac{dC_1}{dt} = - QC_1 \tag{5.20}$$

Integrating equation (5.20) for the time-interval zero to t with an initial condition of $C_1 = C_{1(0)}$ at t = 0, yields

$$C_1 = C_{1(0)} \exp (- t/dt) \tag{5.21}$$

The mass balance for the second lake gives

$$\frac{dC_2}{dt} = \frac{C_1}{t_d} - \frac{C_2}{t_d} \tag{5.22}$$

Substituting equation (5.21) into equation (5.22) and rearranging yields

$$\frac{dC_2}{dt} + \frac{C_2}{t_d} = \frac{C_{1(0)} \exp (-t/dt)}{t_d} \tag{5.23}$$

Equation (5.23) can be solved using the integrating factor method for

$$C_2 = \frac{C_{1(0)}t}{t_d} \exp \left(-t/t_d\right) \tag{5.24}$$

For the third lake, the mass balance yields

$$\frac{dC_3}{dt} = \frac{C_2}{t_d} - \frac{C_3}{t_d} \tag{5.25}$$

Substituting equation (5.24) into equation (5.25) and solving using the integrating factor yields

$$C_3 = \frac{C_{1(0)} t^2}{2t_d^{\,2}} \exp\left(-t/t_d\right) \tag{5.26}$$

Thus, the general formula for n lakes in series that receive an impulse input of conservative tracer is given as

$$C_n = \frac{C_{1(0)}}{(n-1)!} \left(\frac{t}{t_d}\right)^{n-1} \exp\left(-t/t_d\right) \tag{5.27}$$

where t_d is the detention time of an individual lake, V/Q.

In the case that a lake or reactor vessel is segmented into n compartments as shown in Figure 5.03, the effluent response to an impulse input of non-reactive chemical may be given by

$$C_n = \frac{C_0\, n^n}{(n-1)!} \left(\frac{t}{t_d'}\right)^{n-1} \exp\left(-nt/t_d'\right) \tag{5.28}$$

where t_d' represents the detention time of the entire vessel (V_{total}/Q) and C_o is the initial concentration if the impulse input were delivered to the entire vessel (M/V_{total}). The effluent responses with respect to the number of compartment are illustrated in Figure 5.03. As seen, the greater the number of compartment, the greater the tendency towards plug flow conditions.

Equation 5.28 is particularly powerful because it provides effluent responses that are intermediate between the ideal plug-flow model and the ideal completely mixed model ($n = \infty$ and $n = 1$ in Figure 5.03). For lakes and reservoirs that have, in reality, plug flow and dispersion characteristics, equation (5.28) can be used with a hypothetical number of compartments (n) to obtain the best fit to an impulse injection of tracer, and thus obtain the mixing characteristics of the system for modeling of other pollutants.

5.3 PLUG-FLOW SYSTEMS

An ideal plug-flow system is illustrated, using a river as an example, in Figure 5.04. The major assumptions involved in this model are that the bulk of water flows downstream with no longitudinal mixing and that instantaneous mixing occurs in the lateral and vertical directions. It is a one-dimensional model. The mass balance is developed around an incremental volume V and is given as

$$\frac{\Delta(VC)}{\Delta t} = QC - Q(C + \Delta C) - KCV \tag{5.29}$$

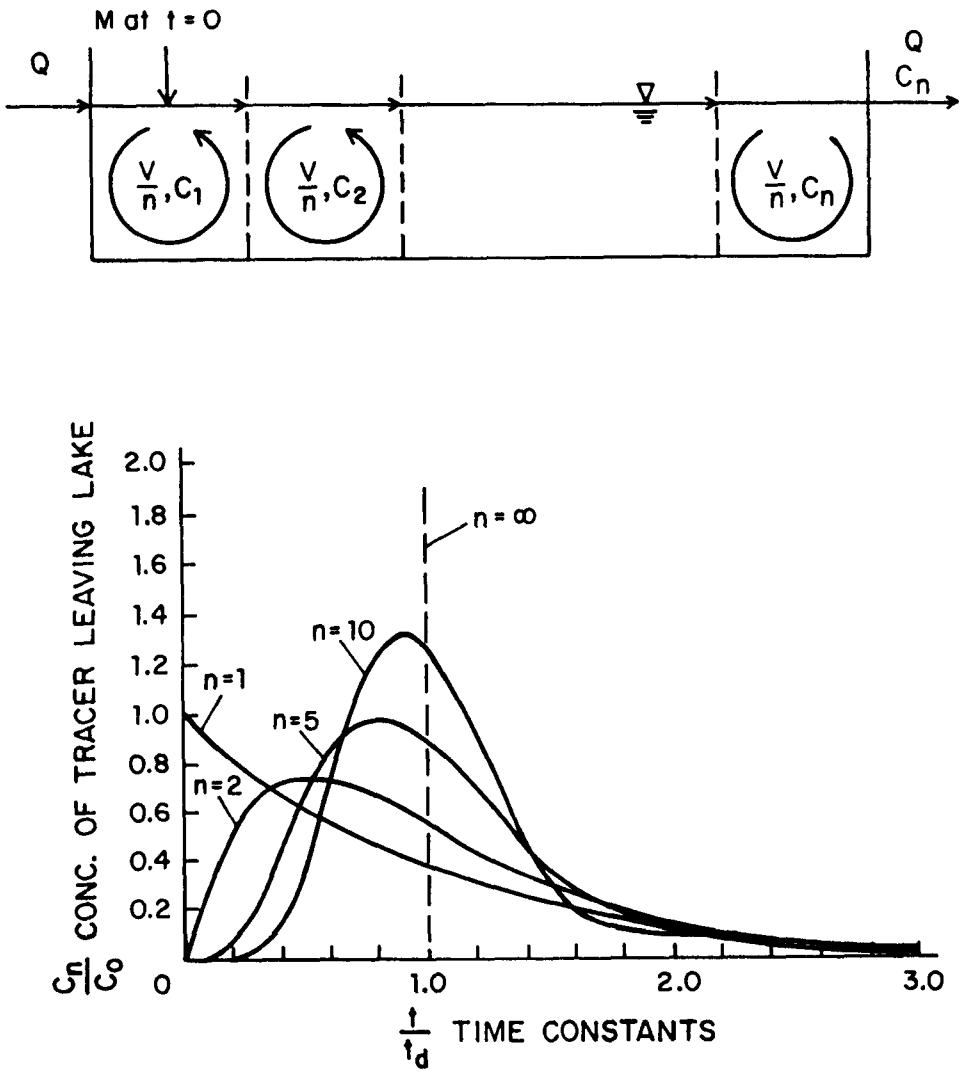

Figure 5.03. A compartmentalized lake and effluent responses to an impulse input of conservative tracer.

where $V = A\Delta X$ (L^2L),
A = cross-sectional area (L^2),
Δx = an increment of finite thickness of the stream (L), and
Δt = a time interval (T), and
K = a first-order decay rate (T^{-1}).

Dividing equation (5.29) by V and simplifying yields

$$\frac{\Delta C}{\Delta t} = -\frac{Q\Delta C}{A\Delta x} - KC \tag{5.30}$$

The limit of equation (5.29) as $\Delta t \to 0$ is:

$$\frac{\partial C}{\partial t} = -\frac{Q}{A}\frac{\partial C}{\partial x} - KC = -u\frac{\partial C}{\partial x} - KC \tag{5.31}$$

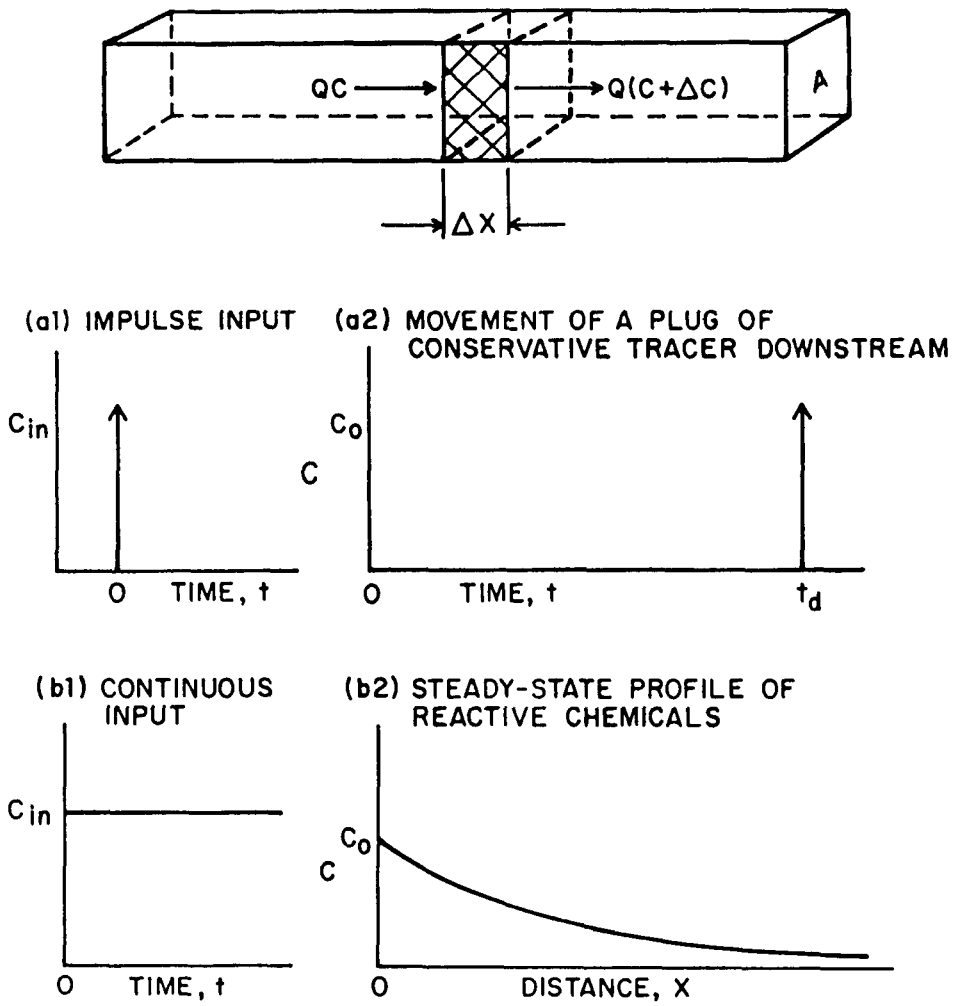

Figure 5.04. Schematic of plug-flow system, with inputs and response profiles.

where u = Q/A = mean velocity. This is the general equation for a plug-flow system. Note that the concentration C is a function of both time, t, and distance, x.

At steady state ($\partial C/\partial t = 0$), equation (5.31) reduces

$$\frac{\partial C}{\partial x} = -\frac{K}{u} C \tag{5.32}$$

With a boundary condition of $C = C_0$ at $x = 0$, equation (5.32) can be integrated by separation of variables to yield

$$C = C_0 \exp(-Kx/u) \tag{5.33}$$

This is the steady-state solution to the plug flow equation. Effluent responses to an impulse and constant inputs are illustrated in Figure 5.4.

5.4 ADVECTIVE-DISPERSIVE SYSTEMS (PLUG FLOW WITH DISPERSION)

An ideal plug-flow system is illustrated, using an estuary as an example, in Figure 5.05. As was done in the plug-flow model, the mass balance is written around an incremental control volume of small but finite volume.

Accumulation	=	Advective transport inputs	+	Dispersive transport inputs		
	-	Advective transport outputs	-	Dispersive transport outputs	±	Reactions

A mass balance over an infinitesimal time interval can be written for the differential volume, $A\Delta x$, as

$$V \frac{\partial C}{\partial t} = (QC + (-EA \frac{\partial C}{\partial x}))$$
$$- (Q(C + \Delta C) + (-EA (\frac{\partial C}{\partial x} + \Delta \frac{\partial C}{\partial x}))) - KCV \qquad (5.34)$$

where $V = A\Delta x$ (L^2L)
E = dispersion coefficient (L^2T^{-1})
K = first-order reaction coefficient (T^{-1})

Simplifying equation (5.34) yields

$$V \frac{\partial C}{\partial t} = - Q \frac{\partial C}{\partial x} \Delta x + EA \frac{\partial}{\partial x} (\frac{\partial C}{\partial x}) \Delta x - KCV \qquad (5.35)$$

Dividing by $V = A\Delta x$

$$\frac{\partial C}{\partial t} = - \frac{Q}{A} \frac{\partial C}{\partial x} + E \frac{\partial}{\partial x} (\frac{\partial C}{\partial x}) - KC$$

or

$$\frac{\partial C}{\partial t} = E \frac{\partial^2 C}{\partial x^2} - u \frac{\partial C}{\partial x} - KC \qquad (5.36)$$

Equation (5.36) is the time-variable equation for advective-dispersive systems with constant coefficients, Q, A, E, and K.

The steady-state equation for an estuary system may be obtained by setting the left-hand side of equation (5.36) equal to zero, $\partial C/\partial t = 0$.

$$0 = E \frac{d^2C}{dx^2} - u \frac{dC}{dx} - KC \qquad (5.37)$$

Equation (5.37) is a second-order, ordinary, homogeneous, linear differential equation, which has the general form:

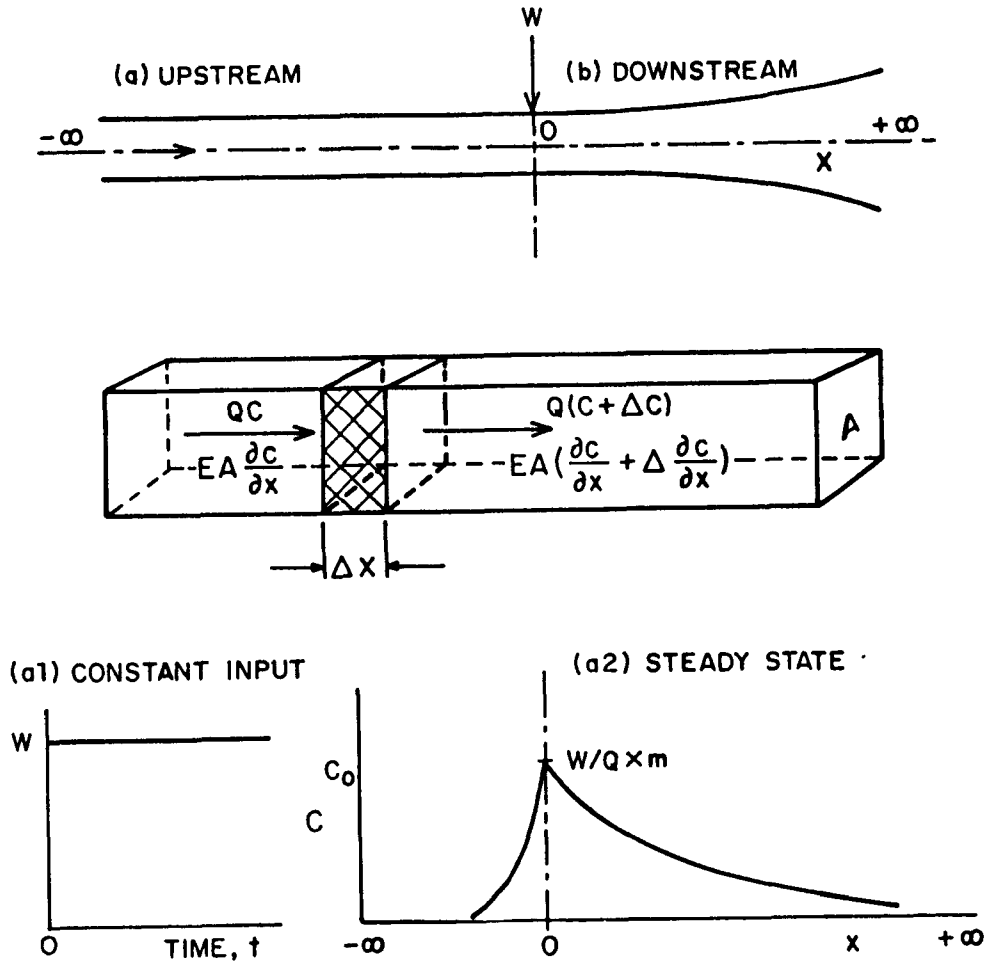

Figure 5.05. Schematic of advective-dispersive system, and input and steady-state profile of reactive chemicals.

$$0 = ay'' + by' + cy$$

where $y = f(x)$, and the general form of the solution is given as

$$y = B \exp(gx) + D \exp(jx)$$

where

$$g \cdot j = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

The roots of the quadratic equation of coefficients gives g and j (g • j), and B and D are integration constants obtained from boundary conditions. Note that g and j refer to positive and negative roots, respectively. Accordingly, the solution of equation (5.37) is obtained as

$$C = B \exp(gx) + D \exp(jx) \tag{5.38}$$

where

$$g \cdot j = \frac{u \pm \sqrt{u^2 + 4EK}}{2E} = \frac{u}{2E}(1 \pm m)$$

$$m = \sqrt{1 + \frac{4EK}{u^2}}$$

In order to solve equation (5.38), boundary conditions must be used. To establish boundary conditions, the estuary system of question may be divided into upstream and downstream segments at the point of chemical discharge (Figure 5.05).

In the upstream segment, we can set two boundary conditions (BC 1 and BC 2) as follows.

BC 1: At the upstream segment, far from the discharge point, the concentration approaches zero, that is, $C = 0$ at $x = -\infty$. Under this condition, we obtain

$$D = 0 \text{ and } C = B \exp(gx) \tag{a1}$$

BC 2: The concentration at the point of discharge is C_0, that is, $C = C_0$ at $x = 0$. Under this condition, we obtain

$$B = C_0$$

Therefore, the concentration in the upstream segment is given as

$$C_a = C_0 \exp(gx) = C_0 \exp\left(\frac{ux}{2E}(1 + m)\right) \tag{a2}$$

In the downstream segment, two additional boundary conditions can be set.

BC 1: The concentration approaches zero downstream, far from the discharge point, that is, $C = 0$ at $x = +\infty$. Under this condition, we obtain

$$B = 0 \text{ and } C = D \exp(jx) \tag{b1}$$

BC 2: At the point of discharge, the concentration is C_0, that is $C = C_0$. Under this condition, we obtain

$$D = C_0$$

Therefore, the concentration in the downstream segment is given as

$$C_b = C_0 \exp(jx) = C_0 \exp\left(\frac{ux}{2E}(1 - m)\right) \tag{b2}$$

The boundary concentration (C_0) at the discharge point can be obtained by making a mass balance at $x = 0$ (Figure 5.06).

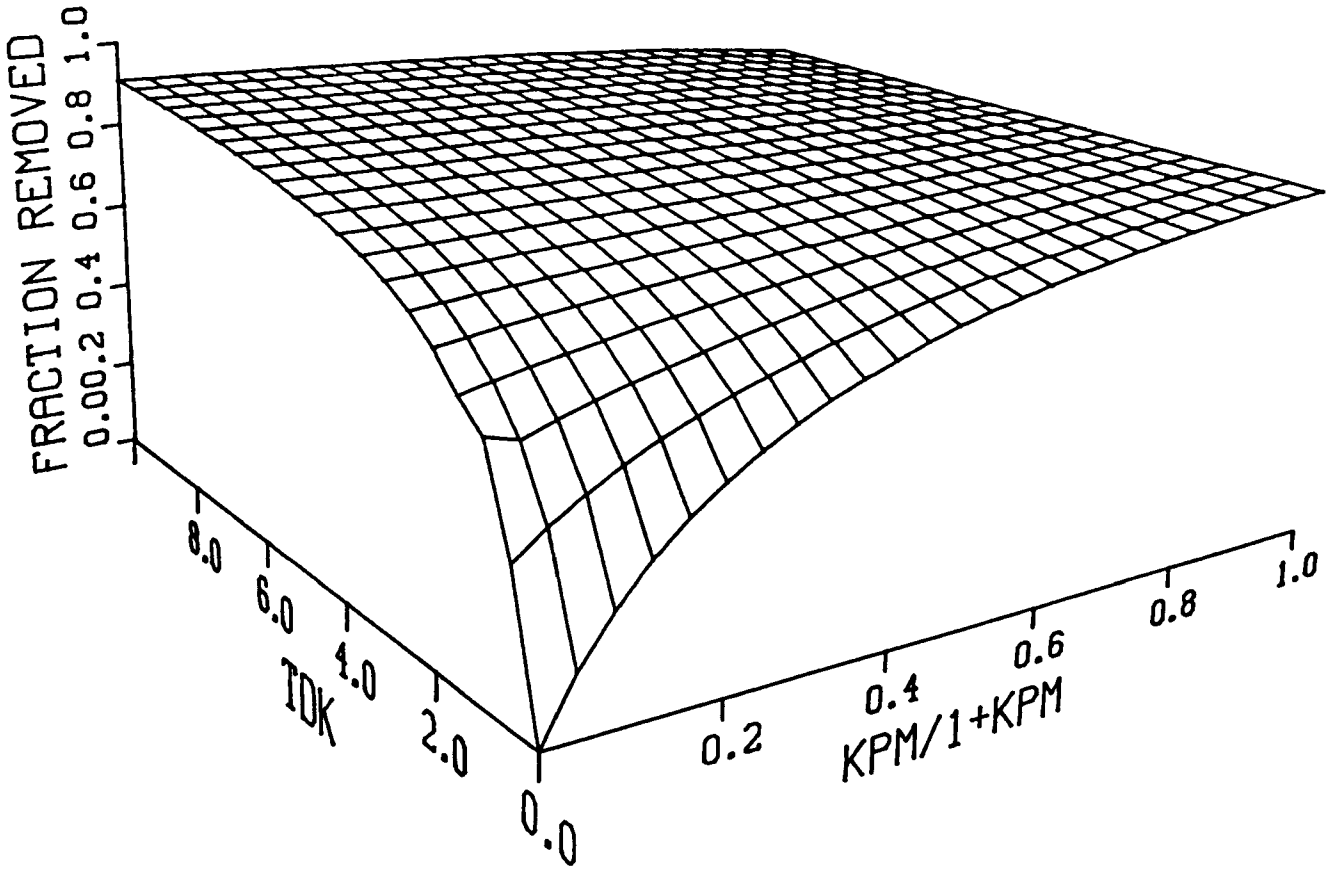

Figure 5.06. Chemical fraction removed versus particulate fraction (KPM/1 + KPM) versus t_d ΣK(TDK) at $K_s t_d$ = 4 at steady-state.

Mass in = Mass out

$$QC_0 - EA \left.\frac{dC_a}{dx}\right|_{x=0} + W = QC_0 - EA \left.\frac{dC_b}{dx}\right|_{x=0} \qquad \text{(c1)}$$

The reaction is negligible because Δx is infinitesimally small. From equation (a1),

$$\left.\frac{dC_a}{dx}\right|_{x=0} = gB \qquad \text{(a1)'}$$

and from equation (b1),

$$\left.\frac{dC_b}{dx}\right|_{x=0} = jD \qquad \text{(b1)'}$$

Substituting equations (a1)' and (a2)' into (c1) yields

$$- EAgB + W = -EAjD$$

Since $B = D = C_0$, we obtain

$$C_0 = \frac{W}{EA(g - j)} \qquad \text{(c2)}$$

Substituting g.j of equation (5.38) into equation (c2) and simplifying yields

$$C_0 = \frac{W}{mQ} \qquad \text{(c3)}$$

The final solution is summarized as follows:

$$C = C_0 \exp(gx) \text{ at } x \leq 0$$
$$C = C_0 \exp(jx) \text{ at } x \geq 0$$

where $C_0 = \frac{W}{mQ}$

$$g \cdot j = \frac{u}{2E}(1 \pm m)$$

$$m = \sqrt{1 + \frac{4KE}{u^2}}$$

The response to a constant input under steady state conditions is presented in Figure 5.05.

5.5 GRAPHICAL SOLUTIONS

Removal efficiencies for toxic chemicals in lakes or reservoirs may be estimated using the graph shown in Figure 5.06. The 3-D graph shows the removal efficiency of a steady-state lake as a function of three

dimensionless terms: $t_d \Sigma K$, $K_s t_d$ and $\frac{K_p M}{1 + K_p M}$. The constant ΣK refers to the sum of all reaction rates of the dissolved chemicals, and K_s refers to the settling rate constant of suspended solids. K_p and M are the partition coefficient and the suspended solids concentration, respectively. It is indicated that the fraction of chemicals removed increases as the dimensionless number $K_p M/(1 + K_p M)$ increases and as the dimensionless number $t_d \Sigma K$ increases.

This relationship can be obtained in a mathematical form applying the same principle used in the modeling a completely mixed system. Mass balance on chemicals around a completely mixed impoundment may be expressed as

$$V \frac{dC_T}{dt} = QC_{T(in)} - QC_T - KC_T V \tag{5.39}$$

Here, the chemical flux is described as $QC_{T(in)}$, which equals the rate of mass input or the loading rate, W. The washout of chemicals is given as QC_T and the mass reacted is expressed as $KC_T V$. The constant K refers to the rate of total sinks of chemicals, which is assumed to be first order with respect to the total chemical concentration. As was discussed in Section 2, toxic chemicals released into receiving waters are associated, to a lesser or greater extent, with suspended and sedimented particles via sorption processes. Assuming that the reactions such as photolysis, volatilization, oxidation, and biodegradation occur primarily in the dissolved phase, and that the adsosrbed chemicals in water are removed predominantly by settling, one can develop the following reaction term.

$$KC_T V = (\Sigma KC + K_s C_p)V \tag{5.40}$$

where ΣK refers to the sum of all reaction rates of the dissolved chemicals, and K_s refers to the settling rate constant of adsorbed chemicals. (Note: For sediments, the reactions are likely to occur in the adsorped phase as well as the dissolved phase.) Incorporating these assumptions, equation (5.39) can be rewritten as

$$V \frac{dC_T}{dt} = W - C_T Q - (\Sigma KC - K_s C_p)V \tag{5.41}$$

Under the condition of sorptive equilibrium, C and C_p may be replaced by their equivalents in terms of C_T. That is,

$$C = \frac{\Sigma K \, C_T}{1 + K_p M} \tag{5.42}$$

and

$$C_p = \frac{K_s K_p M \, C_T}{1 + K_p M}$$

Describing C and C_p as a function of C_T, and dividing by V yields

$$\frac{dC_T}{dt} = \frac{W}{V} - \frac{C_T}{t_d} - \frac{\Sigma K \, C_T}{1 + K_p M} - \frac{K_s K_p M \, C_T}{1 + K_p M} \tag{5.43}$$

Solving for C_T under steady-state condition yields

$$C_T = \frac{\frac{W}{V}}{\frac{1}{t_d} + \frac{1}{1 + K_p M}(\Sigma K + K_p M K_s)} \tag{5.44}$$

Multiplying by t_d and rearranging for dimensionless term, $\frac{C_T}{W/Q}$, the overall chemical removal efficiency may be expressed as

$$e = 1 - \frac{C_T}{W/Q} = 1 - \frac{1}{1 + K_s t_d \left(\frac{K_p M}{1 + K_p M}\right) + \frac{\Sigma K t_d}{1 + K_p M}} \tag{5.45}$$

where e = overall chemical fraction removal.

The sum of the decay rate constants (ΣK) depends on the solubility, volatility, and chemical structure-reactivity. Some heavy metals and some low vapor pressure/high solubility, persistant chemicals would, therefore, not be susceptible to transfer by these mechanisms and equation (5.45) reduces to

$$e = 1 - \frac{C_T}{W/Q} = 1 - \frac{1}{1 + K_s t_d \left(\frac{K_p M}{1 + K_p M}\right)} \tag{5.46}$$

Chemicals that are strongly adsorbed are analogously trapped or removed in reservoirs, but in a lesser amount than suspended solids. The greater is the degree of adsorption, the more equal are the removal efficiencies between the chemical and the suspended solids. This degree of adsorption is described by $K_p M$, the dimensionless product of the partition coefficient times the suspended solids concentration. $K_p M$ is equal to the ratio of adsorbed particulate chemical to dissolved chemical, Cp/C. If $K_p M$ were equal to zero, all of the chemical would be in the dissolved phase, and, in the absence of other reaction decay processes, the fraction removed would be zero. Because steady-state conditions are rarely observed in lakes and reservoirs, the above analysis should be considered as a first approximation or order-of-magnitude solution to the problem of estimating the fate of toxic chemicals in impoundments. Figure 5.06 is plotted based on equation (5.45) for the conditions $K_s t_0 = 4$.

SECTION 6

DESCRIPTION OF MODELS

6.1 INTRODUCTION

The chemical fate models (TOXIWASP, EXAMS II, HSPF) and one chemical equilibrium model (MINTEQ) are described in this chapter. They are supported by the Center for Water Quality Modeling of the Environmental Research Laboratory, U.S. Environmental Protection Agency, Athens, GA. The TOXIWASP, EXAMS II, HSPF models represent tools to predict short-term or long-term effects of toxic chemicals on various aquatic environments. They provide a basis for quantifying the interactions between toxic chemicals and receiving water systems. Each model is uniquely structured to account for relevant transport, transfer and reaction processes, using different spatial and temporal discretization and numerical solution techniques. The MINTEQ model, on the other hand, is designed to compute geochemical equilibria of various inorganics and heavy metals. It calculates aqueous speciation, equilibrium adsorption/desorption, and precipitation/dissolution of solid phases, but it does not simulate chemical kinetics or transfer and transport processes.

6.2 TOXIWASP

TOXIWASP is a dynamic, compartmentalized model that examines the transport and transformation of toxic chemicals in various receiving water bodies. It was developed by combining the transport framework of WASP (Di Toro et al., 1982), with the kinetic structure of EXAMS (Burns et al., 1982), and including a mass balance for solids and sediment. TOXIWASP can be applied to streams, lakes, reservoirs, estuaries, and coastal waters, but it is directed to toxic chemicals, both organics and heavy metals.

The mathematical formulation of TOXIWASP is based on the principle of conservation of mass, as given in Figure 6.01. Equations (6.1) and (6.2) can be used to calculate sediment and chemical concentrations in the water compartment. Transport in TOXIWASP is an advective-dispersive process represented by a flow and a mixing process defined by a dispersion or exchange rate. Equations (6.3) and (6.4) calculate the concentrations of dissolved and sorbed chemicals in the sediment bed. Equation (6.3) accounts for diffusion-dispersion and pore water transport of chemical between the bed and the overlying water. Sediment-water exchange is described as a diffusion or dispersion process. Equation (6.4) accounts for sediment-bound chemical transport by scour from the bed and deposition to the bed. Sediment is assumed to be a conservative constituent which is advected and dispersed among water segments and which can be suspended or fixed in the

sediment bed. As in all the models, the reaction and transformation rates are based on an addition of pseudo-first order rate constants for hydrolysis, oxidation, biodegradation, volatilization, and photolysis of a toxic chemical dissolved in water or sorbed to sediments. Most chemical transformation and reaction rates vary in time and space, depending on chemical characteristics and environmental conditions.

Figure 6.02 presents the phase transfer and reaction kinetics used in TOXIWASP. The overall rate of hydrolysis reaction is given by the sum of three competing reactions: acid-catalyzed, neutral, and base-catalyzed

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TOXIWASP FORMULATION

(1) For chemical and suspended sediment concentration in water compartments.

$$\frac{\partial C_1}{\partial t} = - u\frac{\partial C_1}{\partial x} + \frac{\partial}{\partial x}\left(E\frac{\partial C_1}{\partial x}\right) + \frac{W_1}{V} - K + S_1 \qquad (6.1)$$

$$\frac{\partial C_2}{\partial t} = - u\frac{\partial C_2}{\partial x} + \frac{\partial}{\partial x}\left(E\frac{\partial C_2}{\partial x}\right) + \frac{W_2}{V} - K + S_2 \qquad (6.2)$$

where C_1 = concentration of chemical (ML^{-3})

C_2 = concentration of suspended sediment (ML^{-3})

u = flow velocity of water (LT^{-1})

W_1 = mass loading of chemical (MT^{-1})

W_2 = mass loading of sediment (MT^{-1})

S_1 = net exchange of chemical with bed ($ML^{-3}T^{-1}$)

S_2 = net exchange of sediment with bed ($ML^{-3}T^{-1}$)

x = longitudinal distance (L)

t = time (T)

E = longitudinal dispersion (L^2T^{-1})

V = segment volume (L^3

K = kinetic degradation or transformation rate ($ML^{-3}T^{-1}$)

$$S_2 = \frac{W_s S_b}{L_b} - \frac{W_d S_w}{L_w}$$

where W_s = scour (erosion) velocity of bed sediment (LT^{-1})

W_d = deposition velocity of suspended sediment (LT^{-1})

L_{bv} = depth of active bed sediment layer (L)

L_w = depth of water layer (L)

(2) For the dissolved and particulate chemical concentration in the sediment bed.

$$\frac{\partial C_p}{\partial t} = \frac{\partial}{\partial y}\left(D^b \frac{\partial C_p}{\partial y}\right) - \frac{\partial (U_p C_p)}{\partial y} - R_s - K \qquad (6.3)$$

$$\frac{\partial C_b}{\partial t} = \frac{\partial}{\partial y}\left(D^{bs} \frac{\partial C_b}{\partial y}\right) - \frac{W_s C_b}{L_s} + \frac{W_d C_s}{L_s} + R_s - K \qquad (6.4)$$

where C_p = concentration of dissolved chemical in bed (pore water) (ML^{-3})

C_b = concentration of sorbed chemical in bed (ML^{-3})

D^b = vertical dispersion coefficient for dissolved chemical (L^2T^{-1})

D^{bs} = vertical dispersion coefficient for sorbed chemical (L^2T^{-1})

U_p = velocity of net pore water movement into or out of the bed (LT^{-1})

W_d = deposition velocity of sediment between bed and water column (LT^{-1})

W_s = scour velocity of sediment between bed and water column (LT^{-1})

L_w = depth of water compartment (L)

L_s = depth of active bed layer (L)

y = vertical distance (L)

R_s = net rate of chemical transfer between dissolved and sorbed state ($ML^{-3}T^{-1}$)

K = kinetic degradation or transformation rate ($ML^{-3}T^{-1}$)

$$R_s = S\,(k_s\, C_w' - kdC_s')$$

where k_s = rate constant for sorption ($L^3M^{-1}T^{-1}$)

k_d = rate constant for desorption (T^{-1})

$$C_w' = \frac{C_w}{\phi}$$

$$C_s' = \frac{C_s}{S_w}$$

where C_w = concentration of dissolved chemical in water (ML^{-3})

ϕ = porosity or volume water per volume segment (L^3L^{-3})

C_s = concentration of sorbed chemical in water (ML^{-3})

S_w = concentration of sediment in water (ML^{-3})

S = concentration of sediment (ML^{-3})

Figure 6.01. TOXIWASP formulation.

TRANSFORMATION AND REACTION KINETICS IN TOXIWASP

The overall rate of transformation and reactions:

$$\frac{dC}{dt} = \sum_{j=1}^{n} K_j C$$

where K_j = pseudo-first order rate constant for the jth processes (i.e., hydrolysis, biodegradation, and oxidation, photolysis, and volatilization) which can vary in space and time (T^{-1})

n = number of processes operating on the chemical

C = concentration of chemical of interest (ML^{-3})

(1) Hydrolysis

$$k_{hyd} = k_a[H^+] = k_n + k_b\,[OH^-]$$

where k_{hyd} = pseudo-first order rate constant for hydrolysis (T^{-1})

k_a = second order rate constant for acid-catalyzed hydrolysis ($L^3n^{-1}T^{-1}$)

k_n = first order rate constant for neutral hydrolysis (T^{-1})

k_b = second order rate constant for base-catalyzed hydrolysis ($L^2n^{-1}T^{-1}$)

$[H^+]$ = hydrogen ion concentration (nL^{-3})

$[OH^-]$ = hydroxide ion concentration (nL^{-3})

(2) Biodegradation

$$K_{bio} = k_{bio}B$$

where K_{bio} = pseudo-first order rate constant for the biodegradation (T^{-1})

k_{bio} = second order rate constant for biodegradation ($ML^{-3}T^{-1}$)

B = bacteria concentration (ML^{-3})

(3) Oxidation

$$K_{oxi} = k_{oxi}[RO_2^{\bullet}]$$

where K_{oxi} = pseudo-first order rate constant for oxidation (T^{-1})

k_{oxi} = second order rate constant for oxidation ($L^3n^{-1}T^{-1}$)

$[RO_2^{\bullet}]$ = molar concentration of free radical oxygen (oxidant) (nL^{-3})

(4) Photolysis

$$K_{pho} = k_{pho}[L] \sum_{i=1}^{3} \phi_i \alpha_i$$

where K_{pho} = pseudo-first order rate constant for photolysis (T^{-1})

k_{pho} = average first order photolysis rate constant for water surface during cloudless conditions in summer (day^{-1})

ϕ_i = average reaction quantum yield for compound in form "i" (i.e., dissolved, sediment-sorbed, biosorbed) (moles per einstein)

α_i = attenuation coefficient (L^{-1})

[L] = fraction of cloudless summer surface light intensity in segment (unit less)

$$[L] = \left\{\frac{1 - \exp(-K_e z D_f)}{K_e\ z\ D_f}\right\} \{1 - 0.056(CLOUD)\}\ (FL)(LIGHT)$$

where K_e = segment light extinction coefficient (per meter)

z = depth of water (L)

D_f = ratio of optical path length to vertical depth (unit less)

CLOUD = average cloud cover (tenths)

FL = latitude correction factor

LIGHT = normalized time function for light, representing diurnal or seasonal changes (0-1.0)

(5) Volatilization

$$K_{vol} = k_{vol}$$

where K_{vol} = pseudo-first order rate constant for volatilization (T^{-1})

k_{vol} = first order rate constant for volatilization; mass transfer rate coefficient (k_v) divided by the average depth of the water body (L)

$$k_v = \frac{1}{R_g + R_1} = \text{overall mass transfer coefficient } (LT^{-1})$$

where R_g = vapor-phase transport resistance (TL^{-1})

R_1 = liquid-phase transport resistance (TL^{-1})

$$R_g = \frac{8.206 \times 01^{-5} T}{K_{wv} H \sqrt{18/MW}}$$

where T = Kelvin temperature (degrees Kelvin)

K_{wv} = water vapor exchange constant = 0.1857 + 11.36 (W_v)

H = Henry's Law constant (atm-m^3 per mole)

MW = molecular weight of water,

W_v = wind velocity at 10 cm above the water surface (meters per hour)

$$R_1 = \frac{1}{K_{02}\sqrt{32/MW}}$$

where K_{02} = reaeration velocity in segment or oxygen exchange constant (meters per hour)

$$K_{02} = (0.01\ K_{20})\ 1.024\ \exp\ (T_s - 20.0)$$

where T_s = segment temperature (°C)

In a stream:

When z > 2 feet, $K_{20} = 27.6\ u^{0.67}/z^{0.85}$,

When z < 2 feet, $K_{20} = 14.8\ u^{0.969}z^{0.673}$,

or $K_{20} = 16.4\ u^{0.5}/z^{0.5}$,

where K_{20} = reaeration velocity at 20 degree C (cm per hour)
u = average segment velocity (feet per sec)
z = average segment depth (feet)

In a lake (wind-induced reaeration):

$$K_{20} = -0.46\ W_{(t)} + 0.136\ W^2_{(t)}$$

where $W_{(t)}$ = time-varying wind velocity (meters per sec)

(6) Sorption

$$C_T = C(\alpha_1 + \alpha_2 + \alpha_3)$$

$$\alpha_1 = \frac{1}{1 + K_{p2}\left(\frac{S}{\phi}\right) + K_{p3}\left(\frac{B}{\phi}\right)}$$

$$\alpha_2 = \frac{K_{p2}\left(\frac{S}{\phi}\right)}{1 + K_{p2}\left(\frac{S}{\phi}\right) + K_{p3}\left(\frac{B}{\phi}\right)}$$

$$\alpha_3 = \frac{K_{p3}\left(\frac{B}{\phi}\right)}{1 + K_{p2}\left(\frac{S}{\phi}\right) + K_{p3}\left(\frac{B}{\phi}\right)}$$

where C_T = total chemical concentration in segment (mg/L)
C = dissolved chemical concentration in the segment (mg/L)

K_{p2} = partition coefficient of the chemical on the sediment (L/kg)

K_{p3} = partition coefficient of the chemical with biota (L/kg)

S = concentration of sediment (mg/kg)

B = concentration of biomass (mg/kg)

ϕ = porosity of segment = water volume/total volume

α_1 = fraction of chemical dissolved in water phase of segment

α_2 = fraction of chemical sorbed onto sediment phase of segment

α_3 = fraction of chemical sorbed onto biological phase of segment.

Figure 6.02. Transformation and reaction kinetics in TOXIWASP.

reactions. The rate of biological degradation is expressed using a simplified Monod relationship at low organic substrate concentrations, i.e., a second order reaction proportional to both bacteria and chemical concentrations. The rate of oxidation is also expressed by a second order equation assuming the reaction is proportional to both oxidant and chemical present in the system. The photolysis rate is influenced by both the intensity of solar radiation and structure of the compound through its quantum yield, the efficiency by which a quantum of energy (photon) creates a reaction at the molecular level. Environmental inputs to estimate the photolysis rate include water depth, cloudiness, latitude, and time of the year.

The volatilization kinetics were formulated based on a Lewis-Whitman's two-film resistance model with a uniform layer assumption. Environmental variables for the computation of the volatilization rate include water temperature and local and time-varying wnd speed. TOXIWASP calculates the overall mass transfer coefficient as a function of the longitudinal advective velocity and depth. (EXAMS II requires that the mass transfer coefficient for volatilization be specified by the user.) Adsorption of chemicals to solids (sediment and biomass) is computed assuming local equilibrium using a chemical-specific partition coefficient and the spatially varying environmental organic carbon fractions. The concentrations of total chemical and solids are calculated by finite-difference approximations of their mass balance equations.

The physical, chemical, and biological inputs required for TOXIWASP are listed in Appendix B. The model considers three sorption possibilities (i.e., dissolved, sediment sorbed, and bio-sorbed) for an unionized form of the chemical. (Ionization of chemical is not considered in TOXIWASP.) The model calculates total sediment and chemical concentrations explicitly every time step for every segment. The segments can be arranged in a one-, two-, or three-dimensional configuration. TOXIWASP can handle both point and nonpoint source loads, and can estimate time-varying chemical exposure resulting from pulse chemical loads.

WASTOX is a similar model to TOXIWASP. The largest difference between the two models is in how bioaccumulation is treated. Both TOXIWASP and WASTOX have the unique feature of sediment burial or erosion, based on a mass balance for solids. This feature is required to assess long term behavior of persistent, hydrophobic chemicals such as PCB's, DDT, dioxin, etc. Figures 6.03 and 6.04 illustrate the segments where sediment deposition exceeds scour and where scour exceeds sediment deposition, respectively. The review documents are those by Ambrose et al. (1983), Ambrose et al. (1986), and Connolly and Winfield (1984).

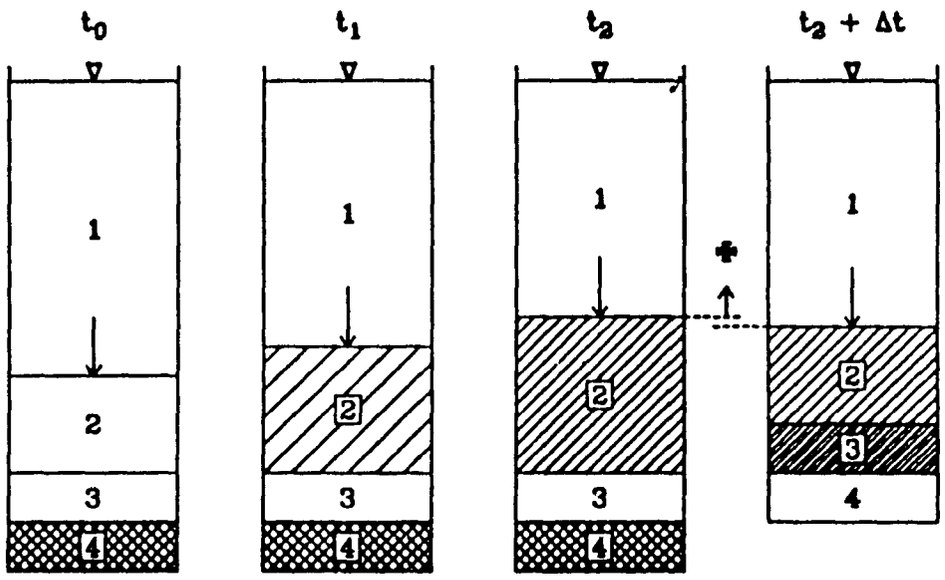
6.3 EXAMS II

The EXposure Analysis Modeling System (EXAMS) (II) is a steady-state or time variable, compartmentalized model that yields exposure, fate and persistence information about organic chemicals in aquatic systems. EXAMS was developed for screening of new chemicals, but it also can be used as a first approximation in site specific cases. It is an interactive program that allows the user to enter and store information on a specific chemical, environment, and loading scheme. It evaluates the chemical behavior and conducts sensitivity analyses on the probable fate in the aquatic environment. EXAMS II also contains a few chemicals and canonical environments that are useful as test cases and are stored on floppy disk (IBM-compatible) with the source code.

As in all the models, the EXAMS II model is formulated based on the principle of conservation of mass. The compartments in the EXAMS II model contain water sediments, biota, dissolved chemicals, and sorbed chemicals under the completely mixed condition. Loadings and exports are represented as mass fluxes across the compartments. Like TOXIWASP, sediment-water exchange is described as a dispersion (Fickian diffusion) process.

EXAMS II sums the overall pseudo-first order reaction rate constants with respect to the chemical concentration. Its kinetic structures are similar to those described for TOXIWASP. A simplified two-resistance model is used to define the process of volatilization. Wind speed, temperature, and compartment dimensions are necessary environmental data. Photochemical transformation is defined with respect to he chemical absorption spectrum and quantum efficiency of the chemical. The solar spectrum is subdivided into 39 wavelength intervals, and the total rate constant is computed as the sum of contributions from each spectral interval.

The environmental inputs for photolysis include concentrations of chlorophyll-like pigments, dissolved organic carbon, and sediments. Water depth is also specified as input. The hydrolysis rate is defined with three competing reactions: acid-catalyzed, neutral and base-catalyzed reactions, as a function of pH. The second order rate of biodegradation is described as a function of chemical concentration and viable degrading microbial population. Environmental inputs are bacterial population density and the proportion of total bacterial population that actively degrades the chemical. The rate of oxidation is also expressed by a second order rate



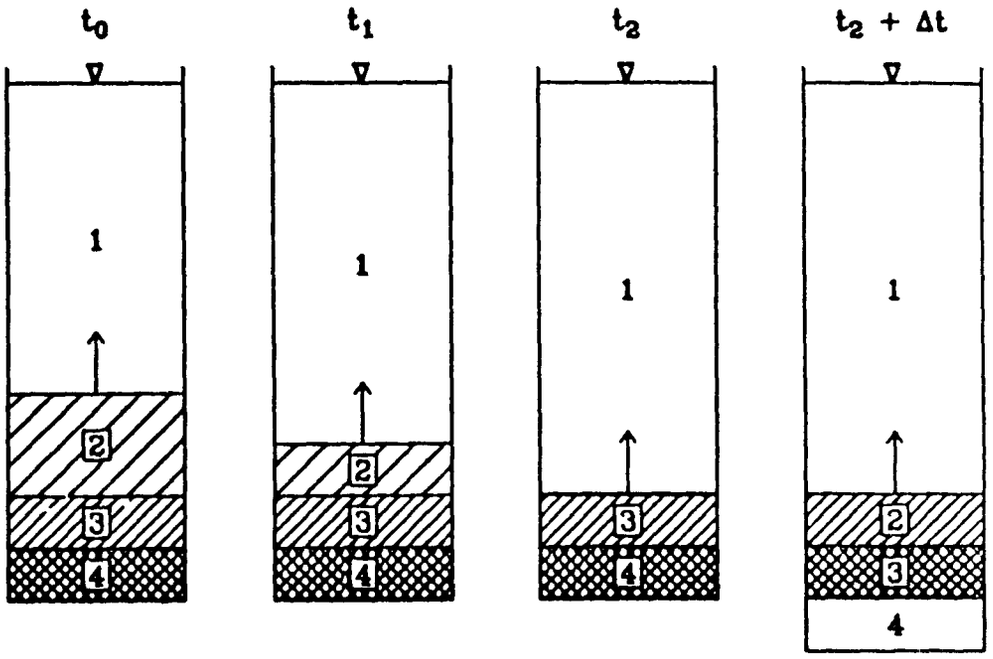
	Time = t_0			Time = t_2			Time = $t_2 + \Delta t$		
Segment	Depth	Density	Conc	Depth	Density	Conc	Depth	Density	Conc
1	d_1	1.0	$C_1(0)$	$d_1 - d_2(2)$	1.0	$C_1(2)$	$d_1 - d_2$	1.0	$C_1(2)$
2	d_2	ρ_2	0.0	$d_2(0) + d_3\frac{\rho_3}{\rho_2}$	ρ_2	$C_2(2)$	d_2	ρ_2	$C_2(2)$
3	d_3	ρ_3	0.0	d_3	ρ_3	0.0	d_3	ρ_3	$C_2(2)\frac{\rho_3}{\rho_2}$
4	d_4	ρ_4	$C_4(0)$	d_4	ρ_4	$C_4(0)$	d_4	ρ_4	0.0

✤ Compaction: SVOL Compacted = $Vol(3)\left[\frac{\rho_3}{\rho_2} - 1\right]$

Pore water volume SVOL squeezed into water column.

Figure 6.03. TOXIWASP sediment burial.
During the time = t_0 to t_1, as sediment and sorbed chemical settle from the water column, the top bed segment (2) increases in volume, depth, chemical mass, and sediment mass. During the time = t_2 to $t_2 + \Delta t$, at the time when the top bed segment depth and volume (2) exceed the initial top two bed segments depth and volume, the top bed segment (2) is compressed into two segment, and the previous segment (4) at time t_2 is buried.

equation as a function of the concentrations of oxidant and chemical to be oxidized. Molar concentration of oxidants is an environmental input. The chemical properties and environmental characteristics that should be provided by the user are listed in Appendix B.



	Time = t_0			Time = t_2			Time = $t_2 + \Delta t$		
Segment	Depth	Density	Conc	Depth	Density	Conc	Depth	Density	Conc
1	d_1	1.0	0.0	$d_1+d_2(0)$	1.0	$C_1(2)$	$d_1+d_2(0)$	1.0	$C_1(2)$
2	d_2	ρ_2	$C_2(0)$	0	ρ_2	$C_2(0)$	d_3	ρ_3	$C_3(2)$
3	d_3	ρ_3	$C_3(0)$	d_3	ρ_3	$C_3(0)$	d_3	ρ_3	$C_4(2)$
4	d_3	ρ_3	$C_4(0)$	d_3	ρ_3	$C_4(0)$	d_3	ρ_3	0.0

Figure 6.04. TOXIWASP sediment erosion.
During the time = t_0 to t_1, as sediment and sorbed chemical erode from the bed, the top bed segment (2) decreases in volume, depth, chemical mass, and segment mass. During the time = t_2 to $t_2 + \Delta t$, at the time when the segment mass in the top bed layer equals zero, then the segments are renumbered, and a new segment (4) is included.

Output from EXAMS II includes up to 20 tables containing the following information: (1) a transport profile of the natural water system, (2) a kinetic profile of the chemical, (3) a canonical profile of the system, (4) the toxicant loading for each system segment, (5) the distribution of the chemical at steady state, (6) the average, maximum, and minimum concentrations at steady state in both water and sediment compartments, (7) an analysis of steady state of the chemical, (8) a simulation of the system response after load ceases, and (9) exposure (fate and persistence) analysis summary. The EXAMS II program can be run in three modes: 1) a constant

"annual average" loading or input that results in a steady state solution, 2) impulse inputs that simulate spills and result in a dynamic solution, and 3) a monthly average input with or without pulses for a period of 12 months.

The EXAMS II code can handle up to 20 compartments (called segments) that can be arranged in an arbitrary fashion of littoral, epilimnetic, hypolimnetic, or benthic compartments. Therefore, rivers, lakes, streams, and ponds can all be simulated including sediment compartments that can be layered vertically such that one can simulate an active, exchanging bed layer and a fixed, deeper sediment compartment. The EXAMS II model, however, does not contain a solids balance in the situation where the bed is aggrading or degrading.

Novel features of the EXAMS II model include the introduction of "canonical" environments, i.e., typical environmental systems and variables that provide the necessary input variables to solve the second-order reaction equations. In addition, 12 chemicals that were studied by Smith et al., (1977) are made available to the user such that rate constants are internally specified and not require as user input. Several canonical environments are available (a eutrophic lake, an oligotrophic lake, a pond, and a river) as well as Lake Zurich. Templates are available for the user to specify a new chemical or new environment. Transformation products are computed for each spatial and temporal segment defined by the user. Unlike other models, EXAMS II accounts for ionization of organic chemicals (Figure 6.05). It allows for molecules of +3, +2, +1, 0 -1, -2, and -3 charge, and each charged state can be either dissolved, adsorbed, or biosorbed for a total 21 different distribution coefficients. Sorbed and biosorbed fractions are available for photolysis, hydrolysis, oxidation, and biological transformations as a user option.

EXAMS II is an extended version of EXAMS suitable for the IBM PC XT or AT. EXAMS II can handle spatial and temporal changes of the transport and transformation processes of products that result from transformation reactions. It provides greater flexibility in specifying the timing and duration of chemical loadings entering a receiving water body. EXAMS II expanded the treatment of ionic speciation and sorption to include trivalent ions and complexation with dissolved organic matter. The inputs to EXAMS II are also expanded to include the effects of seasonal variation by adding monthly environmental data. EXAMS II estimates some quantities which EXAMS requires as input data. For example, EXAMS II generates solar light field from meteorological data. The review documents for EXAMS are those by Lassiter et al. (1978), Burns et al. (1982), and for EXAMS II, the one by Burns and Cline (1985).

6.4 HSPF

The Hydrologic Simulation Program -- FORTRAN (HSPF) is a comprehensive package program designed for continuous simulation of watershed hydrology and receiving water quality. HSPF was developed from the Hydrocomp Simulation Program (HSP) which includes the Agriculture Runoff Management (ARM) model (Donigian and Davis, 1978) and the Nonpoint Source (NPS) model

IONIZATION REACTIONS IN EXAMS II

(1) Basic Reactions:

$$SH_3 + H_2O \leftrightarrow SH_4^+ + OH^- \qquad K_{b1} = \frac{\{SH_4^+\}\{OH^-\}}{\{SH_3\}\{H_2O\}}$$

$$SH_4^+ - H_2O \leftrightarrow SH_5^{2+} + OH^- \qquad K_{b2} = \frac{\{SH_5^{2+}\}\{OH^-\}}{\{SH_4^+\}\{H_2O\}}$$

$$SH_5^{2+} + H_2O \leftrightarrow SH_6^{3+} + OH^- \qquad K_{b3} = \frac{\{SH_6^{3+}\}\{OH^-\}}{\{SH_5^{2+}\}\{H_2O\}}$$

(2) Acidic Reactions:

$$SH_3 + H_2O \leftrightarrow SH_2^- + H_3O^+ \qquad K_{a1} = \frac{\{SH_2^-\}\{H^+\}}{\{SH_3\}\{H_2O\}}$$

$$SH_2^- + H_2O \leftrightarrow SH^{2-} + H_3O^+ \qquad K_{a2} = \frac{\{SH^{2-}\}\{H^+\}}{\{SH_2^-\}\{H_2O\}}$$

$$SH^{2-} + H_2O \leftrightarrow S^{3-} + H_3O^+ \qquad K_{a3} = \frac{\{S^{3-}\}\{H^+\}}{\{SH^{2-}\}\{H_2O\}}$$

where SH_3 = unionized or neutral parent molecule,

SH_4^+, SH_5^{2+}, SH_6^{3+} = singly, doubly, triply charged cation, respectively,

SH_2^-, SH^{2-}, S^{3-} = singly, doubly, triply charged anion, respectively,

K_{b1}, K_{b2}, K_{b3} = equilibrium constants for the basic reactions, and

K_{a1}, K_{a2}, K_{a3} = equilibrium constants for the acidic reactions.

Figure 6.05. Ionization reactions in EXAMS II.

(Donigian and Crawford, 1976) for runoff simulation, and incorporates the SERATRA model (Onishi and Wise, 1982) for sediment transport, pesticide decay, sediment-contaminant partitioning, and risk assessment. The model is fully dynamic and can simulate chemical behavior over an extended period of time, using a constant time step selected by the user.

HSPF includes time series-based simulation modules (PERLIND, IMPLND and RCHRES), and utility modules (COPY, PLTGEN, DISPLAY, DURANL, and GENER). The simulation (application) modules include mathematics for the behavior of processes that occur in a study watershed. The watershed is divided into three segments -- pervious land, impervious land, and a receiving water system (i.e., a single reach of an open channel or a completely mixed impoundment). The module PERLND simulates the pervious land segment with homogeneous hydrologic and climatic characteristics, including snow accumulation and melt, water movement (overland flow, interflow and groundwater flow), sediment erosion and scouring, and water quality (pesticides, nutrients). The IMPLND module simulates the impervious land segment where little or not infiltration occurs. The IMPLND processes include snow and water movements, solids, and water quality constituents. The module RCHRES simulates the segment of receiving water body, including hydrologic behavior, conservative and nonconservative constituents, temperature, sediments, BOD and DO, nitrogen, phosphorus, carbon, and pH. The utility modules perform "house-keeping" operations, designed to provide the user flexibility in managing simulation inputs and outputs. For example, the COPY module manipulates time series.

The HSPF model includes a simplification of the code of SERATRA, which simulates the fate of chemical in the receiving water systems. Mathematical formulation of SERATRA is presented in Figure 6.06. Transport in SERATRA is by advective processes, represented by the horizontal and vertical convections, and vertical diffusion. Equation (6.5) gives the mass balance equation for sediment, which accounts for sediment erosion and deposition. It considers two types of sediments: cohesive sediment (i.e., silt and clay) and noncohesive sediment (i.e., sand) for calculation of scour and deposition. HSPF solves time series from upstream to downstream for 1-D branching networks.

Deposition occurs when shear stress at the bed-water interface is less than the critical shear stress for deposition. When shear stress is greater than the critical shear stress for scour, scouring of cohesive bed sediment occurs. The critical shear stresses for deposition and scour are specified by the user. Noncohesive sediment is scoured from the bed when the amount of sand being transported is less than the capacity of flow to carry the sediment, and deposition occurs when the noncohesive sediment (sand) transport rate exceeds the sediment-carrying capacity of the river.

Equation (6.6) gives the mass balance for dissolved chemical, which accounts for chemical and biological reactions as well as phase transfer (volatilization and sorption) processes. The mass balance equation for adsorbed chemical is given by Equation (6.7), which accounts for processes of sorption, erosion and deposition. A linear sorption between dissolved chemical in the overlying water and organic sediment in the bed is assumed.

Kinetics of the transformation and reaction decay processes used in HSPF are presented in Figure 6.07. The formulations for these processes are similar to the previous two models except that volatilization is related to the molecular diameter of oxygen and the contaminant, and sorption has a kinetic formulation with a Fruendich isotherm at equilibrium. To compute

the biodegradation rate, biomass data are supplied by a constant, monthly, or a time series input. HSPF also allows the user to specify a unique set of biomass data for each chemical (i.e., parent and daughter) compounds.

For computation of the photolysis rate constant, the solar spectrum is subdivided into 18 wavelength intervals. (EXAMS II divides it into 39.) The total rate constant is calculated as the sum of contributions from each spectral interval. Environmental inputs include water-surface shading, light intensity, cloud cover, concentrations of suspended sediment and phytoplankton, and water depth.

Adsorption and desorption processes are specified by the user by one of three methods; (1) first order kinetics, which assume that the chemical adsorbs and desorbs at a rate based on the adsorbed concentration in soil solution and on the suspended particle; (2) the single-value Freundlich isotherm, which makes use of a single adsorption/desorption curve for determining the concentration on the soil and in solution; and (3) the multiple curves method, which is based on a variable Freundlich

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SERATRA FORMULATION

(1) Mass conservation of sediment

$$\underbrace{\frac{\partial}{\partial t}(m_j B\ell)}_{\text{rate of accum.}} + \underbrace{(u_o m_j B - u_i m_{ij} B)}_{\text{horizontal convection}} + \underbrace{\frac{\partial}{\partial B}\{m_i(W - W_{sj})B\ell\}}_{\text{vertical convection (not in HSPF)}}$$

$$= \underbrace{\frac{\partial}{\partial z}\left(E_z \frac{\partial m_j}{\partial z} B\ell\right)}_{\text{vertical diffusion (not in HSPF)}} + \underbrace{\frac{1}{h}\left(S_{Rj} - S_{Dj}\right)}_{\text{sediment erosion or deposition}} \qquad (6.5)$$

where the vertical fall velocity, W_{sj}, is:

$$W_{sj} = K_j'' \; m_j^{4/3}$$

For cohesive sediments, the sediment erosion and deposition rates are defined:

$$S_{Rj} = M_j \left(\frac{\tau}{\tau_{CRj}} - 1\right)$$

$$S_{Dj} = W_{sj} C_j \left(1 - \frac{\tau_b}{\tau_{CDj}}\right)$$

For noncohesive sediments, sediment erosion and deposition rates are defined:

$$S_{Rj} = \frac{Q_T - Q_{Ta}}{A}$$

$$S_{Dj} = \frac{Q_{Ta} - Q_T}{A}$$

(2) Mass conservation of dissolved chemical

$$\underbrace{\frac{\partial}{\partial t}(CB\ell)}_{\text{rate of accum.}} + \underbrace{(u_o CB - u_i C_i B)}_{\text{horizontal advection}} + \underbrace{\frac{\partial}{\partial t}(BCB\ell)}_{\text{vertical advection (not in HSPF)}}$$

$$= \underbrace{\frac{\partial}{\partial z}\left(E_z \frac{\partial C}{\partial z} B\ell\right)}_{\text{vertical diffusion (not in HSPF)}} - \underbrace{\lambda CB\ell}_{\text{radionuclide decay}} - \underbrace{\sum_{i=1}^{5} K_{mi}\, CB\ell}_{\text{chemical/biological decay and volatilization}}$$

$$- \underbrace{\sum_j K_j \left(k_{dj} m_j C - C_{pj}\right) B\ell}_{\text{adsorption to suspended sediments}} - \underbrace{\sum_j K_j \left(K'_{dj}\, m_j C - C_{pj}\right) B\ell}_{\text{desorption from suspended sediments}}$$

$$- \underbrace{\sum_j \gamma_j (1-e) D_j K_{bj} \left(K_{dj} C - C_{pBj}\right)}_{\text{adsorption to bed sediments}} - \underbrace{\sum_j \gamma_j (1-3) D_j K'_{bj} \left(K'_{dj} C - C_{pRj}\right)}_{\text{desorption from bed sediments}} \qquad (6.6)$$

$$K_{dj} \text{ and } K'_{dj} = \frac{f_{sj}/M'_j}{f_w/V_w} = \frac{f_{sj}}{f_w C_j}$$

$$\frac{f_{sj}}{f_w} = \frac{m_j C_{pj}}{C}$$

$$C_{pj} = K_{dj} C \quad \text{or} \quad C_{pj} = K'_{dj} C$$

(3) Mass conservation of adsorbed chemical

$$\underbrace{\frac{\partial}{\partial t}(C_{pj} B\ell)}_{\text{rate of accum.}} + \underbrace{\left(u_o C_{pj} B - u_i C_{pij} B\right)}_{\text{horizontal convection}} + \underbrace{\frac{\partial}{\partial z}\left\{(W - W_{sj})\, C_{pj} B\ell\right\}}_{\text{vertical convection (not in HSPF)}}$$

$$= \underbrace{\frac{\partial}{\partial z}\left(E_z \frac{\partial C_{pj}}{\partial z} B\ell\right)}_{\text{vertical diffusion (not in HSPF)}} - \underbrace{\lambda\, C_{pj} B\ell}_{\text{radionuclide decay}} + \underbrace{K_j \left(K_{dj} C - C_{pj}\right) B\ell}_{\text{adsorption}} \qquad (6.7)$$

$$+ \underbrace{K'_j \left(K'_{dj} C - C_{pj}\right) B\ell}_{\text{desorption}} + \underbrace{\frac{1}{h}\left(C_{pBj}\, S_r - C_{pj} S_D\right)}_{\text{contaminated sediment erosion and deposition}}$$

where

m_j = concentration of sediment of jth size fraction (ML^{-3})

m_{ij} = concentration of sediment of horizontal inflow for jth size fraction (ML^{-3})

S_{Dj} = sediment deposition rate per unit area for jth sediment size fraction (ML^{-3})

S_{Rj} = sediment erosion rate per unit area for jth sediment size fraction (ML^{-3})

B = river width (L)

h = water depth (L)

ℓ = longitudinal distance (L)

t = time (T)

u_i = horizontal inflow velocity (LT^{-1})

u_o = horizontal outflow velocity (LT^{-1})

W = vertical flow velocity (LT^{-1})

W_{sj} = fall velocity of sediment particle of jth size fraction (LT^{-1})

E_z = vertical diffusion coefficient (L^2T^{-1})

z = vertical direction

N = number of sediment size fractions considered (i.e., sand, silt and clay, N=3)

Q_T = sediment transport capacity of flow (ML^{-1})

Q_{Ta} = actual amount of sand being transported in a river water

A = river bed surface area (L^2)

M_j = erodability coefficient for sediment of jth size fraction (ML^{-3})

τ_b = bed shear stress (ML^{-2})

τ_{CDj} = critical shear stress for sediment deposition for jth sediment size fraction (ML^{-2})

τ_{CRj} = critical shear stress for sediment erosion for jth sediment size fraction (ML^{-2})

K_j'' = an empirical constant depending on the sediment type

D_j = diameter of jth sediment (L)

C_{pBj} = particulate chemical concentration (ML^{-3}) per unit weight of sediment in jth sediment size fraction in river bed

γ_j = specific weight of jth sediment (ML^{-3})

C = dissolved chemical concentration (ML^{-3})

C_i = dissolved chemical concentration in horizontal inflow (ML^{-3})

C_{pj} = particulate chemical concentration (ML^{-3}) per unit weight of jth sediment

K_{mi} = first order reaction rate of contaminant degradation due to hydrolysis, oxidation, photolysis, volatilization and biological activities (T^{-1})

K'_{bj} = transfer rate of chemical with jth non-moving sediment in bed (T^{-1})

K_{dj}, K'_{dj} = rate of adsorption and desorption between dissolved contaminant and sediment (suspended and bed load sediments) of jth size fraction, respectively (T^{-1})

K_j, K'_j = transfer rate of contaminants for adsorption and desorption, respectively, with jth sediment in motion (T^{-1})

λ = decay rate constant of radioactive material (T^{-1})

e = porosity of bed sediment

K_{dj}, K'_{dj} = distribution coefficient (LM^{-1})

f_{sj} = fraction of contaminant sorbed by jth sediment

f_w = fraction of contaminant left in solution

M'_j = weight of jth sediment (M)

V_w = volume of water (L^3)

C_{pij} = particulate concentration per unit volume of water associated with the jth sediment size fraction in horizontal inflow (ML^{-3})

Figure 6.06. SERATRA formulation.

TRANSFORMATION AND REACTION KINETICS IN HSPF

(1) Hydrolysis

$$K_{hyd} = k_a[H^+] + k_n + k_b[OH^-]$$

where K_{hyd} = pseudo-first order rate constant for hydrolysis (T^{-1})

k_a = second order rate constant for acid catalyzed hydrolysis ($L^3n^{-1}T^{-1}$)

k_n = first order rate constant for neutral hydrolysis (T^{-1})

k_b = second order rate constant for base-catalyzed hydrolysis ($L^3n^{-1}T^{-1}$)

$[H^+]$ = hydrogen ion concentration (nL^{-3})

$[OH^-]$ = hydroxide ion concentration (nL^{-3})

(2) Biodegradation

$$K_{bio} = k_{bi2}B \qquad \text{or} \qquad K_{bio} = k_{bi1}$$

where K_{bio} = pseudo-first order rate constant for the biodegradation (T^{-1})

k_{bi2} = second order rate constant for biodegradation ($L^3M^{-1}T^{-1}$)

B = concentration of active biomass (ML^{-3})

k_{bi1} = generalized first-order decay rate (T^{-1})

(3) Oxidation

$$K_{oxi} = k_{oxi}\,[RO_2^{\bullet}]$$

where K_{oxi} = pseudo-first order rate constant for oxidation (T^{-1})

k_{oxi} = second order rate constant for oxidation ($L^3n^{-1}T^{-1}$)

$[RO_2^{\bullet}]$ = molar concentration of free radical oxygen (oxidant) (nL^{-3})

(4) Photolysis

$$K_{pho} = \left(C_f \frac{D60}{24.}\right) \phi \sum_{1}^{18} \left\{\left(\frac{\ell_\lambda C_\lambda}{2.76\ K_\lambda Z}\right)\left(1.0 - \exp\left(-2.76\ K_\lambda Z\right)\right)\varepsilon_\lambda\right\}$$

$$K_\lambda = \alpha_\lambda + \gamma_\lambda \cdot m + \delta_\lambda B_{phy}$$

$$C_\lambda = \frac{10.0 - C_c K_{eff}}{10.0}$$

where C_f = factor accounting for surface shading,

D60/24. = conversion from day to hour intervals,

ϕ = reaction quantum yield for photolysis of chemical

ℓ_λ = seasonal day-average, 24 hour light intensity (einstein per cm^2-day)

C_λ = fraction of total light intensity of wavelength λ which is not absorbed or scattered by clouds

α_λ = base absorbance term for the light of wavelength λ for the system (Cm^{-1})

γ_λ = absorbance term for the light absorbed by suspended sediment ($\ell \cdot Cm^{-1} mg^{-1}$)

m = total suspended sediment (ML^{-3})

δ_λ = absorbance term for the light absorbed by suspended phytoplankton ($\ell \cdot cm^{-1} \cdot mg^{-1}$)

B_{pho} = phytoplankton concentration (ML^{-3})

ε_λ = absorbance term for light of wavelength λ absorbed by chemical (L/mol-cm)

z = water depth (cm)

C_c = cloud cover (tenths)

K_{eff} = efficiency of cloud cover in intercepting light of wavelength λ.

(5) Volatilization

$$K_{vol} = (k_0)_w \, r_{vo}$$

where K_{vol} = pseudo-first order rate constant for volatilization (T^{-1})

$(k_0)_w$ = oxygen reaeration rate through water-air interface (T^{-1})

r_{vo} = ratio of volatilization rate to oxygen reaeration rate

(6) Sorption

(a) First order kinetics:

$$F_{ads} = C_{msu} \, K_{ads} \, Th_{ads}(T-35.)$$
$$F_{des} = C_{mad} \, K_{des} \, Th_{des}(T-35.)$$

where F_{ads}, F_{des} = current adsorption and desorption fluxes of chemical, respectively (ML^{-2}) per interval)

C_{mad} = storage of adsorbed chemical (ML^{-2})

C_{msu} = storage of chemical in solution (ML^{-2})

K_{ads} = first order adsorption rate parameter (per interval)

K_{des} = first order desorption rate parameter (per interval)

Th_{ads} = temperature correction parameter for adsorption (unitless)

Th_{des} = temperature correction parameter for desorption (unitless)

T = soil layer temperature (°C)

(b) Single-value Freundlich Parameter:

$$X = K_{f1} \, C \, \exp(1./N1) + X_{fix}$$

where X = chemical adsorbed on soil (ppm of soil)

K_{f1} = single value Freundlich coefficient (unitless)

C = equilibrium chemical concentration in solution (ppm of solution)

$N1$ = single value Freundlich exponent (unitless)

X_{fix} = chemical which is permanently fixed in soil (ppm of soil)

(c) Non-single value Freundlich parameter:

$$X = K_{f2}\, C \exp(1./N2) + X_{fix}$$

$$K_{f2} = \frac{X_{f1}}{X_{jct} - X_{fix}} \exp(N1/N2) \quad (X_{jct} - X_{fix})$$

where K_{f2} = non-single value Freundlich coefficient (unitless)

N_2 = non-single value Freundlich exponent parameter (unitless)

X_{jct} = adsorbed concentration where desorption started (ppm of soil)

Figure 6.07. Transformation and reaction kinetics in HSFP.

coefficient. The HSPF model considers the generation of transformation products, each of which is subject to reaction and transformation processes. "Parent-daughter" relationships allowed in HSPF are that a "daughter chemical-2" may be produced by decay of a "Parent chemical-1," and that a "daughter chemical-3" may be produced by decay of a "chemical-1" and/or "chemical-2."

In order to simulate the hydrologic and receiving water systems, HSPF requires a considerable amount of information. The user must prepare two types of data: time series data and user-controlled inputs. All hydrologic simulations of runoff require time series precipitation and evapotranspiration data. If the user wants to simulate snowmelt for hydrologic studies or to simulate water temperature for water quality studies, then additional time series data of air temperature, wind speed, solar radiation, and dewpoint temperature are needed. The user's control inputs include characteristics of the land surface (e.g., land use patterns, soil types) and agricultural practices. For model applications in which channel processes are important, additional data on stream flow, channel geometry, and instream chemical concentrations are necessary. The chemical and environmental information required in the user's control inputs are listed in Appendix B. Input data must represent the spatial and temporal variations in flow and/or chemical loadings resulting from the combined meteorologic, hydrologic, chemical, and biologic processes of the entire study area.

The results of an HSPF simulation are time histories of the quantity and quality of the runoff (flow rate, suspended and bed sediment load, and

nutrient and pesticide concentrations). The model then takes these results and characteristics of the receiving water and simulates the processes that occur in the aquatic environment. This part of the simulation produces a time history of water quality and quantity at any point in the watershed. The review documents are those by Donigian et al. (1984) and Johanson et al. (1984).

6.5 MINTEQ

MINTEQ is a thermodynamic equilibrium model that computes aqueous speciation, equilibrium adsorption/desorption, and the mass of metal transferred into or out of solution as a result of the dissolution or precipitation of solid phases. It was developed by Felmy et al. (1983) by combining MINEQL (Westall et al., 1976) and WATEQ3 (Ball et al., 1981), for incorporation into MEXAMS (Felmy et al., 1984) to assess the fate of selected priority pollutant metals in aqueous systems. MINTEQ alone, however, does not have the capability of computing kinetic, transfer or transport processes.

The program requires two types of data: (1) thermodynamic data and (2) water quality data. The user is only required to provide the water quality data; thermodynamic data are contained in a MINTEQ data base. The thermodynamic data are equilibrium constants, enthalpies of reaction, and other basic information required to predict the formation of each species or solid phase. The supplemental data include charge, gram formula weight, carbonate alkalinity factor, extended Debye-Huckel parameters, and name and ID number of each species. Although the MINTEQ data base is probably the most thoroughly documented and evaluated thermodynamic data base used in any currently available geochemical model, it is suggested that it should be updated when new and more reliable information is published, or when data for reactions not presently included in the data base become available.

There are Several limitations for efficient use of the model. First, the data base contains equilibrium constants for a limited number of heavy metals and organic ligands (fulvate, fumate). Equilibrium constants of heavy metals included in the data base are those of arsenic, cadmium chromium, copper, lead, mercury, nickel, selenium, thallium, and zinc. The other metals' constants can be inserted into the data base by the user as they become available. A number of organics can form complexes with heavy metals in natural waters, but equilibrium constants for these complexes are widely varying in the literature. Second, the program treats every reaction as if it were at chemical equilibrium. In fact, chemical reactions of precipitation/dissolution and oxidation/reduction are often not at chemical equilibrium. The kinetics of these reactions are slow. Third, the program has not been verified for reactions that would occur in natural waters. Equilibrium constants are based on thermodynamic relationships, assuming a certain set of environmental conditions. If conditions vary, as they do from site to site, conditional stability constants are needed to account for the special chemistry of the site, which is not considered explicitly. There are analytical chemistry problems with verifying the speciation model also. Current analytical techniques do not provide high enough precision to measure separately the activity of individual metal species and complexes.

Pertinent review documents are those by Felmy et al. (1983) and Felmy et al. (1984) for the MINTEQ model, and a recent update by Brown et al. (1987) for MINTEQA1.

6.6 SUMMARY

A summary of the three transport models, TOXIWASP, EXAMS II, and HSPF is given in Table 6.01. All the models are constructed as systems of differential equations organized around mass balances, considering various physical, chemical, and biological processes. HSPF uses a finite-difference numerical solution to the advective equation, whereas TOXIWASP and EXAMS II are completely mixed compartmentalized models with finite-difference solutions to the set of time-variable, ordinary differential equations. TOXIWASP and EXAMS II can provide either the steady-state or time-variable simulation, and can handle both point and nonpoint source loads. The HSPF model is fully dynamic and can be used for evaluation of both short- and long-term migration and fate of a chemical in rivers. In long term simulations where the contaminant source is in-situ (contaminated sediment), it would be necessary to use a model with an explicit solids balance so that sediment burial and scour could be accounted. Both TOXIWASP and HSPF include a mass balance and conserve solids for this purpose.

HSPF computes a time-varying runoff load to the receiving water. TOXIWASP can be used for cases requiring more dynamic transport loading capabilities than EXAMS II, but less detailed and mechanistic sediment predictions that HSPF. Only HSPF can provide quantitative estimates of the non-point source chemical load -- it is the only model that includes a field-to-stream sub-model that can be used to estimate the effects of best management practices (BMPs) in agriculture. For the TOXIWASP and EXAMS II models, the chemical loadings must be specified based on monitoring data in the field or predictions from hydrologic simulation.

EXAMS II is readily generalizable to a wide variety of environmental systems, but it was developed to be used as a screening tool for evaluation of long-term chemical loadings. EXAMS II is modularly programmed, relatively easy to use, and well documented. TOXIWASP is sufficiently general to be applied to all types of natural water systems. HSPF is comprehensive and general enough to applicable to nontidal rivers, streams and narrow impoundments. In general, HSPF is more applicable to upland streams and one-dimensional reservoirs, whereas TOXIWASP is more suited to stratified lakes and reservoirs, large rivers, estuaries, and coastal waters. Both TOXIWASP and EXAMS II can be used to simulate one, two, or three-dimensional segments of aquatic systems by the arbitrary configuration of completely-mixed compartments which is available for user specification.

The EXAMS II model includes a sophisticated kinetic structure that allows a full treatment of ionizable compounds (seven different ionic forms) and ion-specific chemical reactivities (e.g., volatilization, sorption). Similar kinetics are incorporated into TOXIWASP, but no ionization of chemical is considered. TOXIWASP has the unique feature of sediment burial, erosion and scour, based on a mass balance for solids. HSPF and EXAMS II include a process of generation of transformation products.

TABLE 6.01 SUMMARY COMPARISON OF THE MODELS, TOXIWASP, EXAMS II AND HSPF

	TOXIWASP	EXAMS II	HSPF
Types			
Steady state model		x	
Dynamic model	x	x	x
Completely mixed compartments	x	x	
Advective-dispersive model	x	x	
Sediment-water exchange	x	x	x
Applications (r=river, l=lake, e=estuary)	r,l,e	r,l,e	r
Numerical Method			
Gaussian elimination		x	
Finite difference	x	x	x
Order of transformation and reaction			
Ion reactions		x	
Daughter product reactions		x	x
Hydrolysis (acid and base catalyzed, neutral)	x	x	x
Biolysis (second-order)	x	x	x
Oxidation (second-order)	x	x	x
Photolysis (direct, first order)	x	x	x
Volatilization (Lewis-Whitman two-film)	x	x	x
Sorption, equilibrium isotherm	L	L	L & NL
Sorption, kinetic (nonequilibrium)			x
Sediment transport			
Mass balance on solids	x		x
Resuspension/scour	x	x	x
Sedimentation	x		x
Deep-sedimentation	x		
Bed load			x
Cohesive and Noncohesive sediment fractions			x

L = linear isotherm
NL = nonlinear isotherm (Fruendlich)

Physical, chemical, and biological characteristics of chemical and the receiving environment are essential inputs to all the models. Most rate constants for the transformations and reactions are treated as variables that depend on chemical properties and environmental conditions. Table 6.02 lists the environmental inputs for the kinetic constants. EXAMS II has the user advantage of being interactive, which allows convenient data manipulation. TOXIWASP and HSPF must be operated in a batch mode. Environmental data to EXAMS II are contained in a file composed of concise descriptions of the aquatic systems. TOXIWASP and EXAMS II require much less effort for data management than HSPF. Effective use of HSPF requires a considerable amount of data, which may limit wide use of this model. As stated by Grenney et al. (1978), the selection of a model for a particular situation requires a tradeoff between the practicability and economy of the model application and the amount and refinement of information to be provided by the model.

MINTEQ is the only model discussed in this chapter that is applicable expressly for heavy metals. MINTEQ is a geochemical equilibrium model that is capable of calculating heavy metals speciation, adsorption/desorption, and precipitation/dissolution reactions. It was developed to link with EXAMS (for incorporation into MEXAMS) to assess fate and transport of toxic heavy metals in aquatic systems. MINTEQ alone, however, does not have the capacity of simulation of kinetic, transfer and transport processes.

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TABLE 6.02 ENVIRONMENTAL INPUTS FOR COMPUTATION OF THE TRANSFORMATION AND REACTION PROCESSES IN TOXIWASP, EXAMS II AND HSPF

PROCESS	ENVIRONMENTAL INPUT	WATER QUALITY MODELS TOXI WASP	EXAMS II	HSPF
Biodegradation	Active degrading population	x	x	x
	Total bacteria population	x		
	Temperature	x	x	x
Hydrolysis	pH	x	x	x
	Temperature	x	x	x
Photolysis	Depth	x	x	x
	Chlorophyll, phytoplankton		x	x
	Latitude	x	x	x
	Cloudiness	x	x	x
	Dissolved organic carbon		x	
	Suspended Sediment	x	x	x
	Spectral high intensity a surface	x	x	x
	Temperature	x	x	x
	Time of day, year	x	x	x
Oxidation	Temperature	x	x	x
	Oxidant, free radical oxygen concentration	x	x	x
Volatilization	Temperature	x	x	x
	Compartment dimensions, area, depth and volume	x	x	x
	Mixing			
	Wind	x	x	x
	Slope			x
	Water velocity	x		x
Sediment Sorption	Organic carbon content	x	x	
	% water of benthic sediment	x	x	
	Bulk density benthic sediment	x	x	
	Suspended sediment	x	x	x
	Biomass	x	x	x
	Compartment dimensions volume, area, depth	x	x	x
	Particle size			x
	Temperature	x	x	x

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SECTION 7

EXAMPLES AND TEST CASES

7.1 INTRODUCTION

Purposes of this chapter are (1) to show example runs of the EXAMS and HSPF models, and (2) to compare the simulation results of the two models. As test cases, alachlor and DDT dynamics are simulated for the Iowa River and Coralville Reservoir. The Iowa River, located in central Iowa, runs through prime Iowa farm land from northwest to southeast before flowing into the Mississippi River. The low-water profile (elevation above sea level) of the Iowa River is shown in Figure 7.01. Alachlor is a herbicide widely used to control weeds in corn and soybeans in Iowa. DDT is an insecticide that was previously used to control corn rootworm and cutworm in Iowa. DDT, banned in 1970, is no longer used. Properties of alachlor and DDT are summarized in Table 7.01

Alachlor, 2-chloro-2',6'-diethyl-N-(methoxymethyl) acetanilide, is one of the most widely used herbicides in the United States and its use in Iowa has been steadily increasing. It is a preemergence herbicide used for controlling certain broadleaf weeds and yellow nutsedge. Application rate in an emulsified form is 1 to 4 pounds active ingredient per acre (Weed Science Society of America, 1974). Alachlor is much less likely to adsorb to a sediment particle than to remain in solution because of a relatively high solubility (242 mg/ℓ) and low partition coefficient (50-100 ℓ/kg). Literature reviewed by Cartwright (1980) shows that chemical hydrolysis is not significant at normal aquatic pH levels. Photolysis of alachlor may be negligible because alachlor does not absorb radiation above 2800 Angstroms (solar radiation is greater than 2900 Angstrom wavelength). Volatilization is very small because a low Henry's constant (1.3×10^{-6}) reflects the tendency for alachlor to remain in the aqueous phase. Noll (1980) found that bio-uptake of alachlor was non-detectable in sunfish, clams and algae in a microcosm experiment.

Of these processes, the main route by which alachlor is degraded in soil and water is biological transformation by microorganisms. First order kinetics with respect to alachlor concentration have been used by Beestman and Deming (1974) to describe biodegradation of alachlor in soil. Cartwright (1980) reported a first order biological transformation rate constant of 0.05 day^{-1}.

DDT, 1,1,1-trichloro-2,2 bis(p-chlorophenyl)ethane, is a chlorinated hydrocarbon (organochlorine) insecticide. It was used to control insect

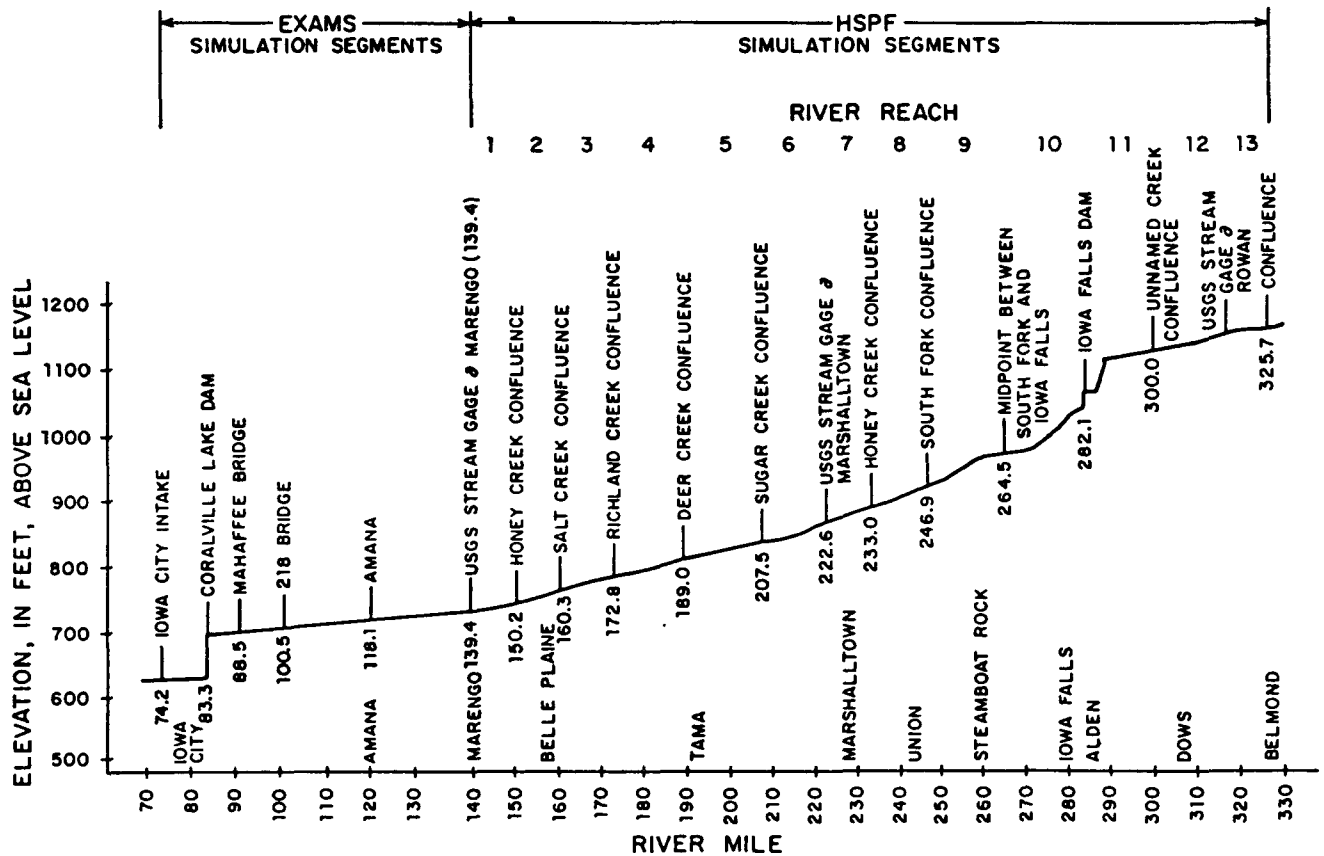


Figure 7.01. Iowa River low-water (elevation above sea level) profile (Donigian, Jr., et al. 1984; U.S.G.S., 1985).

TABLE 7.01 PROPERTIES OF ALACHLOR AND DDT

		Alachlor	DDT
A.	Nomenclature	2-chloro-2',6'-diethy 1-N-(methoxymethyl) acetanilide	1,1,1,-trichloro-2,2 bis(p-chlorophenyl) ethane 1,1'-(2,2,2-Trichloro-ethylidene)bis[4-chlorobenzene]
	Molecular formula	$C_{14}H_{20}ClNO_2$	$C_{14}H_9Cl_5$
	Molecular Weight (gram/mole)	269.8	354.5
B.	Physical and Chemical Properties		
	Melting Point	100 °C at 0.02 mmHg, 135 °C at 0.3 mm Hg	108.5 - 109 °C
	Vapor pressure	2.2×10^{-5} mmHg at 25 °C	1×10^{-7} mmHg at 20 °C
	Water Solubility	242 ppm at 25 °C	1.2×10^{-3} mg/L
	Sediment patition coefficient (L/Kg dry wt.)	50	1×10^5
	Bioconcentration (L/Kg wet wt.)	75	1.3×10^5
C.	Water Quality Criteria and Toxicological Properties		
	Criteria		0.001 ug/L for freshwater and marine aquatic life
	TLM_{96}	2.3 ppm for Rainbow Trout 13.4 ppm for Bluegill	
	LD_{50}(96 hrs)	19.5 ppm for crayfish 6.6 ppm for catfish	
	LC_{50}(96 hrs)		0.24 ug/L for crayfish 2 ug/L largemouth bass 27 ug/L for goldfish

pests in Iowa from the late 1940's until it was banned in 1970. DDT was applied at the rate of 1 to 2 pounds active ingredient per acre. Although no longer used, DDT and its metabolites (DDE, DDD) still exist in sediments and fish of the Iowa River. Freitag (1978) reported DDT concentrations of 145, 90, 60, and 40 ppb in carp, buffalo, catfish, and carp sucker, respectively, in the Iowa River. DDT has significant adsorbing affinity to sediment indicated by its low solubility (1.2 ug/ℓ) in water and high partition coefficient (100,000 ℓ/kg dry wt.). The DDT adsorbing capacity of the sediment is affected by pH, ion exchange capacity, and sediment compositions. The actual volatilization rate is dependent on environmental conditions although potential volatility of DDT is related to its vapor pressure. DDT degrades photochemically in aquatic environments. Because DDT is chemically stable and lipid-soluble, it accumulates in sediments and biota. Bioaccumulation ranges from 10^3 to 10^6. Factors affecting rates and the extent of biomagnification include the water composition and temperature; the exposure route; and the age, sex, size of the organism. Biodegradation is one of the most important processes for self purification of DDT-contaminated streams.

Three examples are given in this section. First, hydraulic flow and fate of alachlor in a 190-mile reach (300 kilometers) of the Iowa River upstream of Marengo, Iowa, were simulated by HSPF. Second, Coralville Reservoir (a 65-mile reach of the Iowa River below Marengo) was simulated for alachlor and DDT using EXAMS. The hydrologic information produced by the above HSPF simulation was used as the EXAMS inputs. A simple comparison was made between the two chemicals. Third, the 190-mile stretch of the Iowa River (upstream of Marengo) was simulated for alachlor by EXAMS, and EXAMS results were compared with the previous HSPF prediction.

7.2 ALACHLOR IN THE IOWA RIVER USING HSPF

The 190-mile reach of the Iowa River upstream of Marengo was divided into 13 segments as shown in Figure 7.01. Segmentation methodology was described in detail by Donigian, Jr. et al. (1984). The simulation was performed using the HSPF program written for the PRIME 750 computer in The University of Iowa, Iowa City, Iowa. Both the time series and the user control input data for the Iowa River reach were provided by U.S. EPA, Washington, D.C. (NCC Data Processing Support MD-24 RTP, NC 27710). The user control input data for alachlor are summarized in Table 7.02. The single-value Freundlich isotherm method was selected for adsorption/desorption processes. Three constant values (XF1, K1, N1) are provided for surface soil, upper soil, lower soil layers, and groundwater. In all the land segments, an alachlor degradation rate (summation) of 0.12 day^{-1} is given for 0.25 inch of surface soil layer, 0.045 day^{-1} for upper soil layer, and 0.04 day^{-1} for lower soil layer and ground water. In the receiving water segments, the degradation rate of 0.04 day^{-1} for water and 0.045 day^{-1} for suspended solids and bed sediments was used.

The simulated flow and associated suspended sediment concentration at Marengo for years 1977 and 1978 are shown in Figures 7.02 and 7.03, respectively. The dissolved, suspended, and sedimented alachlor concentrations at Marengo are presented in Figures 7.04 and 7.05,

TABLE 7.02 HSPF INPUT DATA USED FOR
ALACHLOR SIMULATION IN THE IOWA RIVER

Land Segment Pesticide Parameters for Single Value Freundlich	Surface Soil Layer	Upper Soil Layer	Lower Soil Layer	Groundwater
Method [a]				
XFLX (ppm)	0.0	0.0	0.0	0.0
K1	4.0	4.0	2.0	0.2
N1	1.4	1.4	1.4	1.4
Pesticide Degradation Rate (day^{-1})	0.120	0.045	0.04	0.04
Initial Pesticide Storage (lb/acre)				
Crystal	0.0	0.0	0.0	0.0
Adsorbed	0.0	0.0	0.0	0.0
Solution	0.0	0.0	0.0	0.0
Solid Layer Depth (inch)	0.25	5.71	41.30	60.0
Bulk Density (lb/ft^3)	62.4	79.2	81.7	85.5

Receiving Water Segment	Suspended Sand	Suspended Silt	Suspended Clay	Bed Sediment Sand	Bed Sediment Silt	Bed Sediment Clay
Partition Coefficient (L/Kg)	3.2	9.5	19	3.2	9.5	19.0
Adsorption rate (day^{-1})	36	36	36	0.00001	0.00001	0.00001
Temp correction coeff.	1.0	1.0	1.0	1.0	1.0	1.0
Initial concentration on sediments	0.0	0.0	0.0	0.0	0.0	0.0

	Water	Suspended Solids	Bed Sediment
Pesticide degradation rate (day^{-1}) in receiving water	0.004	0.045	0.045
Temp. corerction factor	1.07	1.07	1.07

a) X = K1 * C ** (1/N1) + XFLX

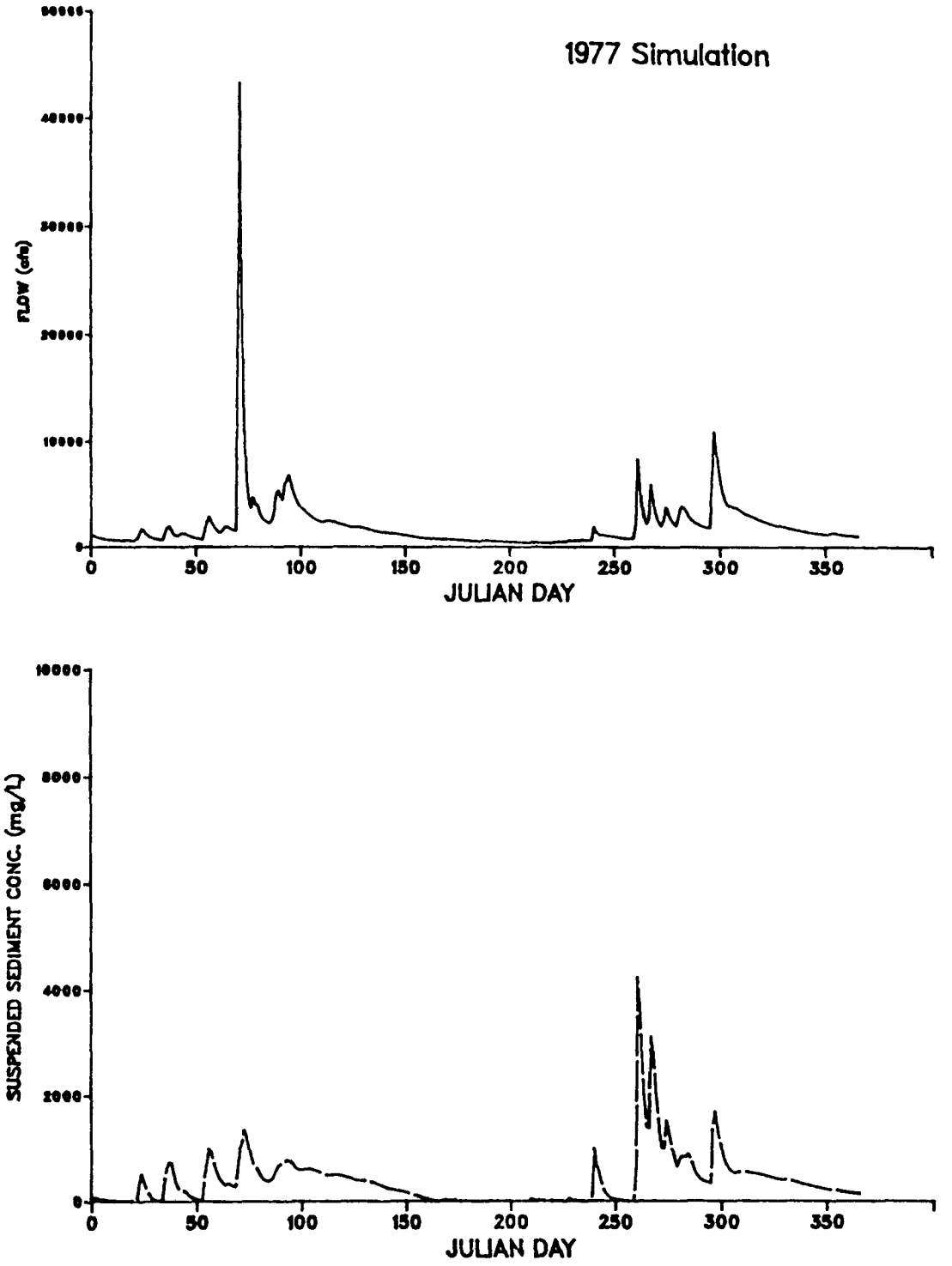


Figure 7.02. Flow and sediment loadings simulated by HSPF for year 1977.

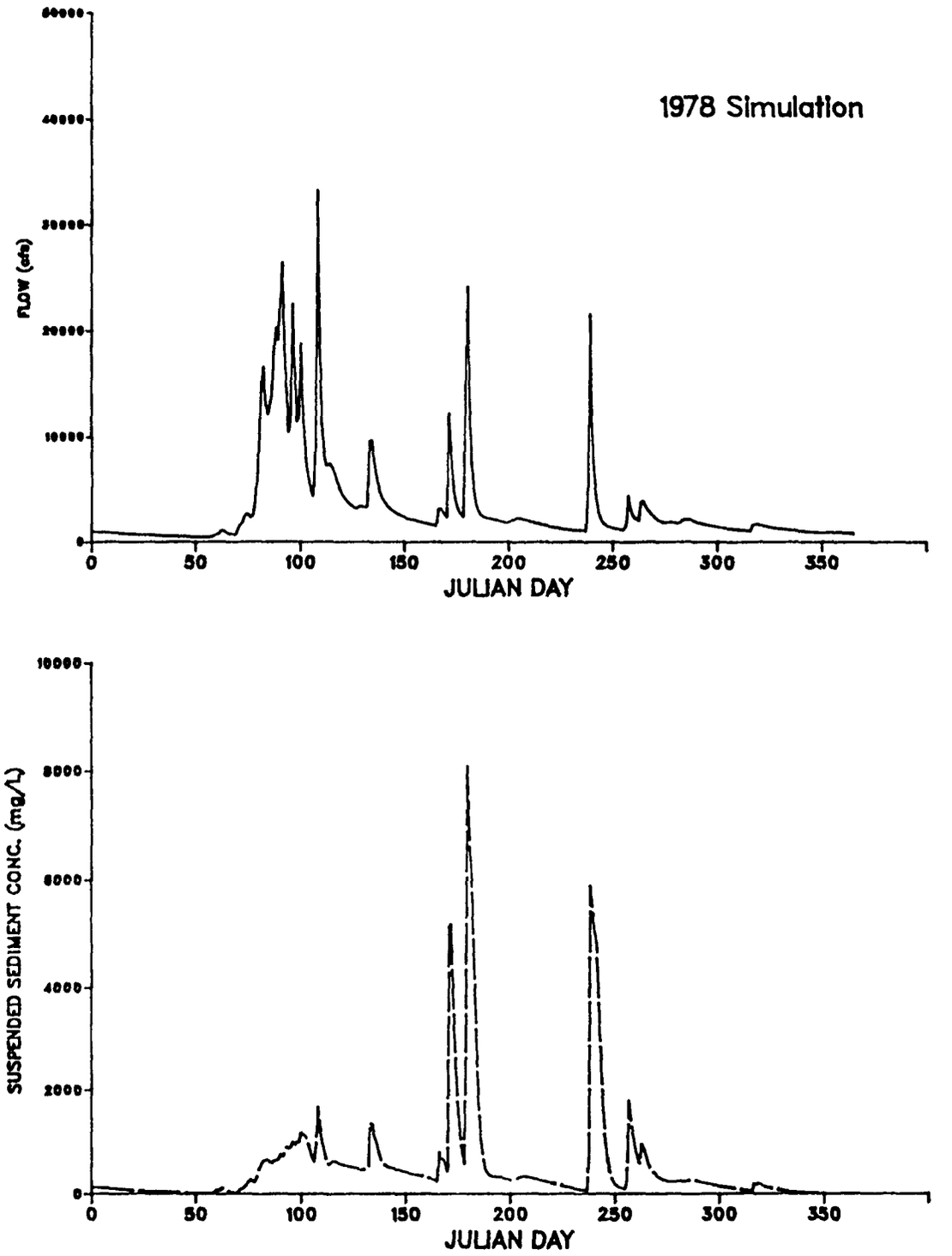


Figure 7.03. Flow and sediment loadings simulated by HSPF for year 1978.

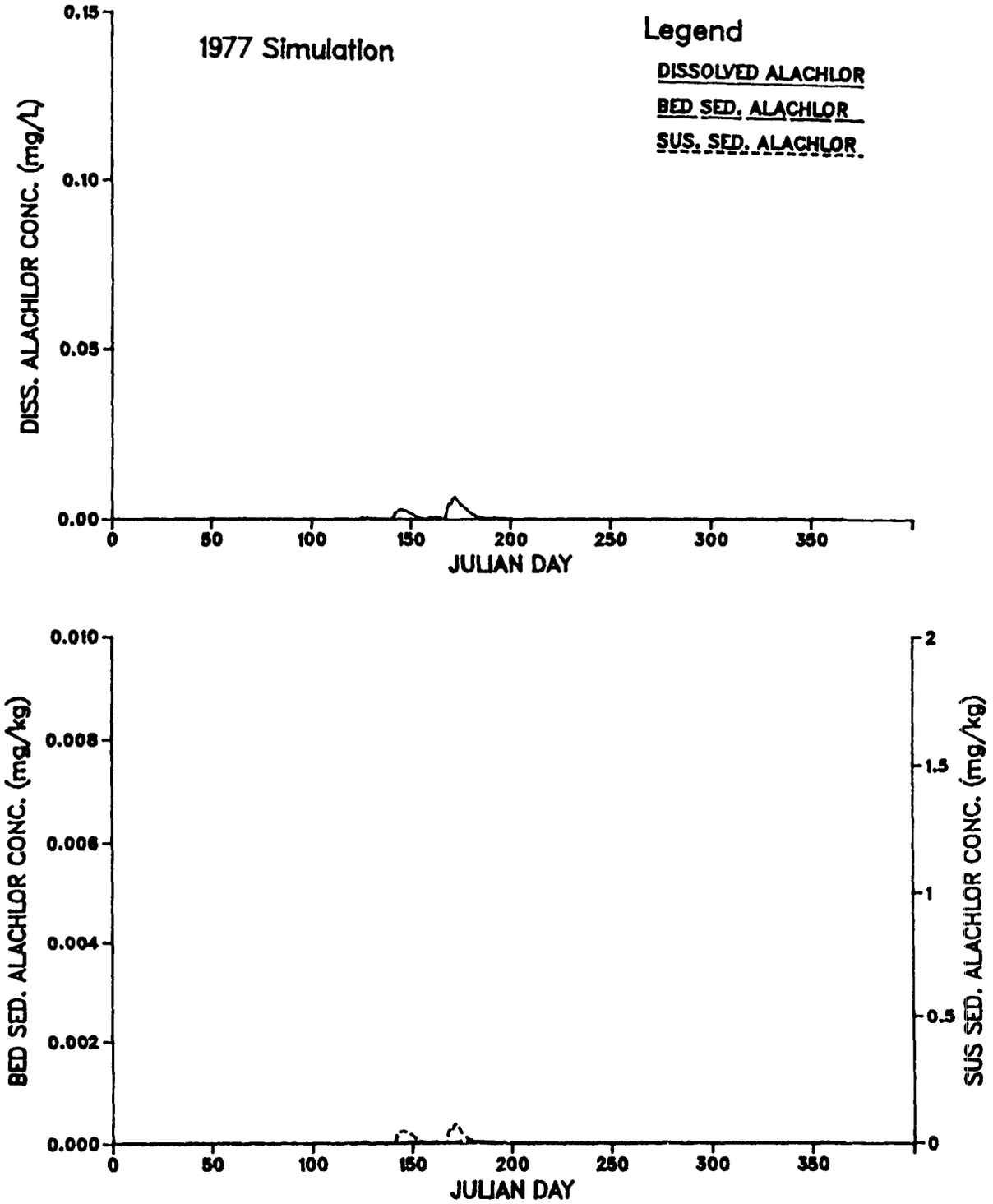


Figure 7.04. Dissolved, suspended and sedimented alachlor concentrations at Marengo, IA, simulated by HSPF for year 1977.

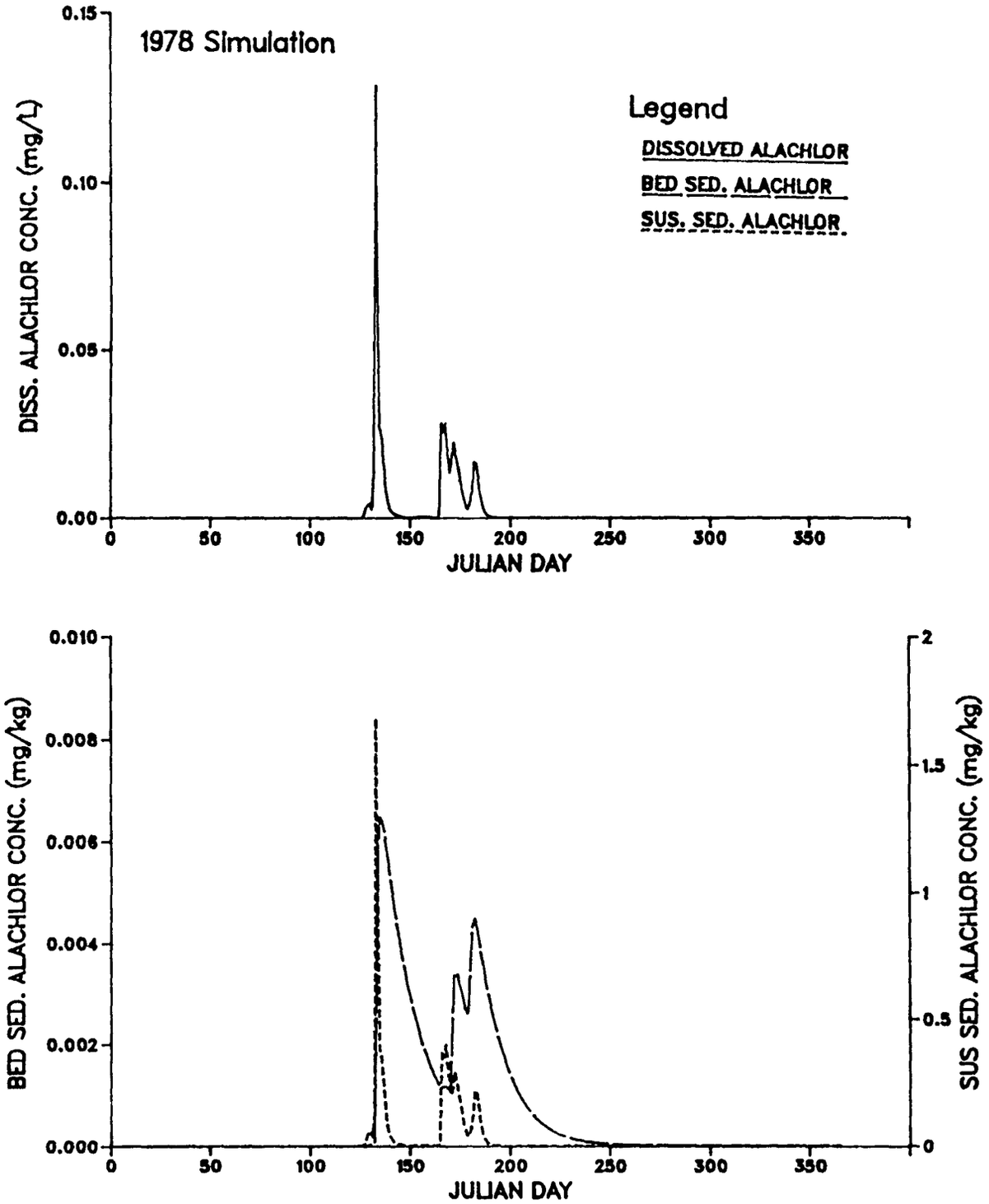


Figure 7.05. Dissolved, suspended and sedimented alachlor concentrations at Marengo, IA, simulated by HSPF for year 1978.

respectively, for years 1977 and 1978. The summer stream flow at Marengo was computed to be very low, which can be explained by a summer.

Consequently, concentrations of alachlor (dissolved, suspended, and bed sediment) in the receiving water are predicted to be extremely low in 1977. The 1978 simulation showed high flow in March, April, June, and August. High suspended solid concentrations are indicated in June and August. Elevated concentrations of alachlor (dissolved, suspended, and bed sediment) are predicted to occur in April and June, but not in August. A peak concentration is calculated to occur at 6.85 ug/ℓ (dissolved) in June 21, 1977. (An average concentration in 1977 was simulated to be 0.266 ug/ℓ). The highest level of alachlor in 1978 was calculated to be 0.128 mg/ℓ, which occurred on May 13. (Average concentration in 1978 is 1.64 ug/ℓ).

The simulation results indicate that high runoff of alachlor occurs directly after the alachlor application followed by a rainfall event. Alachlor dissipated quickly by July. Maximum concentrations measured in 1975 and 1976 were approximately 1.0 ug/ℓ and 1.7 ug/ℓ, respectively (Ruiz 1979). Both concentrations occurred in May. Little alachlor appeared in the runoff after the crop season. Runoff of the alachlor was not necessarily a function of the turbidity or suspended solids because of its high solubility in water. Alachlor runoff is a function of rainfall events shortly after application (generally from April 15 to May 15).

7.3 EXAMS SIMULATIONS FOR ALACHLOR AND DDT IN CORALVILLE RESERVOIR

A 65-mile reach of the Iowa River downstream of Marengo was divided into 5 segments based on river morphology (Table 7.03). The width of the stream channel varies from 35 to 586 meters and the depth from 1.2 to 1.7 meter. Compartment 4 (Table 7.03) represents Coralville Reservoir, which is a mainstream impoundment of the Iowa River and receives extensive agricultural runoff via inflow from upstream. Figure 7.06 shows the physical configurations of the completely mixed compartments defined for the EXAMS application. The IBM.PC.XT version of EXAMS II program was provided

TABLE 7.03 SEGMENTATION OF THE IOWA RIVER STUDY REACH

Compartment	Identified Points	Segment Length m	(mi)	Drainage Area sq. km	(sq. mi)
1	Marengo to Amana	39,816	(21.0)	311	(120)
2	Amana to Route 218 Bridge	33,370	(17.6)	262	(101)
3	R 218 B to Mahaffee Bridge	22,752	(12.0)	179	(69)
4	M.B. to Coralville Dam	9,860	(5.2)	80	(31)
5	C.D. to Iowa City intake	17,255	(9.1)	404	(156)

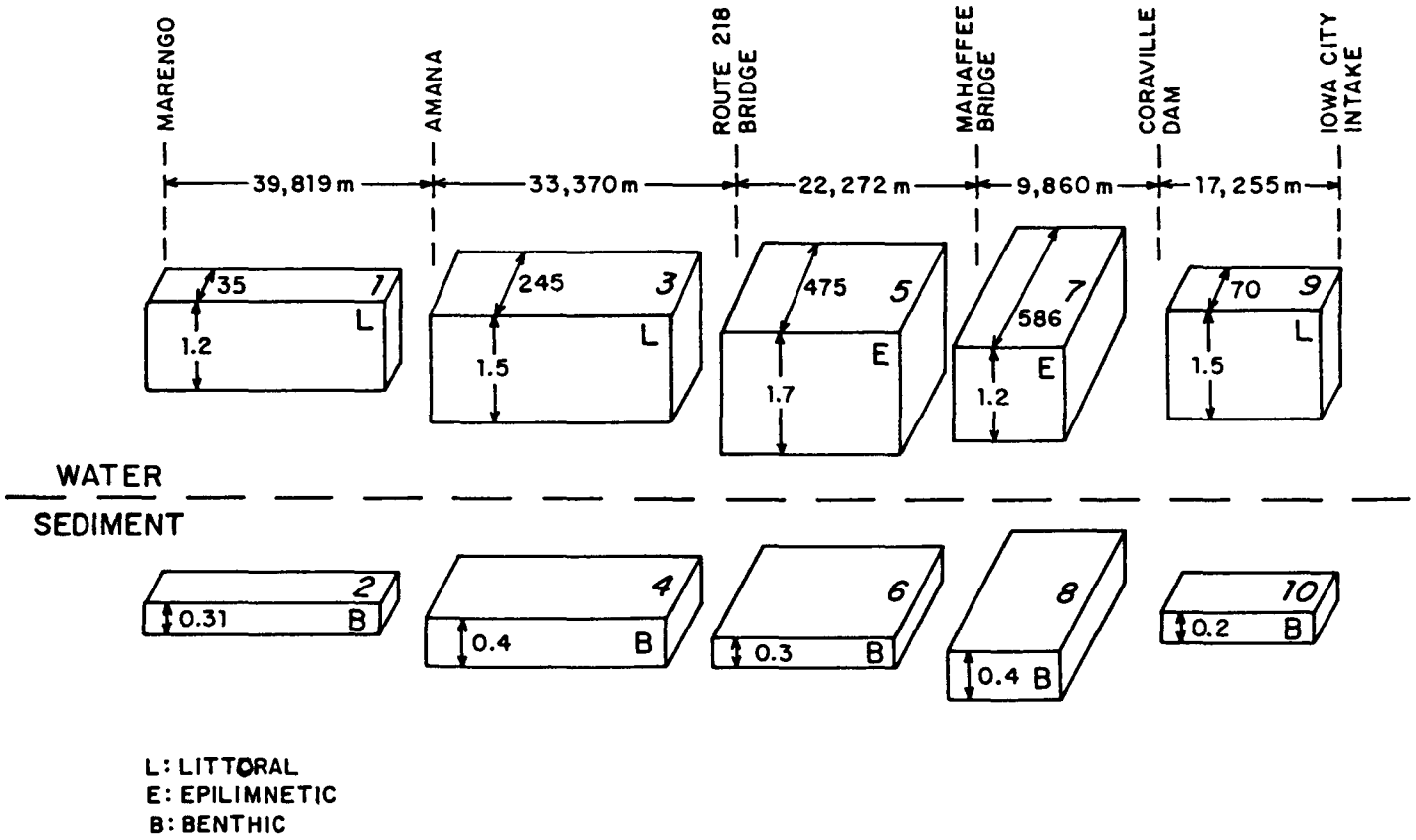


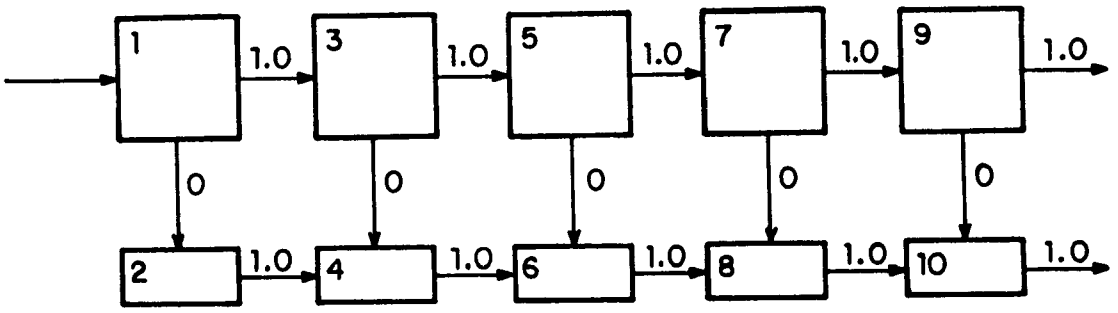
Figure 7.06. Physical configurations of the completely mixed compartments of the Iowa River for EXAMS.

by U.S. EPA, Athens, Georgia. Major inputs to EXAMS II are presented in Table 7.04. Physical dimensional and advective/dispersive parameters are shown in Figures 7.06 and 7.07, respectively.

TABLE 7.04 FLOW, SEDIMENT AND ALACHLOR LOADS USED IN EXAMS SIMULATION IN THE 65 MILES OF THE IOWA RIVER REACh, DOWNSTREAM OF MARENGO, IA.

Descriptive Parameter	(Unit)	EXAMS Parameter	1977	1978
ENVIRONMENT INPUT THROUGH STREAM FLOW				
Stream Flow	(m^3/hr)	STFLO (1,13)	215047	336944
Stream born sediment load	(kg/hr)	STSED (1,13)	50	50
Suspended Sed. Conc.	(mg/L)	SUSED (1,13)	376	507
ENVIRONMENT INPUT THROUGH RUNOFF (NONPOINT)				
Nonpoint sediment load	(m^3/hr)	NPSED (1,13)	2871	2871
Nonpoint flow	(kg/hr)	NPSFL (1,13)	3	3
Suspended sediment Conc.	(mg/L)	NPSED (1,13)	376	507
		NPSED (3,13)	2416	2416
		NPSFL (3,13)	2.5	2.5
		NPSED (3,13)	376	507
		NPSED (5,13)	1650	1650
		NPSFL (5,13)	1.8	1.8
		NPSED (5,13)	60	60
		NPSED (7,13)	740	740
		NPSFL (7,13)	0.8	0.8
		NPSED (7,13)	60	60
		NPSED (9,13)	3732	3732
		NPSFL (9,13)	3.9	3.9
		NPSED (9,13)	190	190
ALACHLOR LOADING INPUT				
Loading through stream flow	(kg/hr)	STRLD (1,1,13)	5.742×10^{-2}	6.530×10^{-1}
Loading through runoff	(kg/hr)	NPSLD (1,1,13)	2.0×10^{-5}	2.0×10^{-5}
		NPSLD (3,1,13)	1.7×10^{-5}	1.7×10^{-5}
		NPSLD (5,1,13)	1.1×10^{-5}	1.1×10^{-5}
		NPSLD (7,1,13)	5.0×10^{-6}	5.0×10^{-6}
		NPSLD (9,1,13)	2.6×10^{-5}	2.6×10^{-5}

(a)



(b)

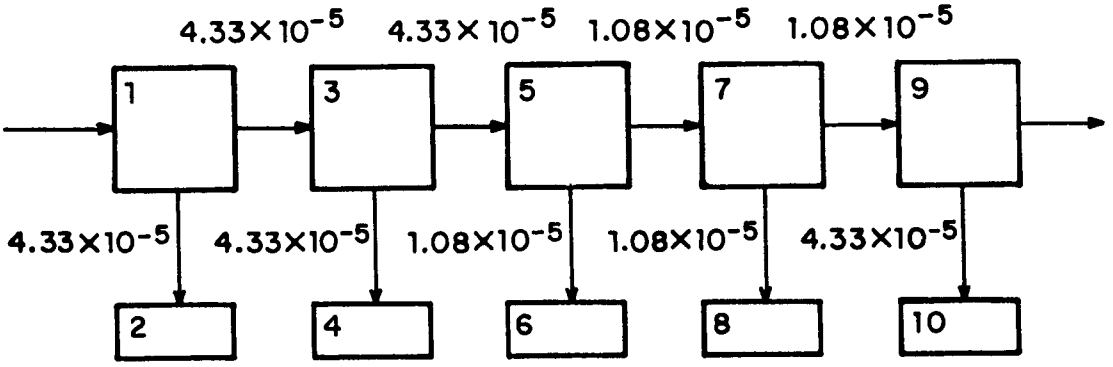


Figure 7.07. Iowa River/Coralville Environment (10 segments) Model Pathways.
(a) Advective Transport Pathways (15 pathways)
Proportion of flow advected (dimensionless)
(b) Dispersive Transport Pathways (9 pathways)
Dispersion Coefficient (m^2/hr)

Values of bulk density of sediments, percent water in sediment, stream flow, stream-born sediment load, suspended sediment concentration, non-point source sediment load, runoff, and bacterial population for 1977 were time-averaged for the entire year. The previous HSPF simulation results at Marengo were used for estimating the alachlor loadings to the new segment below Marengo. Alachlor loading data were entered in the model in the form of a stream-borne load to the littoral segment at the compartment 1, and

non-point source loads entered either the littoral or epilimnetic segments in all five compartments. Stream-borne and runoff values for the alachlor loadings were assumed because no useful information was available. A pseudo first-order biolysis rate of 0.05 day^{-1} was estimated. The other decay reactions are assumed insignificant.

Simulation results (steady-state concentrations) of EXAMS II are shown in Figure 7.08. The drought-like precipitation levels for the summer of 1977 resulted in extremely low alachlor concentrations downstream, although the average flow for the year of 2100 ft^3/sec is considered normal. The average alachlor concentrations in 1977 are 0.266 ug/ℓ at Marengo (HSPF result) and 0.25 ug/ℓ at the Iowa City intake, showing 6% reduction in the 65 miles of the Iowa River segment. In 1978, average alachlor concentrations at Marengo were 1.64 ug/ℓ and 1.56 ug/ℓ at Iowa City intake, indicating 5% reduction. Several mechanisms are responsible for removal of alachlor. Of these, the major means of removal is by microbial degradation. Photolysis and volatilization rates of alachlor were assumed negligible.

The fate of alachlor and DDT in Coralville Reservoir are compared using EXAMS II. All input data, except for chemical data, are the same as the above Coralville Reservoir simulation data of 1977. The chemical input data are summarized in Table 7.05. The calculated alachlor and DDT concentrations are shown in Figure 7.09. DDT shows higher concentration than alachlor in all the water compartments. The DDT concentration decreases slowly. In the bed sediments, DDT concentration is significantly greater than the alachlor concentration, which can be expected due to the DDT's low water solubility and very high partition coefficient. Increased concentrations in the bed segments 6 and 8 occurred due to the high sediment loadings into these segments. DDT concentration in the sediments is influenced dramatically by sediment loadings, but not apparent in the water column. The exposure, fate and persistence of alachlor and DDT estimated by EXAMS are summarized in Table 7.06.

7.4 COMPARISON OF EXAMS AND HSPF FOR IOWA RIVER

In selecting a model, it is important to understand the nature of the results. In making a comparison between the HSPF estimates and the EXAMS predictions, the 190-mile stretch of the Iowa River upstream of Marengo was simulated by EXAMS. The study reach was segmented into 20 compartments (i.e., 10 water compartments and 10 bed sediment compartments), which is the maximum number of compartments allowed by the PC version of EXAMS. In HSPF, the reach was simulated as a continuum and not compartmentalized. The environment and loading data for 1977 and 1978 are presented in Tables 7.07 and 7.08, respectively. Information on advective and dispersive transports are shown in Figure 7.10. It should be noted that the suspended sediment concentration, stream flow, nonpoint flow and loadings (load via stream flow and nonpoint source) were either generated by HSPF simulation or estimated from its output. Chemical data were previously given in Table 7.05.

The computed total alachlor concentrations in the water column and in the bed sediments are shown in Figure 7.11. As discussed above, alachlor

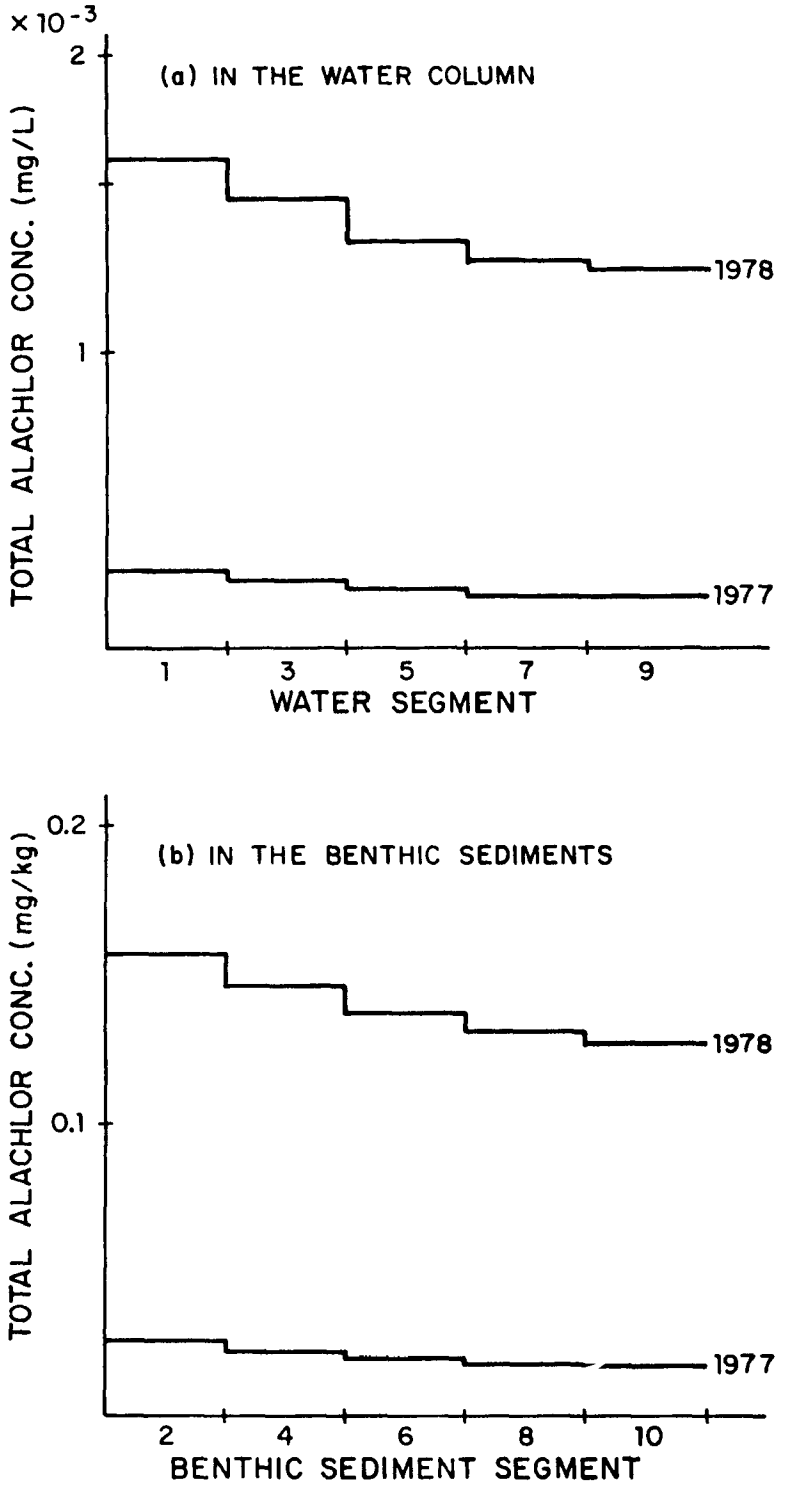


Figure 7.08. Alachlor simulation results by EXAMS.

TABLE 7.05 CHEMICAL INPUT DATA TO EXAMS II FOR ALACHLOR AND DDT

		Alachlor	DDT
Gram molecular weight (g/mole)	MWT(1)	2.700E+02	3.540E+02
Vapor pressure (mmHg)	VAPR(1)	2.200E-05	1.900E-07
Solubility (mg.L)	SOL(1,1)	2.400E+02	1.2
K_p for biomass	KPB(1,1)		1.000E+04
K_p for sediment	KPS(1,1)	1.000E+02	2.380E+05
Acid hydrolysis rate (2nd order)	KAH(1,1,1)		6.840E-06
Base hydrolysis rate (2nd order)	KBH(1,1,1)		9.900E-03
Biolysis rate (2nd order)	KBACW(1,1,1)		2.080E-10
Q10 value for planktonlysis	QTBAS(1,1,1)		2.0
Biolysis by sediment bacteria (2nd order)			2.080E-07
Q10 value for benthic bacterial biolysis			2.0
Mean decadic molar light extinction coefficient in 48 wavelength interval over 280-825 nm (/cm/(mol/L))	ABS(1,1,1) ABS(2,1,1) ABS(3,1,1) ABS(4,4,4) ABS(5,1,1)		4.000E-02 1.600E-02 7.000E-03 3.000E-03 1.300E-03

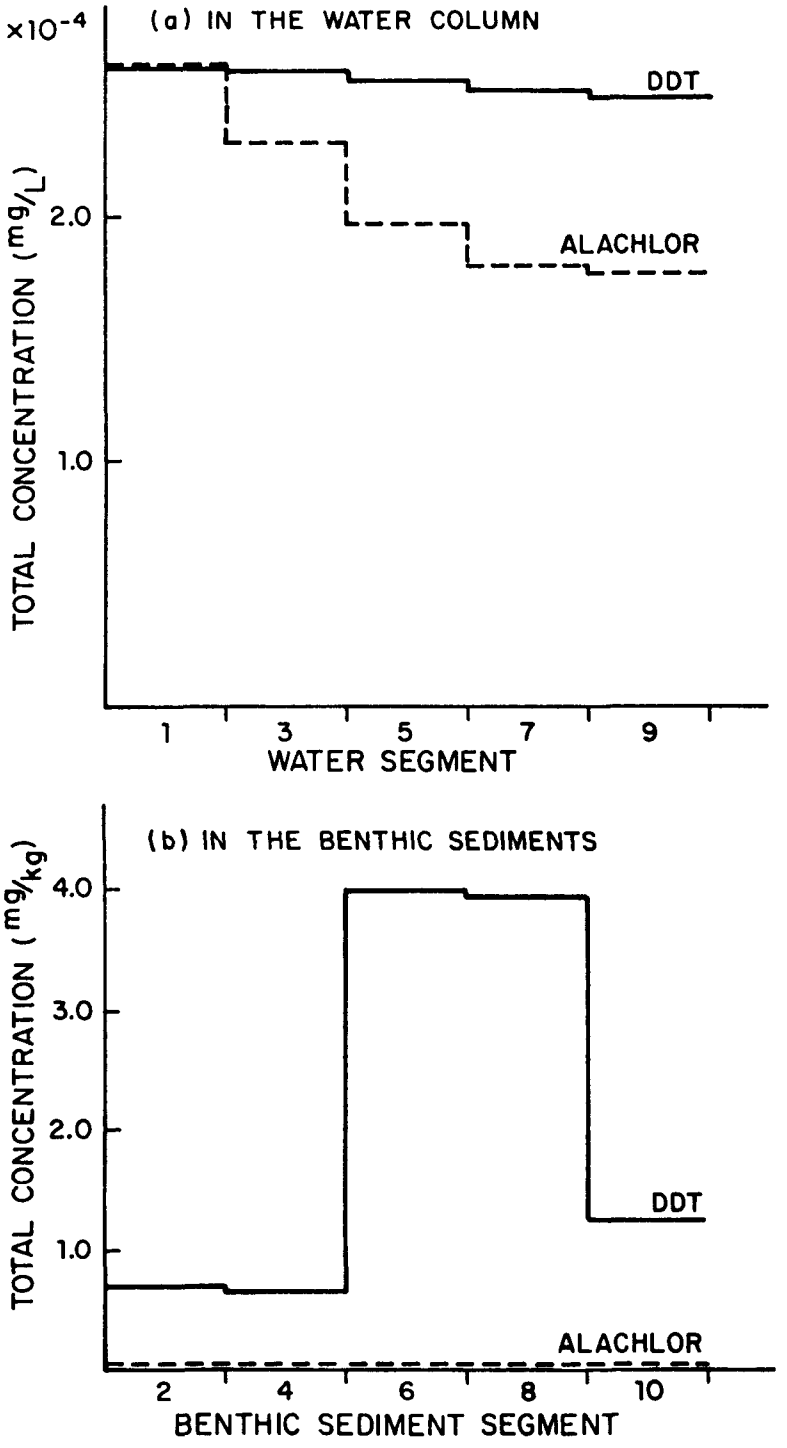


Figure 7.09 Comparison of alachlor and DDT simulations by EXAMS II.

TABLE 7.06 COMPARISON OF EXPOSURE, FATE AND PERSISTENCE BETWEEN ALACHLOR AND DDT (EXAMS II OUTPUTS)

			Alachlor	DDT
EXPOSURE (maximum steady-state concentration)				
Water column:	dissolved	(mg/L)	2.502E-04	1.672E-05
	total	(mg/L)	2.596E-04	2.634E-04
Benthic layer:	dissolved	(mg/L)	2.502E-04	1.672E-05
	total	(mg/Kg dry)	2.522E-02	3.98
FATE				
Total steady-state accumulation			138	1.647E+04
In the water column (%)			6.08	0.06
In the sediments (%)			93.92	99.94
Total chemical load			1.4/Kg/day	504 Kg/Year
Dispositions:				
biotransformed (%)			29.83	1.67
other passway (%)			70.17	98.33
PERSISTENCE				
95% Cleanup time (years)			10	110

concentrations in 1977 were predicted to be much smaller than those in 1978. In the 1978 simulation, increased loading rates in compartments 11, 13, 15, 17, and 19 resulted in elevated alachlor concentrations in water and bed sediments. The comparison between EXAMS and HSPF was made using the dissolved and benthic sediments alachlor concentrations at Rowan (compartments 1 and 2). The simulations for 1977 and 1978 are shown in Figures 7.12 and 7.13, respectively. The alachlor concentrations computed by HSPF are time variable (e.g., daily) values, whereas EXAMS concentrations are steady state (e.g., yearly averaged) values. EXAMS-II has the capability to simulate monthly-average loadings over one year periods, but the steady state mode of EXAMS was used in this comparison. Because runoff of alachlor occurs in slugs, especially concentrated in May and June runoffs, the steady state concentrations of alachlor provide less information for alachlor management purposes. Unfortunately, no measurement data are available for these 2 years to examine the accuracy of the models predictions.

TABLE 7.07. EXAMS INPUT DATA FOR THE 1977 SIMULATION OF THE IOWA RIVER - WATER COMPARTMENT.

Descriptive Parameter	EXAMS Parameter	upstream 1	3	5	water compartment 7	9	11	13	downstream 15	17	19
ENVIRONMENT INPUT											
Stream length (m)	LENG	14970	55200	28320	50690	16740	24300	29770	26070	36370	17380
Stream width (m)	WIDTH	35.4	35.8	38.3	44.6	80.5	51.5	59.0	50.3	54.1	71.7
Stream depth (m)	DEPTH	0.91	1.06	0.98	1.33	1.22	1.65	2.32	1.58	1.65	2.44
Compartment type	TYPE	L	L	L	L	L	L	L	L	L	L
Suspended Sediment conc. (mg/L)	SUSED	(33.0)	63.0	143.0	248.0	(350.2)	355.2	360.2	365.2	372.5	(376.2)
Nonpoint sediment load (kg/hr)	NPSED	0	30.0	80.0	105.0	102.2	5.0	5.0	5.0	7.3	3.7
Nonpoint flow (m^3/hr)	NPSFL	0	3.67×10^4	1.835×10^4	3.665×10^4	1.85×10^4	1.48×10^4	1.48×10^4	1.47×10^4	2.96×10^4	1.47×10^4
Stream flow (m^3/hr)	STFLD	3.14×10^4									
Stream sediment load (kg/hr)	STSED	30.0									
Bacteria popul. (cfu/mℓ)	BACPL	1.00×10^7									
LOADING INPUT											
Load via stream flow (kg/hr)	STRLD	1.088×10^{-2}									
Nonpoint source load (kg/hr)	NPSLD		6.70×10^{-3}	3.69×10^{-3}	7.65×10^{-3}	4.57×10^{-3}	3.63×10^{-3}	5.10×10^{-3}	3.81×10^{-3}	5.69×10^{-3}	3.63×10^{-3}

TABLE 7.07 (continued)

Descriptive Parameter	EXAMS Parameter	upstream			Bed sediment compartment				downstream		
		2	4	6	8	10	12	14	16	18	20
ENVIRONMENT INPUT											
Bulk sediment density (g/cc)	BULKD	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
Water in sediment (%)	PCTWA	180	180	180	180	180	180	180	180	180	180
Compartment type	TYPE	B	B	B	B	B	B	B	B	B	B

( ): values obtained from HSPF simulation

TABLE 7.08. EXAMS INPUT DATA FOR THE 1978 SIMULATION OF THE IOWA RIVER

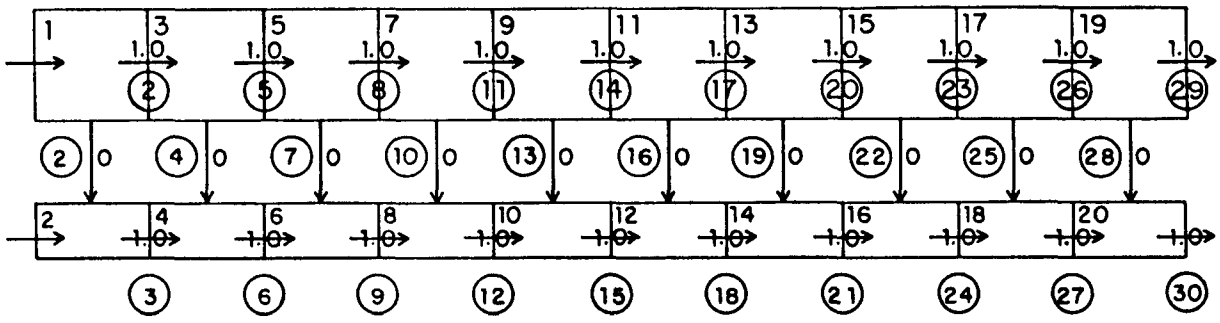
Descriptive Parameter	EXAMS Parameter	upstream 1	3	5	water compartment 7	9	11	13	downstream 15	17	19
ENVIRONMENT INPUT											
Stream length (m)	LENG	14970	55200	28320	50690	16740	24300	29700	26070	36370	17380
Stream width (m)	WIDTH	38.1	38.1	40.4	46.0	87.5	55.0	59.8	53.4	57.5	74.5
Stream depth (m)	DEPTH	1.22	1.27	1.19	1.51	1.52	2.23	2.38	1.95	2.06	2.99
Compartment Type	TYPE	L	L	L	L	L	L	L	L	L	L
Suspended sediment conc. (mg/L)	SUSED	(68.2)	149.2	230.2	34.2	(393.4)	412.4	431.4	450.4	478.9	(507.2)
Nonpoint sediment load (kg/hr)	NPSED	0	81.0	81.0	81.0	82.2	19.0	19.0	19.0	28.5	28.3
Nonpoint flow (m^3/hr)	NPSFL	0	4.078×10^4	2.039×10^4	4.078×10^4	2.571×10^4	2.650×10^4	2.650×10^4	2.650×10^4	5.300×10^4	2.578×10^4
Stream flow (m^3/hr)	STFLD	(5.10×10^4)									
Stream sediment load (kg/hr)	STSED	30.0									
Bacteria popul. (cfu/mℓ)	BACPL	1.00×10^7									
LOADING INPUT											
Load via stream flro (kg/hr)	(STRLD	0.131									
Nonpoint source load (kg/hr)	NPSLD		4.12×10^{-3}	2.26×10^{-3}	4.69×10^{-3}	2.80×10^{-3}	8.42×10^{-2}	1.18×10^{-1}	8.83×10^{-2}	1.32×10^{-1}	8.42×10^{-2}

TABLE 7.08 (continued)

Descriptive Parameter	EXAMS Parameter	upstream 2	4	6	Bed sediment compartment 8	10	12	14	downstream 16	18	20
ENVIRONMENT INPUT											
Bulk sediment density (g/cc)	BULKD	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
Water in sediment (%)	PCTWA	180	180	180	180	180	180	180	180	180	180
Compartment type	TYPE	B	B	B	B	B	B	B	B	B	B

( ): value obtained from HSPF simulation

(a) Advective Tranport pathways (30 pathways)
proportion of flow advected (dimensionless)



(b) Dispersive Transport pathways (19 pathways)
Dispersion coefficient (m^2/hr) --- 4.33×10^{-5}

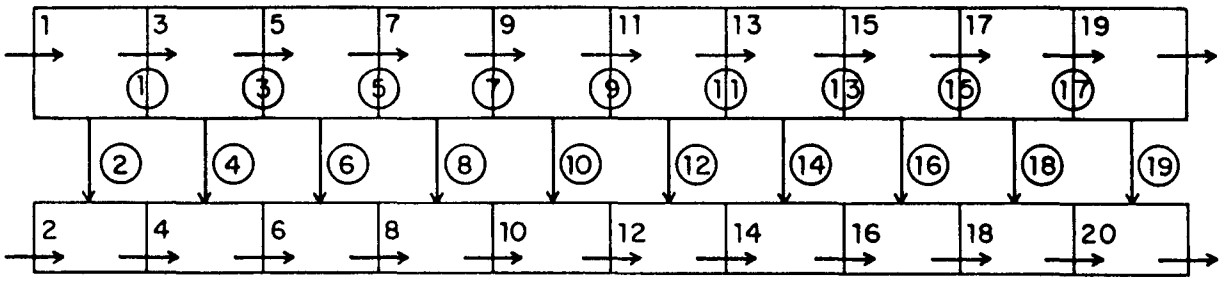


Figure 7.10. The Iowa River (above Marengo) environment model pathways.
(a) Advective transport pathways (30 pathways)
Proportion of flow advected (dimensionless)
(b) Dispersive Transport pathways (19 pathways)
Dispersion coefficient (m^2/hr) >>> $+.33 \times 10^{-5}$

Tables 7.09 and 7.10 give some outputs tables of EXAMS for 1977 and 1978, respectively. As described in the previous section, EXAMS produces not only chemical concentrations, but also summary tables of the results. EXAMS computed, for 1977 data, the maximum exposure concentrations of 0.35 ug/ℓ in water column and 0.28 ug/kg in bed sediment at steady state conditions. About 18% of alachlor was biotransformed; the remaining 82% was transported out of the system. The model also estimated it would take 5 months for 95% recovery after the cessation of inputs. For 1978, the total alachlor concentrations were estimated to be 2.5 ug/ℓ and 2 ug/kg in water column and bed sediments, respectively. Approximately 92% of alachlor is distributed in the water column, and 8% in the benthic sediments. About 12%

is biodegraded and 88% is transported out of the system. A 95% recovery time is estimated to be 6 months.

7.5 HEAVY METAL WASTE LOAD ALLOCATION

With increased industrialization and consequent discharge of toxic metals into the environment, some surface or ground waters could be rendered unusable by contamination. To prevent this situation, permits issued under the National Pollutant Discharge Elimination System should include a waste load allocation based on toxicological data and water quality standards.

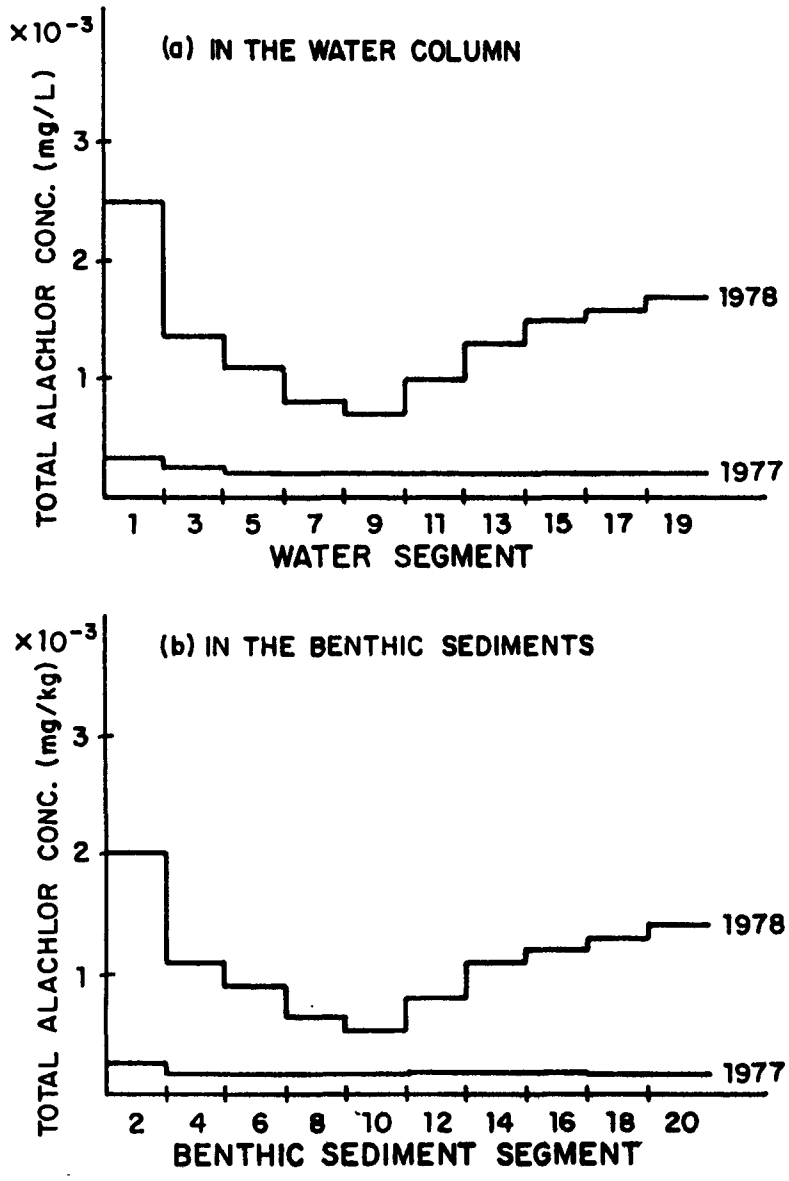


Figure 7.11. Predicted total alachlor concentrations in the water column and in the bed sediments of the Iowa River (190 miles above Marengo).

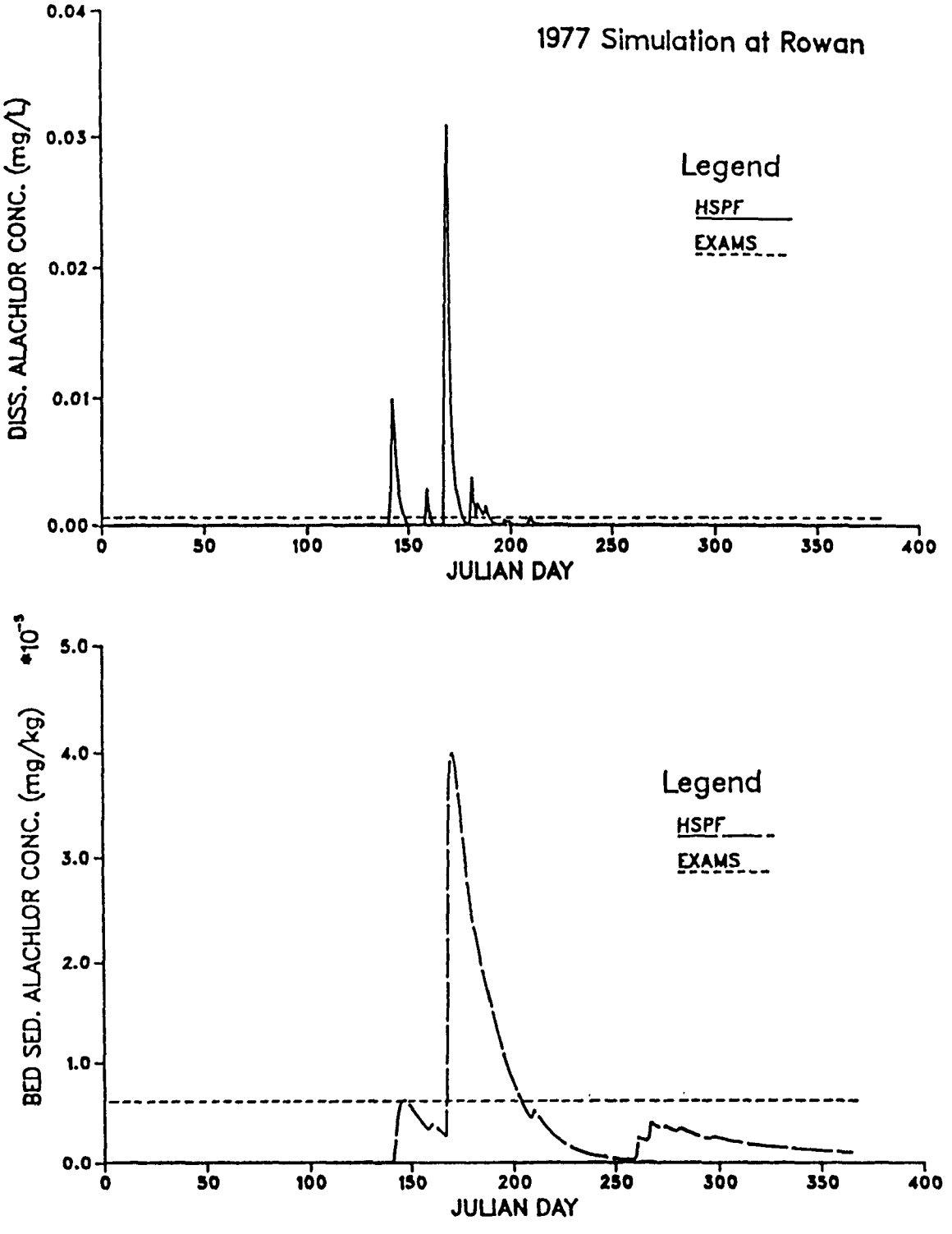


Figure 7.12. 1977 Simulation at Rowan.

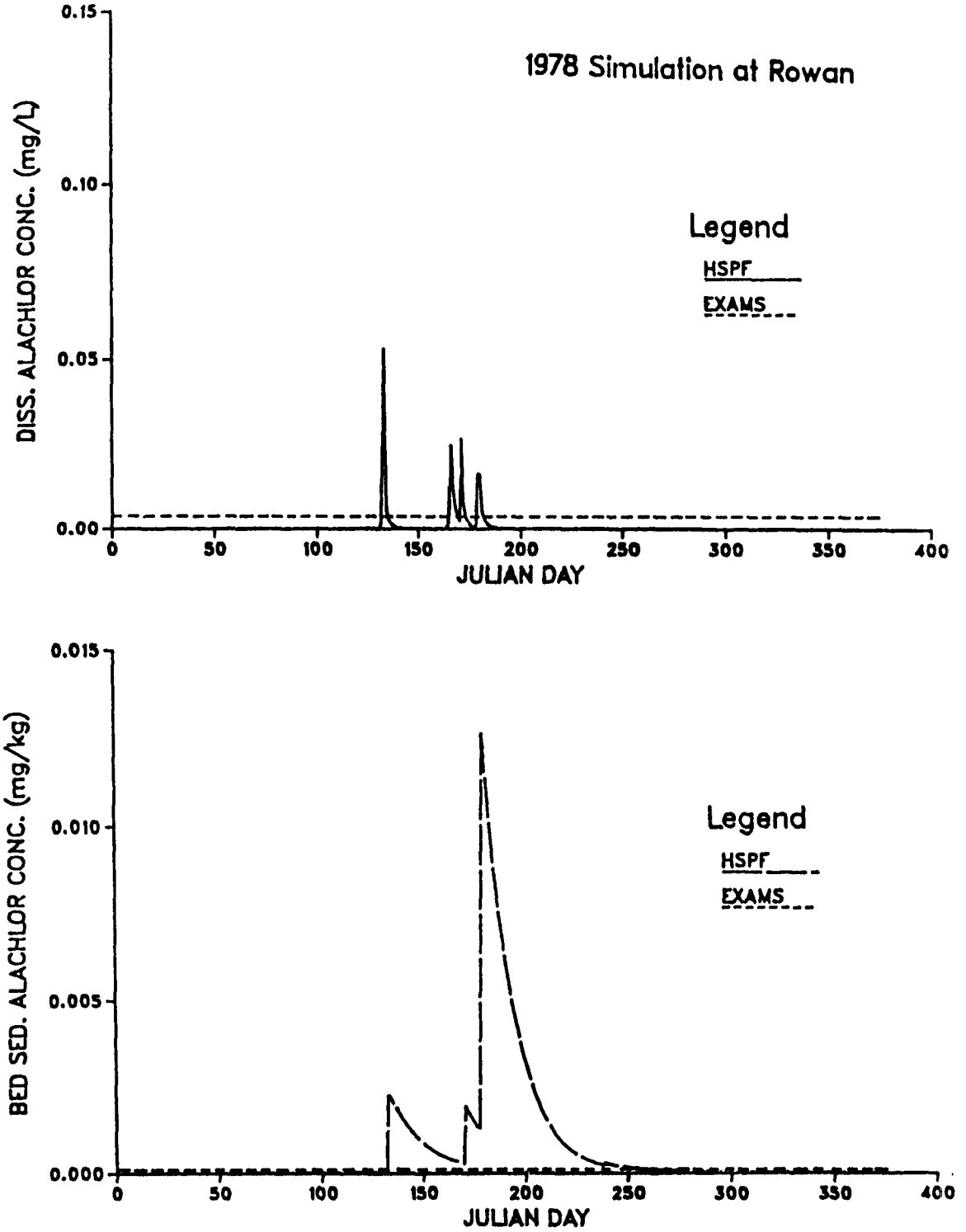


Figure 7.13. 1978 Simulation at Rowan.

TABLE 7.09. THE EXAMS II OUTPUTS FOR THE 1977 SIMULATION OF THE IOWA RIVER FOR ALACHLOR

Table 15.01. Distribution of chemical at steady state.

Seg #	Resident Mass Kilos	Resident Mass %	Chemical Concentrations Total mg/*	Dissolved mg/L **	Sediments mg/kg	Biota ug/g
In the Water Column:						
1	0.16	3.36	3.358E-04	3.358E-04	6.380E-06	0.000E-01
3	0.50	10.34	2.380E-04	2.380E-04	4.522E-06	0.000E-01
5	0.24	4.95	2.243E-04	2.243E-04	4.261E-06	0.000E-01
7	0.63	13.03	2.090E-04	2.090E-04	3.970E-06	0.000E-01
9	0.34	7.12	2.089E-04	2.089E-04	3.969E-06	0.000E-01
11	0.43	8.85	2.067E-04	2.067E-04	3.926E-06	0.000E-01
13	0.85	17.60	2.083E-04	2.083E-04	3.957E-06	0.000E-01
15	0.43	8.92	2.075E-04	2.075E-04	3.942E-06	0.000E-01
17	0.65	13.41	1.992E-04	1.992E-04	3.784E-06	0.000E-01
19	0.60	12.41	1.968E-04	1.968E-04	3.739E-06	0.000E-01
	4.8	90.25				
and in the Benthic Sediments:						
2	2.91E-02	5.60	2.750E-04	3.358E-04	6.380E-06	0.000E-01
4	7.70E-02	14.79	1.949E-04	2.380E-04	4.522E-06	0.000E-01
6	3.98E-02	7.65	1.837E-04	2.243E-04	4.261E-06	0.000E-01
8	7.74E-02	14.86	1.711E-04	2.090E-04	3.970E-06	0.000E-01
10	4.61E-02	8.85	1.711E-04	2.089E-04	3.969E-06	0.000E-01
12	4.24E-02	8.14	1.693E-04	2.067E-04	3.926E-06	0.000E-01
14	5.99E-02	11.51	1.706E-04	2.083E-04	3.957E-06	0.000E-01
16	4.46E-02	8.56	1.699E-04	2.075E-04	3.942E-06	0.000E-01
18	6.42E-02	12.33	1.631E-04	1.992E-04	3.784E-06	0.000E-01
20	4.02E-02	7.71	1.612E-04	1.968E-04	3.739E-06	0.000E-01
	0.52	9.75				

Total Mass (kilograms) = 5.342

* Units: mg/L in Water Column; mg/kg in Benthos.
** Includes complexes with "dissolved" organics.

Table 17.01. Steady-state concentration means and extrema.
Number in parens (Seg) indicates segment where value was found.

	Total Seg	Total mg/*	Dissolved Seg	Dissolved mg/L **	Sediments Seg	Sediments mg/kg	Biota Seg	Biota ug/gram
Water Column:								
Mean		2.234E-04		2.234E-04		4.245E-06		0.000E-01
Max	(1)	3.358E-04	(1)	3.358E-04	(1)	6.380E-06	(1)	0.000E-01
Min	(19)	1.968E-04	(19)	1.968E-04	(19)	3.739E-06	(1)	0.000E-01
Benthic Sediments:								
Mean		1.830E-04		2.234E-04		4.245E-06		0.000E-01
Max	(2)	2.750E-04	(2)	3.358E-04	(2)	6.380E-06	(2)	0.000E-01
Min	(20)	1.612E-04	(20)	1.968E-04	(20)	3.739E-06	(2)	0.000E-01

* Units: mg/L in Water Column; mg/kg in Benthos.
** Includes complexes with "dissolved" organics.

TABLE 7.09 (continued)

Table 18.01. Analysis of steady-state fate of organic chemical.

Steady-state Values by Process	Mass Flux Kg/ hour	% of Load	Half-Life* hours
Hydrolysis			
Reduction			
Radical oxidation			
Direct photolysis			
Singlet oxygen oxidation			
Bacterioplankton	1.0027E-02	18.12	369.2
Benthic Bacteria			
Surface Water-borne Export	4.5323E-02	81.88	81.69
Seepage export			
Volatilization			

Chemical Mass Balance:

Sum of fluxes =	5.5350E-02	
Sum of loadings =	5.5350E-02	
Allochthonous load:		100.0
Autochthonous load:		0.0
Residual Accumulation =	4.66E-09	0.0

* Pseudo-first-order estimates based on flux/resident mass.

Table 19. Summary time-trace of dissipation of steady-state chemical mass, following termination of allochthonous loadings.

Time	Average Chemical Concentrations				Total Chemical Mass	
Hours	Water Column		Benthic Sediments		Water Col	Benthic
	Free-mg/L	Sorb-mg/kg	Pore-mg/L	Sed-mg/kg	Total kg	Total kg
0	2.23E-04	4.25E-06	2.23E-04	4.25E-06	4.8	0.52
11	1.84E-04	3.49E-06	2.23E-04	4.24E-06	4.2	0.52
22	1.54E-04	2.92E-06	2.23E-04	4.24E-06	3.7	0.52
33	1.29E-04	2.46E-06	2.23E-04	4.24E-06	3.2	0.52
44	1.09E-04	2.07E-06	2.23E-04	4.23E-06	2.8	0.52
55	9.15E-05	1.74E-06	2.23E-04	4.23E-06	2.4	0.52
66	7.64E-05	1.45E-06	2.22E-04	4.22E-06	2.0	0.52
77	6.34E-05	1.20E-06	2.22E-04	4.22E-06	1.7	0.52
88	5.22E-05	9.91E-07	2.22E-04	4.21E-06	1.4	0.52
99	4.26E-05	8.09E-07	2.21E-04	4.20E-06	1.2	0.52
110	3.45E-05	6.55E-07	2.21E-04	4.20E-06	0.96	0.52
121	2.77E-05	5.26E-07	2.21E-04	4.19E-06	0.77	0.51
132	2.20E-05	4.19E-07	2.20E-04	4.18E-06	0.62	0.51

Table 20.01. Exposure analysis summary.

Exposure (maximum steady-state concentrations):
Water column: 3.358E-04 mg/L dissolved; total = 3.358E-04 mg/L
Benthic sediments: 3.358E-04 mg/L dissolved in pore water;
maximum total concentration = 2.750E-04 mg/kg (dry weight).
Biota (ug/g dry weight): Plankton: Benthos:

Fate:
Total steady-state accumulation: 5.34 kg, with 90.25% in the water column and 9.75% in the benthic sediments.
Total chemical load: 5.54E-02 kg/ hour. Disposition: 0.00% chemically transformed, 18.12% biotransformed, 0.00% volatilized, and 81.88% exported via other pathways.

Persistence:
After 132. hours of recovery time, the water column had lost 87.11% of its initial chemical burden; the benthic zone had lost 1.32%; system-wide total loss of chemical = 78.7%.
Five half-lives (>95% cleanup) thus require ca. 5. months.

TABLE 7.10. THE EXAMS II OUTPUTS FOR THE 1978 SIMULATION OF THE IOWA RIVER FOR ALACHLOR

Table 15.01. Distribution of chemical at steady state.

Seg #	Resident Mass Kilos	Resident Mass %	******** Chemical Concentrations ******** Total mg/*	Dissolved mg/L **	Sediments mg/kg	Biota ug/g
In the Water Column:						
1	1.7	4.66	2.500E-03	2.500E-03	4.750E-05	0.000E-01
3	3.6	9.68	1.352E-03	1.352E-03	2.569E-05	0.000E-01
5	1.5	4.01	1.098E-03	1.098E-03	2.087E-05	0.000E-01
7	2.8	7.53	7.980E-04	7.980E-04	1.516E-05	0.000E-01
9	1.5	4.07	6.813E-04	6.813E-04	1.294E-05	0.000E-01
11	2.9	7.78	9.742E-04	9.742E-04	1.851E-05	0.000E-01
13	5.6	15.01	1.322E-03	1.322E-03	2.511E-05	0.000E-01
15	4.1	10.88	1.495E-03	1.495E-03	2.841E-05	0.000E-01
17	7.0	18.69	1.618E-03	1.618E-03	3.075E-05	0.000E-01
19	6.6	17.68	1.704E-03	1.704E-03	3.237E-05	0.000E-01
	37.	92.03				
and in the Benthic Sediments:						
2	0.23	7.23	2.047E-03	2.500E-03	4.750E-05	0.000E-01
4	0.47	14.42	1.107E-03	1.352E-03	2.569E-05	0.000E-01
6	0.21	6.38	8.997E-04	1.098E-03	2.087E-05	0.000E-01
8	0.30	9.44	6.536E-04	7.980E-04	1.516E-05	0.000E-01
10	0.16	5.06	5.579E-04	6.813E-04	1.294E-05	0.000E-01
12	0.21	6.61	7.978E-04	9.742E-04	1.851E-05	0.000E-01
14	0.39	11.94	1.083E-03	1.322E-03	2.511E-05	0.000E-01
16	0.34	10.56	1.225E-03	1.495E-03	2.841E-05	0.000E-01
18	0.55	17.17	1.325E-03	1.618E-03	3.075E-05	0.000E-01
20	0.36	11.19	1.395E-03	1.704E-03	3.237E-05	0.000E-01
	3.2	7.97				

Total Mass (kilograms) = 40.53

* Units: mg/L in Water Column; mg/kg in Benthos.
** Includes complexes with "dissolved" organics.

Table 17.01. Steady-state concentration means and extrema.
Number in parens (Seg) indicates segment where value was found.

	Total Seg	Total mg/*	Dissolved Seg	Dissolved mg/L **	Sediments Seg	Sediments mg/kg	Biota Seg	Biota ug/gram
Water Column:								
Mean		1.354E-03		1.354E-03		2.573E-05		0.000E-01
Max	(1)	2.500E-03	(1)	2.500E-03	(1)	4.750E-05	(1)	0.000E-01
Min	(9)	6.813E-04	(9)	6.813E-04	(9)	1.294E-05	(1)	0.000E-01
Benthic Sediments:								
Mean		1.109E-03		1.354E-03		2.573E-05		0.000E-01
Max	(2)	2.047E-03	(2)	2.500E-03	(2)	4.750E-05	(2)	0.000E-01
Min	(10)	5.579E-04	(10)	6.813E-04	(10)	1.294E-05	(2)	0.000E-01

* Units: mg/L in Water Column; mg/kg in Benthos.
** Includes complexes with "dissolved" organics.

TABLE 7.10 (continued)

Table 18.01. Analysis of steady-state fate of organic chemical.

Steady-state Values by Process	Mass Flux Kg/ hour	% of Load	Half-Life* hours
Hydrolysis			
Reduction			
Radical oxidation			
Direct photolysis			
Singlet oxygen oxidation			
Bacterioplankton	7.7589E-02	11.91	362.1
Benthic Bacteria			
Surface Water-borne Export	0.5741	88.09	48.94
Seepage export			
Volatilization			

Chemical Mass Balance:

Sum of fluxes =	0.6517	
Sum of loadings =	0.6517	
Allochthonous load:		100.0
Autochthonous load:		0.0
Residual Accumulation =	7.45E-09	0.0

* Pseudo-first-order estimates based on flux/resident mass.

Table 19. Summary time-trace of dissipation of steady-state chemical mass, following termination of allochthonous loadings.

Time	Average Chemical Concentrations				Total Chemical Mass	
Hours	Water Column		Benthic Sediments		Water Col	Benthic
	Free-mg/L	Sorb-mg/kg	Pore-mg/L	Sed-mg/kg	Total kg	Total kg
0	1.35E-03	2.57E-05	1.35E-03	2.57E-05	37.	3.2
7	1.15E-03	2.18E-05	1.35E-03	2.57E-05	33.	3.2
14	9.85E-04	1.87E-05	1.35E-03	2.57E-05	29.	3.2
21	8.52E-04	1.62E-05	1.35E-03	2.57E-05	26.	3.2
28	7.41E-04	1.41E-05	1.35E-03	2.57E-05	23.	3.2
35	6.47E-04	1.23E-05	1.35E-03	2.57E-05	20.	3.2
42	5.66E-04	1.08E-05	1.35E-03	2.57E-05	18.	3.2
49	4.97E-04	9.45E-06	1.35E-03	2.57E-05	16.	3.2
56	4.37E-04	8.31E-06	1.35E-03	2.56E-05	14.	3.2
63	3.85E-04	7.32E-06	1.35E-03	2.56E-05	12.	3.2
70	3.39E-04	6.45E-06	1.35E-03	2.56E-05	11.	3.2
77	2.99E-04	5.68E-06	1.35E-03	2.56E-05	9.7	3.2
84	2.63E-04	5.00E-06	1.35E-03	2.56E-05	8.6	3.2

Table 20.01. Exposure analysis summary.

Exposure (maximum steady-state concentrations):
Water column: 2.500E-03 mg/L dissolved; total = 2.500E-03 mg/L
Benthic sediments: 2.500E-03 mg/L dissolved in pore water;
maximum total concentration = 2.047E-03 mg/kg (dry weight).
Biota (ug/g dry weight): Plankton: Benthos:

Fate:
Total steady-state accumulation: 40.5 kg, with 92.03% in the water column and 7.97% in the benthic sediments.
Total chemical load: 0.65 kg/ hour. Disposition: 0.00% chemically transformed, 11.91% biotransformed, 0.00% volatilized, and 88.09% exported via other pathways.

Persistence:
After 84.0 hours of recovery time, the water column had lost 76.84% of its initial chemical burden; the benthic zone had lost 0.57%; system-wide total loss of chemical = 70.8%.
Five half-lives (>95% cleanup) thus require ca. 6. months.

Since speciation of a metal in the aquatic environment is an important determinant of its toxic characteristics, however, discharge criteria based on total concentration of the compound may not be adequate.

Fate modeling of heavy metal species after discharge is an important step in establishing a waste load allocation. Model predictions are then coupled with the promulgated standards to estimate allowable discharge limits. Water quality based toxic control can be achieved by establishing a concentration standard for each metal species in the receiving waters. It is necessary, therefore, to be able to predict the concentration of a metal in a water body downstream from the discharge point of a given amount of the pollutant. The model used in this study for heavy metals waste load allocation is:

$$\frac{dC}{dx} = - \frac{k_s M_1 k\ b\ C}{u\left(1 + \frac{b\ C}{1000}\right)} + \frac{k_s M_1 r}{u} \qquad (7.1)$$

where C = dissolved metal concentration (ug/ℓ)
x = distance (mile)
k_s = settling coefficient (1/day)
u = mean velocity in the reach (mile/day)
b = binding constant for adsorption (L/mg)
r = sediment metal concentration (μg/Kg),
k = maximum adsorption capacity (m/kg),
M_1 = suspended solids concentration (kg/ℓ)

The equation may be solved numerically. The solution gives the dissolved concentration of heavy metal in the water column at any location along a stream. The model can be used to predict the level of discharge allowable in order to keep the pollution down to the recommended water quality standard. If the standard for the individual metal species were available, a waste load allocation based on the individual species could be used. This would be a more accurate methodology as each of these chemical species affect toxicity quite differently for the same metal. The species concentration can be calculated using the existing MINTEQ model and imposing the total metal concentration already available or calculated. The data used to calibrate this model were obtained from the Deep River study conducted by the North Carolina Department of Natural Resources and Community Development in cooperation with the EPA (1985). The computer model, in conjunction with the waste load allocation methodology, was applied for Cu and Zn.

The Deep River originates in eastern Forsyth County and flows through Piedmont, North Carolina to its confluence with the Haw River at the Catham-Lee County line. The upper Deep River from High Point Lake to the town of Randleman was the primary focus of this study. The study was conducted during August and September, 1983. At the time of the study, the Deep River was used extensively as a receiving stream for waste discharges. From its source to the Worthville Dam, the river receives 41 NPDES-permitted point source discharges. The majority of the facilities are small domestic discharges. There are several cooling water discharges to the river.

To evaluate the compliance with the standards, concentrations outside of the mixing zone were used. Usually the length of the mixing zone is specified on a case to case basis. We used the following equation

$$x_m = \frac{m\ W\ u^2}{D_y} \tag{7.2}$$

where x_m = flow distance required to achieve complete mixing
m = a parameter that varies from 0.4 to 0.5 (95% mixing)
D_y = lateral dispersion coefficient
W = width of the stream
u = flow velocity
D_y = 0.6 d u* ± 50%
d = water depth
u^* = shear velocity = $(gdS)^{0.5}$
g = acceleration due to gravity
S = slope of the channel

Because this was a slow flowing river, a slope of 1:1000 was assumed. An average width of 40 ft was used for the initial stretch of the stream where excessive pollution was observed. The mean water depth was 0.2 m and the velocity was 0.021 m/sec. The mixing length was calculated to be 12.1 m, i.e., about 0.01 miles. For the purpose of this waste load allocation, however, the concentrations after 0.25 miles from the discharge point were to be checked for compliance. The total initial concentration, the concentration after implementation of the waste load allocation, and the standard are plotted in Figures 7.14 and 7.15. It can be seen that copper clearly exceeds the standards between the 3 mile and 7 mile reaches. Zinc concentrations are rather high and range from 0.1 mg/ℓ to 0.4 mg/ℓ for 5 miles of the reach. A large amount of the water from the river is used for drinking water. There is not much evidence that zinc is deleterious to humans in these concentrations. It is seen that by reducing the concentration in the Jamestown discharge to 0.048 mg/ℓ from 0.250 mg/ℓ, the total copper concentration is brought down to the required standard of 0.02 mg/ℓ. The zinc concentration in the Jamestown discharge needs to be reduced from 0.465 mg/ℓ to 0.093 mg/ℓ to bring it below 0.05 mg/ℓ in the river. For the rest of the river, none of the metals exceeded the water quality standards.

If water quality criteria and standards were given for each chemical species rather than total heavy metal concentration, the waste load allocation would need to include chemical speciation. The speciation of copper and zinc were calculated at various points along the river using MINTEQ. The speciation of the dissolved metal was calculated first in the absence of organic ligands (e.g., fulvic acid) and then with a hypothetical organic ligand concentration of $10^{-4.5}$ M, which is a relatively large concentration. The results are listed in Table 7.11. In Table 7.11, with an absence of organic ligands, zinc was predominantly in the free Zn^{2+} form, whereas copper (II) was present mostly as the neutral hydroxy complex $Cu(OH)_2(aq)$ at pH around 7.2 and alkalinity averaging 100 mg/ℓ in the Deep River. When $10^{-4.5}$ M organic acid is assumed to be present, copper associated strongly with fulvic acid and upwards of 50% of the metal was

complexed as Cu>fulvate. Zinc was associated in Zn>fulvate to the extent of around 12%.

A waste load allocation for zinc would not be much affected by organic> Zn complexation, but an allocatin for copper would be significantly affected. If the complexed form of copper is not toxic, then the allowable discharge could be almost twice as large when organics are present at the $10^{>4.5}$ M concentration (probably a brown water system).

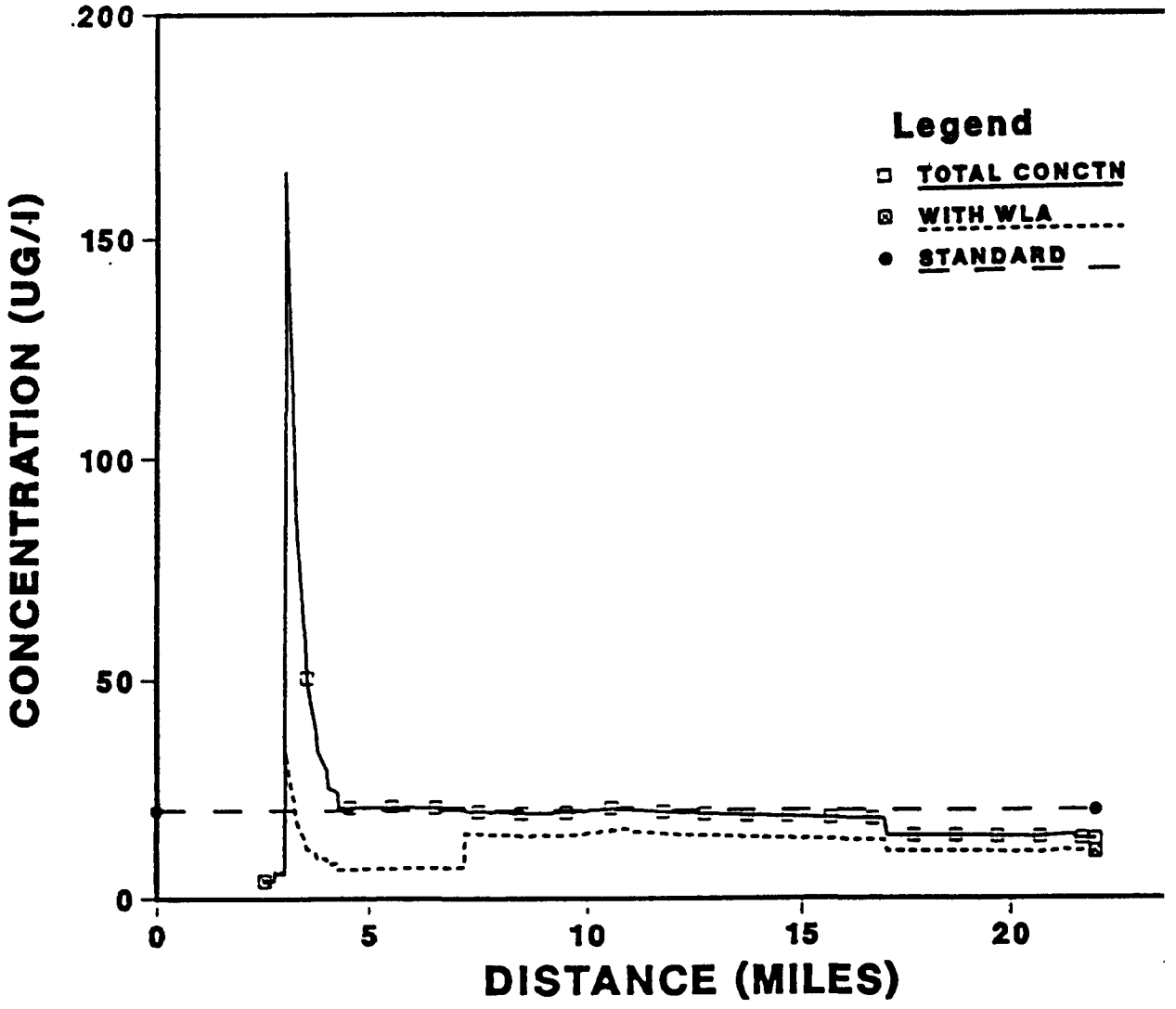


Figure 7.14. Total copper concentration: Initial and with WLA.

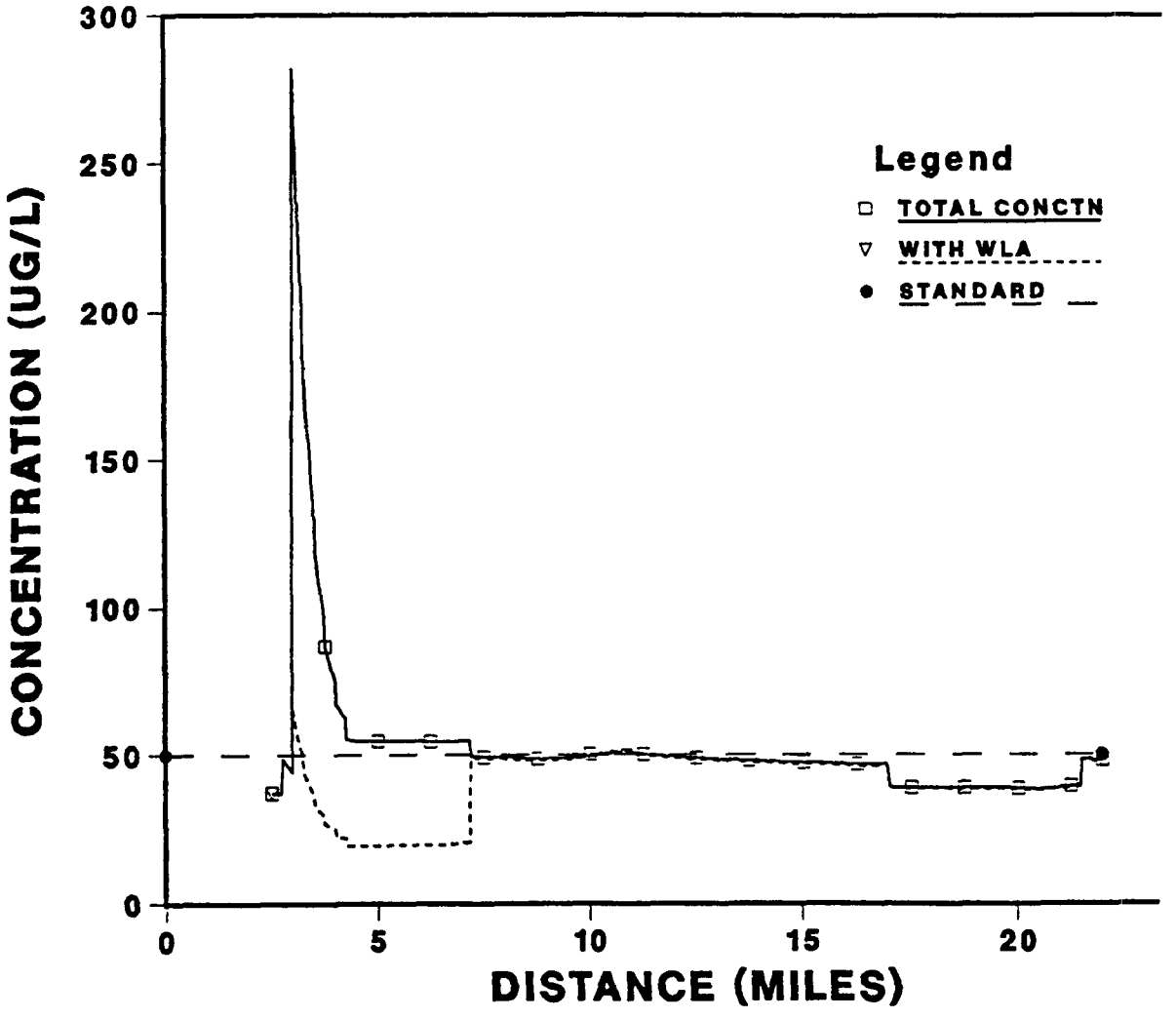


Figure 7.15. Total zinc concentration: Initial and wiwth WLA.

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Table 7.11. CHEMICAL SPECIES OF METALS AT VARIOUS SITES

(WITHOUT ORGANICS)
PERCENT OF THE TOTAL DISSOLVED METAL

Species	STATION D1	D3	D4	D5	D9	D10	D19	D21	D25	D26
Zn^{2+}	53.2	37.5	47.5	59.0	58.9	54.2	69.9	56.4	70.3	79.2
$ZnOH_+$	1.9	-	-	1.3	-	1.1	-	1.6	-	-
$ZnSO_4(aq)$	5.6	1.5	4.0	6.6	5.8	3.9	5.3	6.4	5.2	5.1
$ZnHCO_3^+$	8.3	17.3	19.6	10.2	14.4	13.5	13.7	9.2	15.7	10.7
$ZnCO_3(aq)$	27.1	34.7	24.9	20.9	18.5	24.6	10.0	23.7	8.1	4.5
$Zn(CO_3)_2^{2-}$	2.9	7.9	3.2	1.6	1.3	2.4	-2.1	-	-	
Cu^{2+}	2.2	2.5	4.7	4.3	6.5	4.2	13.6	3.1	17.0	27.2
$CuCO_3(aq)$	29.8	63.2	65.7	40.7	55.2	51.0	52.8	35.1	52.8	41.4
$Cu(OH)_2(aq)$	65.5	28.1	20.5	50.5	30.3	39.4	20.8	58.4	12.9	13.9
$CuHCO_3^+$	1.4	4.7	7.7	2.9	6.3	4.1	10.7	2.0	15.1	14.7
$CuOH^+$	-	-	-	-	-	-	1.1	-	-	1.3
$CuSO_4(aq)$	-	-	-	-	-	-	-	-	1.1	1.5

(FULVIC ACID = $10^{-4.5}$M)
PERCENT OF TOTAL DISSOLVED METAL

Species	STATION D1	D3	D4	D5	D9	D10
Zn^{2+}	46.8	34.7	43.1	51.4	51.5	47.7
$ZnOH_+$	1.7	-	-	1.1	-	-
$ZnSO_4(aq)$	4.9	1.4	3.6	5.7	5.1	3.4
$ZnHCO_3^+$	7.3	16.0	17.8	8.9	12.6	11.8
$ZnCO_3(aq)$	23.8	32.1	22.6	18.2	16.2	21.6
Zn-Fulvate	12.1	7.4	9.3	12.8	12.6	12.1
$Zn(CO_3)_2^{2-}$	2.5	7.3	2.9	1.4	1.1	2.1
Cu^{2+}	1.4	1.6	2.3	2.1	2.5	2.0
$CuCO_3(aq)$	19.1	41.0	32.8	19.7	21.3	24.8
$Cu(OH)_2(aq)$	42.0	18.2	10.2	24.4	11.7	19.2
$CuHCO_3^+$	-	3.0	3.8	1.4	2.5	2.0
Cu-Fulvate	36.0	35.2	50.1	51.6	61.6	51.3

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SECTION 8

SUMMARY

Each model has its proper application and limitation. As shown in Table 6.06, the EXAMS-II model is ideally suited for screening studies of toxic organics. It is modularly programmed and easy to use as a steady-state or time-variable model. TOXIWASP is best applied to toxic organic or heavy metal problems that are time-variable and may involve a contaminated sediment regime. It is particularly useful in the assessment of in-place pollutants, contamination, and bioaccumulation. HSPF is by far the most detailed and data intensive of the four models. It can be used for toxic organics or heavy metals, and it is the only model that tracks the fate of pollutants all the way from field to stream. Thus, it can best be used for nonpoint source problems that are highly dynamic. MINTEQ is the only model discussed for heavy metals speciation under chemical equilibrium conditions. It does not include transport or kinetics, but a test case showed how it is easily coupled with a simple transport model. It is well suited for site-specific water quality management of heavy metal pollutants.

Table 8.01 is a summary of the reaction and transport characteristics of the four models. As a chemical equilibrium model, MINTEQ has neither advective nor dispersive transport. EXAMS-II and TOXIWASP are compartmentalized models in which the user can specify an arbitrary arrangement for the compartments. In EXAMS-II, it is necessary to specify concentrations of suspended solids in each compartment, but in HSPF and TOXIWASP, the sediment concentrations are calculated as state variables from input parameters and initial conditions. Table 2.01 provides a summary of literature values for longitudinal velocity and dispersion characteristics in streams, and Table 2.02 provides vertical dispersivities for lakes.

Benthic sediment compartments can be layered in EXAMS-II and TOXIWASP because of the user-specified arrangement of compartments. HSPF has only one surficial, active sediment layer without the possibility of sediment burial. EXAMS-II is limited to a total of 20 compartments.

The chemical kinetics of EXAMS-II are second-order or pseudo-first order reactions, and it is possible to follow transformation products (e.g., metabolites or daughter products). In TOXIWASP and HSPF, it is possible to specify either first or second order kinetics for transformation reactions. MINTEQ has no kinetics, only chemical equilibrium. EXAMS-II allows for ionizations and acid-base reactions for up to a tri-protic system. MINTEQ includes all ionization and complexation reactions to be considered for heavy metal pollutants. All of the models assume a local

TABLE 8.01 TRANSPORT AND REACTION CHARACTERISTICS OF SELECTED FATE MODELS

Model	Advective Transport	Sediment Balance	Benthic Sediment	Kinetics	Ionization	Sorption
EXAMS-II	I	I	L	S,T	E	E
TOXIWASP, WASTOX	I,S I	S	L	F,S	-	E
HSPF	S	S	S_u	F,S,T	-	K
MINTEQ	-	-	-	E	E	E
	Input, Simulated		Surficial, Layered	First-order (empirical), Second-order, Transformation product		Equilibrium, Kinetic

equilibrium for sorption with suspended solids and bed sediment (sorption reactions are rapid relative to other transport and chemical reactions), but HSPF also has a kinetic option. The rate constants for the forward reaction (sorption) and backward reaction (desorption) must be known or calibrated.

Table 8.02 provides a summary of the reactions data provided in this manual from literature sources through 1986. For most carbamates and organo-P pesticides, like the pesticides carbofuran and parathion, chemical hydrolysis and biologically-mediated hydrolysis are the predominant reactions.

The fate of hydrophobic and persistent chemicals, such as DDT and PCBs and pentachlorophenol, is largely determined by sorption reactions over short time periods (days to a few years). These chemicals are quite resistant to reaction, have a large octanol/water partition coefficient, and are long-lived. Over time periods of years to decades, slow but significant processes become important, such as volatilization and biotransformation. The major challenge of predicting the fate and exposure concentrations for these chemicals is to properly quantify the slow transformation reactions that occur in the sediment over long periods of time, as well as gas transfer or volatilization with the atmosphere. There remains considerable uncertainty in estimating gas transfer/volatilization rates in large lakes for isomeric mixtures like PCBs and pesticides (e.g., chlordane) because the driving force for the reaction is often a small difference between two

TABLE 8.02. SUMMARY TABLE OF SIGNIFICANT REACTIONS IN THE LITERATURE.

	Biotrans-formations	Chemical Hydrolysis	Chemical Oxidation	Phototrans-formations	Volatili-zation	Sorption/ Bioconc.
Pesticides						
Carbofuran	x	x				
DDT	x	x			x	x
Parathion	x	x		x		
PCBs						
Aroclor 1248	x				x	x
Halogenated aliphatic hydrocarbons						
Chloroform	x	x			x	
Halogenated ethers						
2-Chloroethyl vinyl ether	x	x			x	
Monocyclic aromatics						
2,4-Dimethylphenol	x					
Pentachlorophenol	x			x		x
Phthalate esters						
Bis(2-ethylhexyl)phthalate	x	x				x
Polycyclic aromatic hydrocarbons						
Anthracene	x		x	x	x	x
Benzo[a]pyrene	x		x	x		x
Nitrosamines & Miscellaneous						
Benzidine			x	x		x
Dimethyl nitrosamine	x					

relatively large numbers (the polluted atmospheric gas phase concentration and the aqueous phase lake concentration).

For many organic chemicals with intermediate octanol/water partition coefficients, the most important reactions are biotransformation reactions (Table 8.02). This is true for halogenated aliphatic hydrocarbons, aromatics and phthalate esters. Some of the chemicals undergo a variety of reactions including hydrolysis, phototransformation and volatilization, but biological transformations are often the most important. Because biological transformations are so important, there is no substitute for laboratory and field studies on biotransformation rates. Theory on prediction of biotransformation rates from structure activity relationships is not so advanced to give much guidance.

In summary, to determine the fate of an organic chemical in a given transport regime, there are three important parameters: the octanol/water partition coefficient (K_{ow}), the volatilization rate constant which is dependent on Henry's constant (H), and the sum of the pseudo-first order rate constants for all other reactions (Σk). The octanol/water partition coefficient provides an estimate of sorption and bioconcentration. K_{ow} values are presented in Table 3.07 and Appendix A2. Henry's constants (and the solubility and vapor pressure data needed to estimate Henry's constants) are given in Table 3.06 and Appendix A5. Other rate constants in the literature, including biotransformation, are provided in Appendix A. Section 7 shows the considerable difference in fate of a hydrophobic, persistent chemical (DDT) and a pesticide (alachlor) that undergoes biological transformation. The dynamic nature of pesticide runoff events could only be captured by HSPF.

Table 8.03 is a summary of the most important reactions for the eight heavy metals discussed in this report. Two of the metals, arsenic and selenium, often occur as anions in aerobic environments, arsenate and selenate. All of the metals are known to undergo ion exchange or sorption with iron oxide and aluminum oxide coating in sediments, but cadmium, lead, zinc and copper are the most reported in the literature. All of the metals that exist as cations (Cd, Hg, Pb, Ba, Zn, Cu) take on hydroxyl-groups and inorganic ligands such as chloride, sulfate, and carbonate. They are hydrated in water and normally have a coordination number of four (two times their valence) in complexation reactions. Organic complexation is a particularly important reaction, and difficult to quantify, for copper and (to a lesser extent) for cadmium, mercury, lead and zinc. Surrogate organics (salicylate, oxalate, humic acids) can be used to investigate the strength of organic-metal complexes, but knowledge of the conditional stability of complex formation in the surface water being modeled is strongly advised.

Perhaps the heavy metal reactions that are most difficult to quantify are the methylation reactions (for Hg and As) and other redox reactions (for As, Se, and Pb). These reactions are slow compared to the other acid-base and complexation reactions. It is not appropriate to use a chemical equilibrium thermodynamic model for these reactions, so the kinetic rate

constants must be known or calibrated from field measurements and model simulations.

Because water quality standards and maximum contaminant levels (MCLs) for drinking water have been adopted for most heavy metals, future modeling for waste load allocations is imminent. MINTEQ can be combined with another fate model such as EXAMS-II, TOXIWASP, or a simple analytic model (Section 5 and 7.5) to estimate the chemical concentrations and speciation. A recursive scheme could be developed in which the fate model would be used to estimate the total metal concentration and MINTEQ would be used to partition the metal and determine the concentration of each species.

This report should aid the modeler in understanding and choosing appropriate models, in determining rate constants for input to the models, and in interpreting the results.

TABLE 8.03 SUMMARY TABLE OF SIGNIFICANT HEAVY METAL REACTIONS

	Anion Exchange	Sorption Potential	Acid-Base Hydrolysis	Complexation w/Inorganic Ligands	Complexation w/Organic Ligands	Methylation or Redox Rxns.
Cadmium		x	x	x	x	
Arsenic	x					x
Mercury		x	x	x	x	x
Selenium	x					x
Lead		x	x	x	x	x
Barium			x	x		
Zinc		x	x	x	x	
Copper		x	x	x	x	

TABLE A1. BIODEGRADATION

Chemical	First-Order Decay Rate	Population cells/ml	Concentration µg/ℓ	Chemical Aerobic Conditions	Reference
1,1,1-Trichloroethane	0.0154/hr	primary sewage	10,000	yes	Tabak, 1981
1,1,1-Trichloroethane	0.002/hr	primary sewage	5,000	yes	Tabak, 1981
1,1,2,2-Tetrachloroethane	0	primary sewage	10,000	yes	Tabak, 1981
1,1,2,2-Tetrachloroethane	0	primary sewage	5,000	yes	Tabak, 1981
1,1,2-Trichloroethane	0	primary sewage	10,000	yes	Tabak, 1981
1,1,2-Trichloroethane	0.00038/hr	primary sewage	5,000	yes	Tabak, 1981
1,1-Dichloroethane	0.002/hr	primary sewage	10,000	yes	Tabak, 1981
1,1-Dichloroethane	0.0041/hr	primary sewage	5,000	yes	Tabak, 1981
1,1-Dichloroethylene	0.009/hr	primary sewage	5,000	yes	Tabak, 1981
1,1-Dichloroethylene	0.0035/hr	primary sewage	10,000	yes	Tabak, 1981
1,2,4-Trichlorobenzene	0.0033/hr	primary sewage	10,000	yes	Tabak, 1981
1,2,4-Trichlorobenzene	0.0046/hr	primary sewage	5,000	yes	Tabak, 1981
1,2,4-Trichlorobenzene	0.00083/hr*	activated sludge			Callahan, 1979, p. 76-6
1,2,4-Trichlorobenzene	0.0019/hr*	industrial wastewater	2,600		Callahan, 1979, p. 76-6
1,2,4-Trichlorobenzene	0.0033/hr*	industrial wastewater	1,700		Callahan, 1979, p. 76-6
1,2-Benzanthracene	0	primary sewage	10,000	yes	Tabak, 1981
1,2-Benzanthracene	0.00104/hr	primary sewage	5,000	yes	Tabak, 1981
1,2-Dichlorobenzene	0.00133/hr	primary sewage	10,000	yes	Tabak, 1981
1,2-Dichlorobenzene	0.00354/hr	primary sewage	5,000	yes	Tabak, 1981
1,2-Dichloroethane	0.0018/hr	primary sewage	5,000	yes	Tabak, 1981
1,2-Dichloroethane	0.00133/hr	primary sewage	10,000	yes	Tabak, 1981
1,2-Dichloroethylene-cis	0.0033/hr	primary sewage	10,000	yes	Tabak, 1981
1,2-Dichloroethylene-cis	0.0096/hr	primary sewage	5,000	yes	Tabak, 1981
1,2-Dichloroethylene-trans	0.0066/hr	primary sewage	5,000	yes	Tabak, 1981
1,2-Dichloroethylene-trans	0.00304/hr	primary sewage	10,000	yes	Tabak, 1981
1,2-Dichloropropane	0.00325/hr	primary sewage	5,000	yes	Tabak, 1981
1,2-Dichloropropane	0.0026/hr	primary sewage	10,000	yes	Tabak, 1981
1,2-Diphenylhydrazine	0.0076/hr	primary sewage	10,000	yes	Tabak, 1981
1,2-Diphenylhydrazine	0.0096/hr	primary sewage	5,000	yes	Tabak, 1981
1,3-Dichlorobenzene	0.00516/hr	primary sewage	10,000	yes	Tabak, 1981
1,3-Dichlorobenzene	0.0053/hr	primary sewage	5,000	yes	Tabak, 1981
1,3-Dichloropropene	0.0046/hr	primary sewage	10,000	yes	Tabak, 1981
1,3-Dichloropropene	0.00475/hr	primary sewage	5,000	yes	Tabak, 1981
1,4-Chlorophenol	0.0096/hr	aquatic systems			Scow, 1982

TABLE A1 (continued)

Chemical	First-Order Decay Rate	Population cells/ml	Chemical Concentration µg/ℓ	Aerobic Conditions	Reference
1,4-Dichlorobenzene	0.00475/hr	primary sewage	5,000	yes	Tabak, 1981
1,4-Dichlorobenzene	0.0028/hr	primary sewage	10,000	yes	Tabak, 1981
2,2',4,4'-PCB	no biodegradation observed				Bailey, Gonsior & Rhinehart, 1983
2,4,5-T	0.348/hr*	200,000,000	1,000	yes	Kilbane, 1982
2,4-D	18.5/hr	180,000,000,000	1,000	yes	Paris, 1981
2,4-D	0.297/hr	2,100,000,000	1,000	yes	Paris, 1981
2,4-D	0.0095/hr	10,000,000	10,000	yes	Liu, Thomson & Strachan, 1981
2,4-D	4.22/hr	26,000,000,000	100	yes	Paris, 1981
2,4-D	0.56/hr	1,900,000,000	100,10	yes	Paris, 1981
2,4-D	0.00116/hr*	500,000	50,000	yes	Nesbitt & Watson, 1980
2,4-D	34.8/hr	200,000,000,000	100	yes	Paris, 1981
2,4-D	7.71/hr	41,000,000,000	10	yes	Paris, 1981
2,4-D	0.517/hr	2,900,000,000	100	yes	Paris, 1981
2,4-D	1.92/hr	14,000,000,000	1,000	yes	Paris, 1981
2,4-D	19/hr	180,000,000,000	10	yes	Paris, 1981
2,4-D	0.00021/hr	10,000,000	10,000	no	Liu, Thomson & Strachan, 1981
2,4-Dichlorophenol	0.0274/hr	primary sewage	10,000	yes	Tabak, 1981
2,4-Dimethylphenol	0.0234/hr*	activated sludge	50	yes	Petrasek, 1983
2,4-Dimethylphenol	0.0274/hr	primary sewage	10,000	yes	Tabak, 1981
2,4-Dinitrophenol	0.0068/hr	primary sewage	10,000	yes	Tabak, 1981
2,4-Dinitrophenol	0.00546/hr	primary sewage	5,000	yes	Tabak, 1981
2,4-Dinitrotoluene	0.00875/hr	primary sewage	5,000	yes	Tabak, 1981
2,4-Dinitrotoluene	0.00413/hr	primary sewage	10,000	yes	Tabak, 1981
2,6-Dinitrotoluene	0.0102/hr	primary sewage	5,000	yes	Tabak, 1981
2,6-Dinitrotoluene	0.00504/hr	primary sewage	10,000	yes	Tabak, 1981
2,6-Dinitrotoluene	0.001/hr	primary sewage	10,000	no	Hallas & Alexander, 1983
2-Acetylaminofluorene	0.00092/hr*				Fochtman, 1981
2-Chlorobiphenyl	0.0069/hr	lake water baacteria			Callahan, 1979, p. 36-13
2-Chloroethyl vinyl ether	0.00438/hr	primary sewage	10,000	yes	Tabak, 1981
2-Chloroethyl vinyl ether	0.0085/hr	primary sewage	5,000	yes	Tabak, 1981
2-Chlorophenol	0.0105/hr	primary sewage	10,000	yes	Tabak, 1981
2-Chlorophenol	0.0117/hr	primary sewage	5,000	yes	Tabak, 1981
2-Ethylhexyl diphenyl phosphate	0.0144/hr*				Saeger, 1979
4,6-Dinitrophenol	0	primary sewage	10,000	yes	Tabak, 1981

TABLE A1 (continued)

Chemical	First-Order Decay Rate	Population cells/ml	Chemical Concentration µg/ℓ	Aerobic Conditions	Reference
4,6-Dinitrophenol	0.00438/hr	primary sewage	5,000	yes	Tabak, 1981
4-Aminobiphenyl	0.00413/hr*				Fochtman, 1981
4-Bromodiphenyl ether	0	primary sewage	10,000	yes	Tabak, 1981
4-Bromodiphenyl ether	0	primary sewage	5,000	yes	Tabak, 1981
4-Chlorobiphenyl	0.0039/hr				Callahan, 1979, p. 36-13
4-Chloroethyl vinyl ether	0	primary sewage	10,000	yes	Tabak, 1981
4-Chloroethyl vinyl ether	0	primary sewage	5,000	yes	Tabak, 1981
4-Chlorophenyl phenyl ehter	0.173/hr	activated sludge			Callahan, 1979, p. 68-4
Acenaphthene	0.0044/hr*	activated sludge	50	yes	Petrasek, 1983
Acenaphthene	0.0178/hr	primary sewage	5,000	yes	Tabak, 1981
Acenaphthylene	0.0167/hr	primary sewage	10,000	yes	Tabak, 1981
Alachlor	0.0023/hr				Cartwright, 1980
Aldrin	0.00138/hr*	river water		yes	Callahan, 1979, p. 21-8
Aldrin	0	primary sewage	10,000	yes	Tabak, 1981
Aldrin	0	primary sewage	5,000	yes	Tabak, 1981
Anthracene	0.00179/hr	primary sewage	10,000	yes	Tabak, 1981
Anthracene	~0*	activated sludge	50	yes	Petrasek, 1983
Anthracene	0.00333/hr	primary sewage	5,000	yes	Tabak, 1981
Anthracene	0.612/hr	river water			Callahan, 1979, p. 95-11
Anthracene	2.9-22.9E-4/hr	aquatic systems			Scow, 1982
Aroclor 1016	0.00346/hr	primary sewage	5,000	yes	Tabak, 1981
Aroclor 1016	0.00208/hr	primary sewage	10,000	yes	Tabak, 1981
Aroclor 1016	0.0083/hr*	activated sludge			Callahan, 1979, p. 36-12
Aroclor 1221	0.0274/hr	primary sewage	10,000	yes	Tabak, 1981
Aroclor 1221	0.0346/hr*	activated sludge			Callahan, 1979, p. 36-12
Aroclor 1242	0.00246/hr	primary sewage	10,000	yes	Tabak, 1981
Aroclor 1242	0.00275/hr	primary sewage	5,000	yes	Tabak, 1981
Aroclor 1242	0.00625/hr*	activated sludge			Callahan, 1979, p. 36-12
Aroclor 1248	0	primary sewage	5,000	yes	Tabak, 1981
Aroclor 1248	0	primary sewage	10,000	yes	Tabak, 1981
Aroclor 1254	0*	activated sludge	150	yes	Petrasek, 1983
Aroclor 1254	0.000708/hr	primary sewage	5,000	yes	Tabak, 1981
Aroclor 1254	0.000625/hr	primary sewage	10,000	yes	Tabak, 1981
Aroclor 1254	0.00438/hr*	activated sludge			Callahan, 1979, p. 36-12

TABLE A1 (continued)

Chemical	First-Order Decay Rate	Population cells/ml	Chemical Concentration µg/ℓ	Aerobic Conditions	Reference
Aroclor 1260	0	primary sewage	5,000	yes	Tabak, 1981
Aroclor 1260	0	primary sewage	10,000	yes	Tabak, 1981
Atrazine	0.00899/hr	aquatic systems			Scow, 1982
Benzene	0.004/hr	primary sewage	5,000	yes	Tabak, 1981
Benzene	0.00275/hr	primary sewage	10,000	yes	Tabak, 1981
Benzene	0.00458/hr	aquatic systems			Scow, 1982
Benzo[a]anthracene	0.0022/hr*	activated sludge	50	yes	Petrasek, 1983
Benzo[a]anthracene	0	aquatic systems			Scow, 1982
Benzo[a]pyrene	0	aquatic systems			Scow, 1982
Benzo[a]pyrene	0.00312/hr*				Fochtman, 1981
Bezo[ghi]perylene	0.00546/hr*				Fochtman, 1981
Benzo[k]fluoranthene	0.00463/hr*				Fochtman, 1981
Bis(2-chloroethoxy)methane	0	primary sewage	10,000	yes	Tabak, 1981
Bis(2-chloroisopropyl)ether	0.0113/hr	primary sewage	5,000	yes	Tabak, 1981
Bis(2-chloroisopropyl)ether	0.0059/hr	primary sewage	10,000	yes	Tabak, 1981
Bis(2-ethylhexyl)phthalate	0*	activated sludge	50	yes	Petrasek, 1983
Bis(2-ethylhexyl)phthalate	0.00008/hr	sediment microbiota	18.2	yes	Johnson & Heitkamp, 1984
Bis(2-ethylhexyl)phthalate	0.000133/hr	sediment microbiota	18.2	yes	Johnson & Heitkamp, 1984
Bis(2-ethylhexyl)phthalate	0	primary sewage	10,000	yes	Tabak, 1981
Bis(2-ethylhexyl)phthalate	0.00011/hr	sediment microbiota	182	yes	Johnson & Heitkamp, 1984
Bis(2-ethylhexyl)phthalate	0.000104/hr	sediment microbiota	1,820	yes	Johnson & Heitkamp, 1984
Bis(2-ethylhexyl)phthalate	0	primary sewage	5,000	yes	Tabak, 1981
Bis(2-ethylhexyl)phthalate	0.000225/hr	sediment microbiota	10,000	yes	Johnson & Heitkamp, 1984
Bis(2-ethylhexyl)phthalate	0.00103/hr	river water			Callahan, 1979, p. 94-12
Bis(2-ethylhexyl)phthalate	0.0058/hr*	shake culture	0.8%		Callahan, 1979, p. 94-12
Bromoform	0.00067/hr	primary sewage	5,000	yes	Tabak, 1981
Bromoform	0.00025/hr	primary sewage	10,000	yes	Tabak, 1981
Butylbenzylphthalate	0*	activated sludge	50	yes	Petrasek, 1983
Butylbenzylphthalate	0.0144/hr		9.73		Gledhill, 1980
Butylbenzylphthalate	>0.0144/hr	river water			Callahan, 1979, p. 94-12
Carbaryl	0.00525/hr*	activated sludge	10,000	yes	Monnig, 1980
Carbaryl	0.00825/hr	river water	5,000		Sharom, 1980
Carbofuran	0.001375/hr	river water	5,000		Sharom, 1980
Carbon tetrachloride	0.0096/hr	primary sewage	10,000	yes	Tabak, 1981

TABLE A1 (continued)

Chemical	First-Order Decay Rate	Population cells/ml	Chemical Concentration µg/ℓ	Aerobic Conditions	Reference
Carbon tetrachloride	0.0121/hr	primary sewage	5,000	yes	Tabak, 1981
Chlordane	0	primary sewage	5,000	yes	Tabak, 1981
Chlordane	0	primary sewage	10,000	yes	Tabak, 1981
Chlorobenzene	0.0131/hr	primary sewage	5,000	yes	Tabak, 1981
Chlorobenzene	0.00212/hr	primary sewage	10,000	yes	Tabak, 1981
Chlorobenzene	0.00038/hr	sediment			Scow, 1982
Chlorobenzene	0.000188/hr	aquatic systems			Scow, 1982
Chlorodibromomethane	0.0017/hr	primary sewage	5,000	yes	Tabak, 1981
Chlorodibromomethane	0.00063/hr	primary sewage	10,000	yes	Tabak, 1981
Chloroform	0.004/hr	primary sewage	5,000	yes	Tabak, 1981
Chloroform	0.0037/hr	primary sewage	10,000	yes	Tabak, 1981
Chyrsene	0.00038/hr	primary sewage	5,000	yes	Tabak, 1981
Chrysene	0.00054/hr*	activated sludge	50	yes	Petrasek, 1983
Chrysene	0	primary sewage	10,000	yes	Tabak, 1981
Cresyl diphenyl phosphate	0.00962/hr*				Saeger, 1979
DDD	0	primary sewage	10,000	yes	Tabak, 1981
DDD	0	primary sewage	5,000	yes	Tabak, 1981
DDE	0	primary sewage	5,000	yes	Tabak, 1981
DDE	0	primary sewage	10,000	yes	Tabak, 1981
DDE	0.000025/hr	aquatic systems			Scow, 1982
DDT	0.00344/hr	river water	100	yes	Sharom & Miles, 1981
DDT	0	primary sewage	5,000	yes	Tabak, 1981
DDT	0	primary sewage	10,000	yes	Tabak, 1981
DDT	0.00413/hr	river water	100		Sharom, 1980
Di-isooctyl phthalate	0.000167/hr	sediment microbiota	10,000	yes	Johnson & Heitkamp, 1984
Di-isooctyl phthalate	0.000055/hr	sediment microbiota	19.7	yes	Johnson & Heitkamp, 1984
Di-isooctyl phthalate	0.000053/hr	sediment microbiota	1,970	yes	Johnson & Heitkamp, 1984
Di-isooctyl phthalate	0.00004/hr	sediment microbiota	18.3	yes	Johnson & Heitkamp, 1984
Di-isooctyl phthalate	0.000058/hr	sediment microbiota	197	yes	Johnson & Heitkamp, 1984
Di-n-butyl phthalate	0.00525/hr	sediment microbiota	82	yes	Johnson & Heitkamp, 1984
Di-n-butyl phthalate	0.00577/hr	sediment microbiota	82	yes	Johnson & Heitkamp, 1984
Di-n-butyl phthalate	0.00346/hr*	activated sludge	50	yes	Petrasek, 1983
Di-n-butyl phthalate	0.00525/hr	sediment microbiota	820	yes	Johnson & Heitkamp, 1984
Di-n-octyl phthalate	0	primary sewage	5,000	yes	Tabak, 1981

TABLE A1 (continued)

Chemical	First-Order Decay Rate	Population cells/ml	Chemical Concentration µg/ℓ	Aerobic Conditions	Reference
Di-n-octyl phthalate	0	activated sludge	50	yes	Petrasek, 1983
Di-n-octyl phthalate	0	primary sewage	10,000	yes	Tabak, 1981
Di-n-octyl phthalate	0.000962/hr				Callahan, 1979, p. 94-12
Diazinon	0.000156/hr	aquatic systems			Scow, 1982
Diazinon	0.000825/hr	river water	5,000		Sharom, 1980
Dibenzo[ah]anthracene	0.00546/hr*				Fochtman, 1981
Dibutyl phenyl phosphate	0.00825/hr*				Saeger, 1979
Dichlorobromomethane	0.00258/hr	primary sewage	5,000	yes	Tabak, 1981
Dichlorobromomethane	0.00256/hr	primary sewage	10,000	yes	Tabak, 1981
Dieldrin	0	primary sewage	5,000	yes	Tabak, 1981
Dieldrin	0	primary sewage	10,000	yes	Tabak, 1981
Dieldrin	0.000079/hr	river water	2,000		Sharom, 1980
Diethyl phthalate	0.00988/hr*	activated sludge	50	yes	Petrasek, 1983
Dimethyl phthalate	0.0191/hr*	activated sludge	50	yes	Petrasek, 1983
Dioxin	0.000048/hr	sediment	710-1830	no	Ward & Matsumura, 1978
Dioxin	2-2.8E-5/hr*	lake water	710-1830	no	Ward & Matsumura, 1978
Endosulfan	0.00412/hr	100,000 [Pseudomonas]		yes	Callahan, 1979, p. 27-9
Endosulfan	0.00361/hr	river water	200		Walker, 1984
Endosulfan sulfate	0	primary sewage	10,000	yes	Tabak, 1981
Endosulfan-alpha	0	primary sewage	10,000	yes	Tabak, 1981
Endosulfan-alpha	0	primary sewage	5,000	yes	Tabak, 1981
Endosulfan-beta	0	primary sewage	5,000	yes	Tabak, 1981
Endosulfan-beta	0	primary sewage	10,000	yes	Tabak, 1981
Endrin	0	primary sewage	5,000	yes	Tabak, 1981
Endrin	0	primary sewage	10,000	yes	Tabak, 1981
Endrin	0.000108/hr	river water	2,000		Sharom, 1980
Ethyl benzene	0.00696/hr	primary sewage	10,000	yes	Tabak, 1981
Fluoranthene	0*	activated sludge	50	yes	Petrasek, 1983
Fluoranthene	0	primary sewage	5,000	yes	Tabak, 1981
Fluoranthene	0	primary sewage	10,000	yes	Tabak, 1981
Fluorene	0.0102/hr	primary sewage	5,000	yes	Tabak, 1981
Fluorene	0.00625/hr	primary sewage	10,000	yes	Tabak, 1981
Fluorene	0.00325/hr	activated sludge	50	yes	Petrasek, 1983
Heptachlor	-0*	activated sludge	50	yes	Petrasek, 983

TABLE A1 (continued)

Chemical	First-Order Decay Rate	Population cells/ml	Chemical Concentration µg/ℓ	Aerobic Conditions	Reference
Heptachlor	0	primary sewage	10,000	yes	Tabak, 1981
Heptachlor	0	primary sewage	5,000	yes	Tabak, 1981
Heptachlor epoxide	0	primary sewage	5,000	yes	Tabak, 1981
Heptachlor epoxide	0	primary sewage	10,000	yes	Tabak, 1981
Hexachlorobenzene	0.00142/hr	primary sewage	10,000	yes	Tabak, 1981
Hexachlorobenzene	0.00488/hr	primary sewage	5,000	yes	Tabak, 1981
Hexachlorocyclohexane alpha	0	primary sewage	10,000	yes	Tabak, 1981
Hexachlorocyclohexane alpha	0	primary sewage	5,000	yes	Tabak, 1981
Hexachlorocyclohexane beta	0	primary sewage	5,000	yes	Tabak, 1981
Hexachlorocyclohexane beta	0	primary sewage	10,000	yes	Tabak, 1981
Hexachlorocyclohexane delta	0	primary sewage	5,000	yes	Tabak, 1981
Hexachlorocyclohexane delta	0	primary sewage	10,000	yes	Tabak, 1981
Isodecyl diphenyl phosphate	0.0024/hr*				Saeger, 1979
Isopropylphenyl diphenyl phosphate	0.00825/hr*				Saeger, 1979
Lindane	0.00171/hr*	activated sludge	50	yes	Petrasek, 1983
Lindane	0	primary sewage	10,000	yes	Tabak, 1981
Lindane	0	primary sewage	5,000	yes	Tabak, 1981
Lindane	0.000687/hr	river water	2,000		Sharom, 1980
N-nitroso-di-n-propylamine	0.00188/hr	primary sewage	5,000	yes	Tabak, 1981
N-nitroso-di-n-propylamine	0	primary sewage	10,000	yes	Tabak, 1981
N-nitrosodiphenylamine	0.0038/hr	primary sewage	10,000	yes	Tabak, 1981
N-nitrosodiphenylamine	0.0121/hr	primary sewage	5,000	yes	Tabak, 1981
Naphthalene	0.00875/hr*	activated sludge	50	yes	Petrasek, 1983
Nitrobenzene	0.0121/hr	primary sewage	10,000	yes	Tabak, 1981
Nitrobenzene	0.0032/hr*			yes	Hallas & Alexander, 1983
Nitrobenzene	0.00192/hr*			no	Hallas & Alexander, 1983
Parathion	0.0048/hr	river water	5,000	yes	Sharom & Miles, 1981
Parathion	0.004125/hr	river water	5,000		Sharom, 1980
Parathion	<0.0000068/hr	aquatic systems			Scow, 1982
Pentachlorophenol	0.00155/hr	pond water w/o sediment	1,400	yes	Boyle, 1980
Pentachlorophenol	0*	activated sludge	50	yes	Petrasek, 1983
Pentachlorophenol	0.0024/hr	littoral microcosm	41	yes	Knowlton & Huckins, 1983
Pentachlorophenol	0.01155/hr*	9,300,000	32.6	yes	Pignatello, 1983
Pentachlorophenol	0.00104/hr	primary sewage	10,000	yes	Tabak, 1981
Pentachlorophenol	0.00125/hr	primary sewage	5,000	yes	Tabak, 1981

TABLE A1 (continued)

Chemical	First-Order Decay Rate	Population cells/ml	Chemical Concentration µg/ℓ	Aerobic Conditions	Reference
Pentachlorophenol	0.0198/hr*	9,300,000	76	yes	Pignatello, 1983
Pentachlorophenol	0.00208/hr	pond water & sediment	1,500	yes	Boyle, 1980
Pentachlorophenol	1.074/hr	activated sludge	2,000	yes	Liu, Thomson & Strachan, 1981
Pentachlorophenol	0.05776/hr*	9,300,000	199	yes	Pignatello, 1983
Pentachlorophenol	1.4/hr	acclimated activated	2,000	no	Liu, Thomson & Strachan, 1981
Pentachlorophenol	0.00225/hr	pond water & sediment	1,200	no	Boyle,1980
Pentachlorophenol	0.00036/hr	pond water w/o sediment	1,300	no	Boyle, 1980
Pentachlorophenol	7.5-34E-5/hr*	anaerobic digestors	1,000-1,500	no	Guthrie, 1984
Phenanthrene	0.00275/hr*	activated sludge	50	yes	Petrasek, 1983
Phenol	0.0137/hr*	activated sludge	50	yes	Petrasek, 1983
Phenol	0.0191/hr	primary sewage	5,000	yes	Tabak, 1981
Phenol	0.0209/hr	primary sewage	10,000	yes	Tabak, 1981
Phenol	0.0329/hr	aquatic systems			Scow, 1982
Pyrene	0.00738/hr	primary sewage	5,000	yes	Tabak, 1981
Pyrene	0.000708/hr	primary sewage	10,000	yes	Tabak, 1981
Pyrene	0*	activated sludge	50	yes	Petrasek, 1983
Terbutryn	0.00012/hr	pond water	1,000	yes	Muir, 1982
Terbutryn	0.00016/hr	river water	1,000	yes	Muir, 1982
Terbutryn	0.000076/hr	sediment	1,000	yes	Muir, 1982
Tert-butylphenyl diphenyl	0.0072/hr*				Saeger, 1979
Tetrachloroethylene	0.00212/hr	primary sewage	10,000	yes	Tabak, 1981
Tetrachloroethylene	0.00354/hr	primary sewage	5,000	yes	Tabak, 1981
Toxaphene	-0*	activated sludge	150	yes	Petrasek, 1983
Toxaphene	0.00067/hr*	sediment		no	Callahan, 1979, p. 35-6
Tributyl phosphate	0.00577/hr*				Saeger, 1979
Trichloroethylene	0.00283/hr	primary sewage	10,000	yes	Tabak, 1981
Trichloroethylene	0.00608/hr	primary sewage	5,000	yes	Tabak, 1981
Trichlorofluoromethane	0.00529/hr	primary sewage	5,000	yes	Tabak, 1981
Trichlorofluoromethane	0.00283/hr	primary sewage	10,000	yes	Tabak, 1981
Tricresyl phosphate	0.0096/hr*				Saeger, 1979
Trifluralin	0.00385/hr	river water	200		Walker, 1984
Triphenyl phosphate	0.0144/hr*				Saeger, 1979
p-Chloro-m-cresol	0.0085/hr	primary sewage	10,000	yes	Tabak, 1981
p-Chloro-m-cresol	0.009/hr	primary sewage	5,000	yes	Tabak, 1981

* Calculated from data presented

TABLE A1 (continued)

Chemical	Zero-Order Reaction Rate	Second-Order Reaction Rate	Microbial Population cells/mℓ	Chemical Concentration µg/ℓ	Aerobic Conditions	Reference
1,1,2-Trichloroethane		3E-15 ℓ/cell-hr (e)				Mabey et al., 1982
1,1,2,2-Tetrachloroethane		3E-15 ℓ/cell-hr (e)				Mabey et al., 1982
1,2,4-Trichlorobenzene		1E-13 ℓ/cell-hr (e)				Mabey et al., 1982
1,2-Dichlorobenzene		1E-13 ℓ/cell-hr (e)				Mabey et al., 1982
1,2-Dichloroethane		1E-13 ℓ/cell-hr (e)				Mabey et al., 1982
1,2-Dichloropropane		1E-13 ℓ/cell-hr (e)				Mabey et al., 1982
1,2-Diphenylhydrazine		1E-13 ℓ/cell-hr (e)				Mabey et al., 1982
1,3-Dichlorobenzene		1E-13 ℓ/cell-hr (e)				Mabey et al., 1982
1,3-Dichloropropene		1E-13 ℓ/cell-hr (e)				Mabey et al., 1982
1,4-Dichlorobenzene		1E-13 ℓ/cell-hr (e)				Mabey et al., 1982
2,2',3,3'-PCB	7.3 nM/ml-hr		440,000,000	146		Furukawa, 1982
2,2',3,3'-PCB	8.7 nM/ml-hr		2,000,000,000	146		Furukawa, 1982
2,3,4,5-PCB	25.8 nM/ml-hr		2,000,000,000	146		Furukawa, 1982
2,3,4,5-PCB	19 nM/ml-hr		440,000,000	146		Furukawa, 1982
2,3,4-PCB	32 nM/ml-hr		440,000,000	128.8		Furukawa, 1982
2,3,4-PCB	35.1 nM/ml-hr		2,000,000,000	128.8		Furukawa, 1982
2,3,5,6-PCB	0 nM/ml-hr		2,000,000,000	146		Furukawa, 1982
2,3,5,6-PCB	0 nM/ml-hr		440,000,000	146		Furukawa, 1982
2,3,6-PCB	0 nM/ml-hr		440,000,000	128.8		Furukawa, 1982
2,3,6-PCB	0 nM/ml-hr		2,000,000 000	146		Furukawa, 1982
2,2',4,4'-PCB	0 nM/ml-hr		440,000,000	146		Furukawa, 1982
2,2',4,4'-PCB	0 nM/ml-hr		2,000,000,000	146		Furukawa, 1982
2,3',4,4'-PCB	0 nM/ml-hr		2,000,000,000	146		Furukawa, 1982
2,3',4,4'-PCB	0 nM/ml-hr		440,000,000	128.8		Furukawa, 1982
2,4,4'-PCB	41.3 nM/ml-hr		2,000,000,000	128.8		Furukawa, 1982
2,4,4'-PCB	40.2 nM/ml-hr		440,000,000	163.3		Furukawa, 1982
2,2',4,5,5'-PCB	0 nM/ml-hr		440,000,000	163.3		Furukawa, 1982
2,2',4,5,5'-PCB	0.6 nM/ml-hr		2,000,000,000	163.3		Furukawa, 1982
2,4,5-PCB	32.4 nM/ml-hr		440,000,000	128.8		Furukawa, 1982
2,4,5-PCB	46 nM/ml-hr		2,000,000,000	128.8		Furukawa, 1982
2,4,6-PCB	46 nM/ml-hr		440,000,000	128.8		Furukawa, 1982
2,4,6-PCB	3.1 nM/ml-hr		2,000,000,000	128.8		Furukawa, 1982
2,4-D		7E-10 ℓ/cell-hr	natural water	(100,10)	yes	Paris, 1981
2,4-D		2E-10 ℓ/cell-hr	natural water	(100,10)	yes	Paris, 1981
2,4-D		6E-10 ℓ/cell-hr	natural water	(100,10)	yes	Paris, 1981

TABLE A1 (continued)

Chemical	Zero-Order Reaction Rates	Second-Order Reaction Rates	Microbial Population cells/mℓ	Chemical Concentration µg/ℓ	Aerobic Conditions	Reference
2,4-D		1.2E-10 ℓ/cell-hr	natural water	(100,10)	yes	Paris, 1981
2,4-D		6E-10 ℓ/cell-hr	natural water	(100,10)	yes	Paris, 1981
2,4-D		7E-10 ℓ/cell-hr	natural water	(100,10)	yes	Paris, 1981
2,4-D		4E-10 ℓ/cell-hr	natural water	(100,10)	yes	Paris, 1981
2,4-D		5E-10 ℓ/cell-hr	natural water	(100,10)	yes	Paris, 1981
2,4-D		3E-10 ℓ/cell-hr	natural water	(100,10)	yes	Paris, 1981
2,4-D		2.3E-10 ℓ/cell-hr	natural water	(100,10)	yes	Paris, 1981
2,4-D		5E-10 ℓ/cell-hr	natural water	(100,10)	yes	Paris, 1981
2,4-D		4E-10 ℓ/cell-hr	natural water	(100,10)	yes	Paris, 1981
2,4-D		8E-10 ℓ/cell-hr	natural water	(100,10)	yes	Paris, 1981
2,4-D		9E-10 ℓ/cell-hr	natural water	(100,10)	yes	Paris, 1981
2,4-D		8E-10 ℓ/cell-hr	natural water	(100,10)	yes	Paris, 1981
2,4-D	2.58E-6/ml(cell)-hr		aquatic systems			Scow, 1982
2,4-D	2.6-10E-7/ml(cell)-hr		aquatic systems			Scow, 1982
2,4-D	4E-8/ml(cell)-hr		aquatic systems			Scow, 1982
2,4-Dichlorophenol		1E-10 ℓ/cell-hr[e]				Mabey et al., 1982
2,4-Dinitrotoluene		1E-10 ℓ/cell-hr[e]				Mabey et al., 1982
2,4-Dimethyl phenol		1E-10 ℓ/cell-hr[e]				Mabey et al., 1982
2,4-Dinitrophenol		3E-12 ℓ/cell-hr[e]				Mabey et al., 1982
2,2',5,5'-PCB	3.5 nM/ml-hr		440,000,000	146		Furukawa, 1982
2,2',5,5'-PCB	0 nM/ml-hr		2,000,000,000	146		Furukawa, 1982
2,2',5-PCB	122.4 nM/ml-hr		440,000,000	128.8		Furukawa, 1982
2,2',5-PCB	38.4 nM/ml-hr		2,000,000,000	128.8		Furukawa, 1982
2,3',5-PCB	991.2 nM/ml-hr		440,000,000	128.8		Furukawa, 1982
2,3',5-PCB	1010.4 nM/ml-hr		2,000,000,000	128.8		Furukawa, 1982
2,4',5-PCB	729.6 nM/ml-hr		440,000,000	128.8		Furukawa, 1982
2,4',5-PCB	523.2 nM/ml-hr		2,000,000,000	128.8		Furukawa, 1982
2,4,6-Trichlorophenol		3E-12 ℓ/cell-hr[e]				Mabey et al., 1982
2,2',6,6'-PCB	0 nM/ml-hr		440,000,000	146		Furukawa, 1982
2,2',6,6'-PCB	33.6 nM/ml-hr		2,000,000,000	146		Furukawa, 1982
2',3,4-PCB	926.4 nM/ml-hr		440,000,000	128.75		Furukawa, 1982
2',3,4-PCB	374.4 nM/ml-hr		2,000,000,000	128.75		Furukawa, 1982
2,6-Dinitrotoluene		1E-13 ℓ/cell-hr[e]				Mabey et al., 1982
2-Chloroethyl vinyl ether		1E-13 ℓ/cell-hr[e]				Mabey et al., 1982
2-Chloronaphthalene		3E-12 ℓ/cell-hr[e]				Mabey et al., 1982

TABLE A1 (continued)

Chemical	Zero-Order Reaction Rates	Second-Order Reaction Rates	Microbial Population cells/mℓ	Chemical Concentration µg/ℓ	Aerobic Conditions	Reference
2-Chlorophenol		1E-10 ℓ/cell-hr[e]				Mabey et al., 1982
2-Nitrophenol		3E-12 ℓ/cell-hr[e]				Mabey et al., 1982
3,3',4,4'-PCB	0 nM/ml-hr		2,000,000,000	146		Furukawa, 1982
3,3',4,4'-PCB	0 nM/ml-hr		440,000,000	146		Furukawa, 1982
3,3'-Dichlorobenzidine		3E-15 ℓ/cell-hr[e]				Mabey et al., 1982
4,6-Dinitro-o-cresol		3E-12 ℓ/cell-hr[e]				Mabey et al., 1982
4-Bromophenyl phenyl ether		1E-12 ℓ/cell-hr[e]				Mabey et al., 1982
4-Chlorophenyl phenyl ether		1E-10 ℓ/cell-hr[e]				Mabey et al., 1982
4-Nitrophenol		1E-10 ℓ/cell-hr[e]				Mabey et al., 1982
Acenaphthene		3E-12 ℓ/cell-hr[e]				Mabey et al., 1982
Acenaphthylene		3E-12 ℓ/cell-hr[e]				Mabey et al., 1982
Acrolein		3E-12 ℓ/cell-hr[e]				Mabey et al., 1982
Acrylonitrile		3E-12 ℓ/cell-hr[e]				Mabey et al., 1982
Alachlor	0.267µg/1-hr					Cartwright, 1980
Aldrin		3E-12 ℓ/cell-hr[e]				Mabey et al., 1982
Anthracene		3E-12 ℓ/cell-hr[e]				Mabey et al., 1982
Aroclor 1016		3E-12 ~ 3E-15 ℓ/cell-hr[e]				Mabey et al., 1982
Aroclor 1221		3E-12 ~ 3E-15 ℓ/cell-hr[e]				Mabey et al., 1982
Aroclor 1232		3E-12 ~ 3E-15 ℓ/cell-hr[e]				Mabey et al., 1982
Aroclor 1242		3E-12 ~ 3E-15 ℓ/cell-hr[e]				Mabey et al., 1982
Aroclor 1248		3E-12 ~ 3E-15 ℓ/cell-hr[e]				Mabey et al., 1982
Aroclor 1254		3E-12 ~ 3E-15 ℓ/cell-hr[e]				Mabey et al., 1982
Aroclor 1260		3E-12 ~ 3E-15 ℓ/cell-hr[e]				Mabey et al., 1982
Benzene		1E-10 ℓ/cell-hr[e]				Mabey et al., 1982
Benzidine		1E-13 ℓ/cell-hr[e]				Mabey et al., 1982
Benzo[a]anthracene		1E-13 ℓ/cell-hr[e]				Mabey et al., 1982
Benzo[a]pyrene	0.13 µM/hr					Callahan, 1979, p. 98-
Benzo[a]pyrene	0.02 µM/hr		E. coli			Callahan, 1979, p. 98-
Benzo[a]pyrene		3E-15 ℓ/cell-hr[e]				Mabey et al., 1982
Benzo[b]fluoranthene		3E-15 ℓ/cell-hr[e]				Mabey et al., 1982
Benzo[k]fluoranthene		3E-15 ℓ/cell-hr[e]				Mabey et al., 1982
Benzo[ghi]perylene		3E-15 ℓ/cell-hr[e]				Mabey et al., 1982
Bis(2-chloroethoxy)methane		3E-15 ℓ/cell-hr[e]				Mabey et al., 1982
Bis(2-chloroethyl)ether		3E-12 ℓ/cell-hr[e]				Mabey et al., 1982
Bis(2-chloroisopropyl)ether		1E-13 ℓ/cell-hr[e]				Mabey et al., 1982

TABLE A1 (continued)

Chemical	Zero-Order Reaction Rates	Second-Order Reaction Rates	Microbial Population cells/mℓ	Chemical Concentration µg/ℓ	Aerobic Conditions	Reference
Bis(2-ethylhexyl)phthalate	4.167E-11/ml(cell)-hr		aquatic systems			Scow, 1982
Bis(2-ethylhexyl)phthalate		4.2E-15 ℓ/cell-hr				Mabey et al., 1982
Bromodichloromethane		1E-13 ℓ/cell-hr(e)				Mabey et al., 1982
Butyl benzyl phthalate		3E-12 ℓ/cell-hr(e)				Mabey et al., 1982
Chlordane		3E-15 ℓ/cell-hr(e)				Mabey et al., 1982
Chlorobenzene		3E-12 ℓ/cell-hr(e)				Mabey et al., 1982
Chrysene		1E-13 ℓ/cell-hr(e)				Mabey et al., 1982
DDD		1E-13 ℓ/cell-hr(e)				Mabey et al., 1982
DDE		3E-15 ℓ/cell-hr(e)				Mabey et al., 1982
DDT		3E-15 ℓ/cell-hr(e)				Mabey et al., 1982
Di-n-butyl phthalate	3.08E-8/ml(cell)-hr		aquatic systems			Scow, 1982
Di-n-butyl phthalate		(1.9 - 4.4)E-11 ℓ/cell-hr				Mabey et al., 1982
Di-n-octyl phthalate	3.08E-10/ml(cell)-hr		aquatic systems			Scow, 1982
Di-n-octyl phthalate		3.1E-13 ℓ/cell-hr				Mabey et al., 1982
Di-n-propyl nitrosamine		3E-15 ℓ/cell-hr(e)				Mabey et al., 1982
Dibenzo[a,h]anthracene		3E-15 ℓ/cell-hr(e)				Mabey et al., 1982
Dibromochloromethane		1E-13 ℓ/cell-hr(e)				Mabey et al., 1982
Dieldrin		3E-15 ℓ/cell-hr(e)				Mabey et al., 1982
Diethyl phthalate		1E-10 ℓ/cell-hr(e)				Mabey et al., 1982
Dimethyl nitrosamine		3E-15 ℓ/cell-hr(e)				Mabey et al., 1982
Dimethyl phthalate	5E-6/ml(cell)-hr		aquatic systems			Scow, 1982
Dimethyl phthalate		5.2E-9 ℓ/cell-hr				Mabey et al., 1982
Diphenyl nitrosamine		1E-13 ℓ/cell-hr(e)				Mabey et al., 1982
α-Endosulfan		3E-12 ℓ/cell-hr(e)				Mabey et al., 1982
β-Endosulfan		3E-12 ℓ/cell-hr(e)				Mabey et al., 1982
Endosulfan sulfate		1E-13 ℓ/cell-hr(e)				Mabey et al., 1982
Endrin		1E-13 ℓ/cell-hr(e)				Mabey et al., 1982
Endrin aldehyde		3E-12 ℓ/cell-hr(e)				Mabey et al., 1982
Ethylbenzene		3E-12 ℓ/cell-hr(e)				Mabey et al., 1982
Fluoranthene	2.2E-3 µM/hr-mg bact		Pseudomonas			Callahan, 1979, p. 96-
Fluoranthene		1E-13 ℓ/cell-hr(e)				Mabey et al., 1982
Fluorene		3E-12 ℓ/cell-hr(e)				Mabey et al., 1982
α-Hexachlorocyclohexane		1E-13 ℓ/cell-hr(e)				Mabey et al., 1982
β-Hexachlorocyclohexane		1E-13 ℓ/cell-hr(e)				Mabey et al., 1982
δ-Hexachlorocyclohexane		1E-13 ℓ/cell-hr(e)				Mabey et al., 1982

TABLE A1 (continued)

Chemical	Zero-Order Reaction Rates	Second-Order Reaction Rates	Microbial Population cells/mℓ	Chemical Concentration µg/ℓ	Aerobic Conditions	Reference
γ-Hexachlorocyclohexane		1E-13 ℓ/cell-hr(e)				Mabey et al., 1982
Heptachlor epoxide		3E-15 ℓ/cell-hr(e)				Mabey et al., 1982
Hexachlorobenzene		3E-15 ℓ/cell-hr(e)				Mabey et al., 1982
Hexachlorobutadiene		1E-13 ℓ/cell-hr(e)				Mabey et al., 1982
Hexachlorocyclopentadiene		1E-13 ℓ/cell-hr(e)				Mabey et al., 1982
Hexachloroethane		1E-13 ℓ/cell-hr(e)				Mabey et al., 1982
Indeno[1,2,3-cd]pyrene		3E-15 ℓ/cell-hr(e)				Mabey et al., 1982
Isophorone		3E-12 ℓ/cell-hr(e)				Mabey et al., 1982
Malathion		4.58E-11 ℓ/cell-hr	natural water	(100,10)	yes	Paris, 1981
Malathion		4.17E-11 ℓ/cell-hr	natural water	(100,10)	yes	Paris, 1981
Malathion		5.83E-11 ℓ/cell-hr	natural water	(100,10)	yes	Paris, 1981
Malathion		5.42E-11 ℓ/cell-hr	natural water	(100,10)	yes	Paris, 1981
Malathion	2.58E-9/ml(cell)-hr		aquatic systems			Scow, 1982
Malathion	2.08E-9/ml(cell)-hr		aquatic systems			Scow, 1982
Malathion	0.0079/mg(g fungi)-hr		aquatic systems			Scow, 1982
Malathion	1.08-6.71E-8/ml(cell)-hr		aquatic systems			Scow, 1982
Naphthalene	0.0017-0.1375µg/1-hr					Callahan, 1979, p. 95-
Naphthalene	0.167µg/1-hr		river water			Callahan, 1979, p. 95-
Naphthalene		1E-10 ℓ/cell-hr(e)				Mabey et al., 1982
Nitrobenzene		3E-12 ℓ/cell-hr(e)				Mabey et al., 1982
Pentachlorophenol		3E-12 ℓ/cell-hr(e)				Mabey et al., 1982
Phenanthrene		1.6E-10 ℓ/cell-hr(e)				Mabey et al., 1982
Phenol		3E-9 ℓ/cell-hr(e)				Mabey et al., 1982
Pyrene		1E-13 ℓ/cell-hr(e)				Mabey et al., 1982
TCDD		1E-13 ℓ/cell-hr(e)				Mabey et al., 1982
Tetrachloroethene		1E-13 ℓ/cell-hr(e)				Mabey et al., 1982
Tetrachloromethane		1E-13 ℓ/cell-hr(e)				Mabey et al., 1982
Toluene		1E-10 ℓ/cell-hr(e)				Mabey et al., 1982
Toxaphene		3E-15 ℓ/cell-hr(e)				Mabey et al., 1982
Tribromomethane		1E-13 ℓ/cell-hr(e)				Mabey et al., 1982
Trichloroethene		1E-13 ℓ/cell-hr(e)				Mabey et al., 1982
p-Chloro-m-cresol		3E-12 ℓ/cell-hr(e)				Mabey et al., 1982
p-Cresol	5.167E-7/ml(cell)-hr		aquatic systems			Scow, 1982

(e) Estimated value

TABLE A2. CHEMICAL HYDROLYSIS

Chemical	Chemical Concentration µg/ℓ	Hydrolysis Rate Constant	Reference
1,1-Dichloroethane		0/M-hr (acid)	Mabey et al., 1982
1,1-Dichloroethane		1.15×10^{-7} (25°C) (neut)	Mabey et al., 1982
1,1-Dichloroethane		0/M-hr (alk)	Mabey et al., 1982
1,1-Dichloroethane		0/M-hr (acid)	Mabey et al., 1982
1,1-Dichloroethane		0/M-hr (neut)	Mabey et al., 1982
1,1,1-Trichloroethane		0.000158/hr	Callahan, 1979, p. 43-3
1,1,1-Trichloroethane		0/M-hr (acid)	Mabey et al., 1982
1,1,1-Trichloroethane		1.7×10^{-4} (25°C) (neut)	Mabey et al., 1982
1,1,2-Trichloroethane		0/M-hr (acid)	Mabey et al., 1982
1,1,2-Trichloroethane		1.2×10^{-7} (25°C) (neut)	Mabey et al., 1982
1,1,2,2-Tetrachloroethane		0/M-hr (acid)	Mabey et al., 1982
1,1,2,2-Tetrachloroethane		1.2×10^{-7} (25°C) (neut)	Mabey et al., 1982
1,2-Dichlorobenzene		0/M-hr (alk)	Mabey et al., 1982
1,2-Dichlorobenzene		0/M-hr (acid)	Mabey et al., 1982
1,2-Dichlorobenzene		0/M-hr (neut)	Mabey et al., 1982
1,2-Dichloroethane		0/M-hr (acid)	Mabey et al., 1982
1,2-Dichloroethane		1.8×10^{-9} (25°C) (neut)	Mabey et al., 1982
1,2-Dichloroethane		1.58E-9/hr	Callahan, 1979, p. 43-4
1,2-Diphenylhydrazine		0/M-hr (alk)	Mabey et al., 1982
1,2-Diphenylhydrazine		0/M-hr (acid)	Mabey et al., 1982
1,2-Diphenylhydrazine		0/M-hr (neut)	Mabey et al., 1982
1,2-Dichloropropane		0/M-hr (acid)	Mabey et al., 1982
1,2-Dichloropropane		7.2×10^{-4} (25°C) (neut)	Mabey et al., 1982
1,2-trans-Dichloroethene		0/M-hr (alk)	Mabey et al., 1982
1,2-trans-Dichloroethene		0/M-hr (acid)	Mabey et al., 1982
1,2-trans-Dichloroethene		0/M-hr (neut)	Mabey et al., 1982
1,2,4-Trichlorobenzene		0/M-hr (alk)	Mabey et al., 1982
1,2,4-Trichlorobenzene		0/M-hr (acid)	Mabey et al., 1982
1,2,4-Trichlorobenzene		0/M-hr (neut)	Mabey et al., 1982
1,3-Dichlorobenzene		0/M-hr (alk)	Mabey et al., 1982
1,3-Dichlorobenzene		0/M-hr (acid)	Mabey et al., 1982
1,3-Dichlorobenzene		0/M-hr (neut)	Mabey et al., 1982
1,3-Dichloropropene		0/M-hr (acid)	Mabey et al., 1982
1,3-Dichloropropene		4.2×10^{-4} (25°C) (neut)	Mabey et al., 1982

TABLE A2 (continued)

Chemical	Chemical Concentration µg/ℓ	Hydrolysis Rate Constant	Reference
1,4-Dichlorobenzene		0/M-hr (alk)	Mabey et al., 1982
1,4-Dichlorobenzene		0/M-hr (acid)	Mabey et al., 1982
1,4-Dichlorobenzene		0/M-hr (neut)	Mabey et al., 1982
2-Chloroethyl vinyl ether		$4x10^{-6}$(25°C) (neut)	Mabey et al., 1982
2-Chloroethyl vinyl ether		1.584E-6/hr	Callahan, 1979, p. 67-3
2-Chlorophenol		0/M-hr (alk)	Mabey et al., 1982
2-Chlorophenol		0/M-hr (acid)	Mabey et al., 1982
2-Chlorophenol		0/M-hr (neut)	Mabey et al., 1982
2-Chloronaphthalene		0/M-hr (alk)	Mabey et al., 1982
2-Chloronaphthalene		0/M-hr (acid)	Mabey et al., 1982
2-Chloronaphthalene		0/M-hr (neut)	Mabey et al., 1982
2-Nitrophenol		0/M-hr (alk)	Mabey et al., 1982
2-Nitrophenol		0/M-hr (acid)	Mabey et al., 1982
2-Nitrophenol		0/M-hr (neut)	Mabey et al., 1982
2,4-Dichlorophenol		0/M-hr (alk)	Mabey et al., 1982
2,4-Dichlorophenol		0/M-hr (acid)	Mabey et al., 1982
2,4-Dichlorophenol		0/M-hr (neut)	Mabey et al., 1982
2,4-Dimethyl phenol		0/M-hr (alk)	Mabey et al., 1982
2,4-Dimethyl phenol		0/M-hr (acid)	Mabey et al., 1982
2,4-Dimethyl phenol		0/M-hr (neut)	Mabey et al., 1982
2,4-Dinitrophenol		0/M-hr (alk)	Mabey et al., 1982
2,4-Dinitrophenol		0/M-hr (acid)	Mabey et al., 1982
2,4-Dinitrophenol		0/M-hr (neut)	Mabey et al., 1982
2,4-Dinitrotoluene		0/M-hr (alk)	Mabey et al., 1982
2,4-Dinitrotoluene		0/M-hr (acid)	Mabey et al., 1982
2,4-Dinitrotoluene		0/M-hr (neut)	Mabey et al., 1982
2,4,6-Trichlorophenol		0/M-hr (alk)	Mabey et al., 1982
2,4,6-Trichlorophenol		0/M-hr (acid)	Mabey et al., 1982
2,4,6-Trichlorophenol		0/M-hr (neut)	Mabey et al., 1982
2,6-Dinitrotoluene		0/M-hr (alk)	Mabey et al., 1982
2,6-Dinitrotoluene		0/M-hr (acid)	Mabey et al., 1982
2,6-Dinitrotoluene		0/M-hr (neut)	Mabey et al., 1982
3,3'-Dichlorobenzidine		0/M-hr (alk)	Mabey et al., 1982
3,3'-Dichlorobenzidine		0/M-hr (acid)	Mabey et al., 1982

TABLE A2 (continued)

Chemical	Chemical Concentration µg/ℓ	Hydrolysis Rate Constant	Reference
3,3'-Dichlorobenzidine		0/M-hr (neut)	Mabey et al., 1982
4-Bromophenyl phenyl ether		0/M-hr (alk)	Mabey et al., 1982
4-Bromophenyl phenyl ether		0/M-hr (acid)	Mabey et al., 1982
4-Bromophenyl phenyl ether		0/M-hr (neut)	Mabey et al., 1982
4-Chlorophenyl phenyl ether		0/M-hr (alk)	Mabey et al., 1982
4-Chlorophenyl phenyl ether		0/M-hr (acid)	Mabey et al., 1982
4-Chlorophenyl phenyl ether		0/M-hr (neut)	Mabey et al., 1982
4-Nitrophenol		0/M-hr (alk)	Mabey et al., 1982
4-Nitrophenol		0/M-hr (acid)	Mabey et al., 1982
4-Nitrophenol		0/M-hr (neut)	Mabey et al., 1982
4,6-Dinitro-o-cresol		0/M-hr (alk)	Mabey et al., 1982
4,6-Dinitro-o-cresol		0/M-hr (acid)	Mabey et al., 1982
4,6-Dinitro-o-cresol		0/M-hr (neut)	Mabey et al., 1982
Acenaphthene		0/M-hr (alk)	Mabey et al., 1982
Acenaphthene		0/M-hr (acid)	Mabey et al., 1982
Acenaphthene		0/M-hr (neut)	Mabey et al., 1982
Acenaphthylene		0/M-hr (alk)	Mabey et al., 1982
Acenaphthylene		0/M-hr (acid)	Mabey et al., 1982
Acenaphthylene		0/M-hr (neut)	Mabey et al., 1982
Acrolein		0/M-hr (alk)	Mabey et al., 1982
Acrolein		0/M-hr (acid)	Mabey et al., 1982
Acrolein		0/M-hr (neut)	Mabey et al., 1982
Acrylonitrile		0/M-hr (alk)	Mabey et al., 1982
Acrylonitrile		0/M-hr (acid)	Mabey et al., 1982
Acrylonitrile		0/M-hr (neut)	Mabey et al., 1982
Aldicarb	37	5.616E+1 ℓ-M/hr (alk)	Lemley & Zhong, 1983
Aldrin		0/M-hr (alk)	Mabey et al., 1982
Aldrin		0/M-hr (acid)	Mabey et al., 1982
Aldrin		0/M-hr (neut)	Mabey et al., 1982
Anthracene		0/M-hr (alk)	Mabey et al., 1982
Anthracene		0/M-hr (acid)	Mabey et al., 1982
Anthracene		0/M-hr (neut)	Mabey et al., 1982
Aroclor 1016		0/M-hr (alk)	Mabey et al., 1982
Aroclor 1016		0/M-hr (acid)	Mabey et al., 1982

TABLE A2 (continued)

Chemical	Chemical Concentration µg/ℓ	Hydrolysis Rate Constant	Reference
Aroclor 1016		0/M-hr (neut)	Mabey et al., 1982
Aroclor 1221		0/M-hr (alk)	Mabey et al., 1982
Aroclor 1221		0/M-hr (acid)	Mabey et al., 1982
Aroclor 1221		0/M-hr (neut)	Mabey et al., 1982
Aroclor 1232		0/M-hr (alk)	Mabey et al., 1982
Aroclor 1232		0/M-hr (acid)	Mabey et al., 1982
Aroclor 1232		0/M-hr (neut)	Mabey et al., 1982
Aroclor 1242		0/M-hr (alk)	Mabey et al., 1982
Aroclor 1242		0/M-hr (acid)	Mabey et al., 1982
Aroclor 1242		0/M-hr (neut)	Mabey et al., 1982
Aroclor 1248		0/M-hr (alk)	Mabey et al., 1982
Aroclor 1248		0/M-hr (acid)	Mabey et al., 1982
Aroclor 1248		0/M-hr (neut)	Mabey et al., 1982
Aroclor 1254		0/M-hr (alk)	Mabey et al., 1982
Aroclor 1254		0/M-hr (acid)	Mabey et al., 1982
Aroclor 1254		0/M-hr (neut)	Mabey et al., 1982
Aroclor 1260		0/M-hr (alk)	Mabey et al., 1982
Aroclor 1260		0/M-hr (acid)	Mabey et al., 1982
Aroclor 1260		0/M-hr (neut)	Mabey et al., 1982
Atrazine	32,355	hr (acid) 1.67E-1	Khan, 1978
Atrazine	32,355	hr (neut) 3.892E-2	Khan, 1978
Benzene		0/M-hr (alk)	Mabey et al., 1982
Benzene		0/M-hr (acid)	Mabey et al., 1982
Benzene		0/M-hr (neut)	Mabey et al., 1982
Benzidine		0/M-hr (alk)	Mabey et al., 1982
Benzidine		0/M-hr (acid)	Mabey et al., 1982
Benzidine		0/M-hr (neut)	Mabey et al., 1982
Benzo(a)anthracene		0/M-hr (alk)	Mabey et al., 1982
Benzo(a)anthracene		0/M-hr (acid)	Mabey et al., 1982
Benzo(a)anthracene		0/M-hr (neut)	Mabey et al., 1982
Benzo(b)fluoranthene		0/M-hr (alk)	Mabey et al., 1982
Benzo(b)fluoranthene		0/M-hr (acid)	Mabey et al., 1982
Benzo(b)fluoranthene		0/M-hr (neut)	Mabey et al., 1982
Benzo(k)fluoranthene		0/M-hr (alk)	Mabey et al., 1982

TABLE A2 (continued)

Chemical	Chemical Concentration µg/ℓ	Hydrolysis Rate Constant	Reference
Benzo(k)fluoranthene		0/M-hr (acid)	Mabey et al., 1982
Benzo(k)fluoranthene		0/M-hr (neut)	Mabey et al., 1982
Benzo(ghi)perylene		0/M-hr (alk)	Mabey et al., 1982
Benzo(ghi)perylene		0/M-hr (acid)	Mabey et al., 1982
Benzo(ghi)perylene		0/M-hr (neut)	Mabey et al., 1982
Benzo(a)pyrene		0/M-hr (alk)	Mabey et al., 1982
Benzo(a)pyrene		0/M-hr (acid)	Mabey et al., 1982
Benzo(a)pyrene		0/M-hr (neut)	Mabey et al., 1982
Bis(2-chloroethoxy)methane		9.108E-3 ℓ/M-hr (acid)	Callahan, 1979, p. 70-2
Bis(2-chloroethyl)ether		$4x10^{-6}$(25°C) (neut)	Mabey et al., 1982
Bis(chloromethyl)ether		65 (25°C) (neut)	Mabey et al., 1982
Bis(2-ethylhexyl)phthalate		0.4 (30°C) (alk)	Mabey et al., 1982
Bis(2-ethylhexyl)phthalate		$4.0x10^{-5}$ (30°C) (acid)	Mabey et al., 1982
Bis(2-ethylhexyl)phthalate		0/M-hr (neut)	Mabey et al., 1982
Bis(2-ethylhexyl)phthalate		3.95E-8/hr	Callahan, 1979, p. 94-22
Bis(2-chloroethoxy)methane		$4x10^{-6}$ (25°C) (neut)	Mabey et al., 1982
Bis(2-chloroisopropyl)ether		$4x10^{-6}$(25°C) (neut)	Mabey et al., 1982
Bis(chloromethyl)ether		6.98E+1/hr	Callahan, 1979, p. 64-2
Bromodichloromethane		5.76 (alk)	Mabey et al., 1982
Bromodichloromethane		0/M-hr (acid)	Mabey et al., 1982
Bromodichloromethane		$5.76x10^{-8}$ (25°C) (neut)	Mabey et al., 1982
Bromodichloromethane		5.77E-7/hr	Callahan, 1979, p. 59-2
Bromoform		1.15E-7/hr	Callahan, 1979, p. 61-2
Bromomethane		0/M-hr (acid)	Mabey et al., 1982
Bromomethane		$1.44x10^{-3}$ (25°C) (neut)	Mabey et al., 1982
Bromomethane		0.00144/hr	Callahan, 1979, p. 58-3
Butyl benzyl phthalate		79.2 (30°C) (alk)	Mabey et al., 1982
Butyl benzyl phthalate		$7.97x10^{-3}$ (30°C) (acid)	Mabey et al., 1982
Butyl benzyl phthalate		0/M-hr (neut)	Mabey et al., 1982
Butyl benzyl phthalate	9.73	<0.000289/hr	Gledhill, 1980
Carbaryl	2.01	2.772E+4/M-hr (alk)	Harris, 1982b
Carbaryl		1.807E+4/M-hr (alk)	Wolfe, Zepp & Paris, 1978
Carbon tetrachloride	1000	1.13E-8/hr	Callahan, 1979, p. 41-3
Chlordane		1.975E-5/hr	Callahan, 1979, p. 22-6

TABLE A2 (continued)

Chemical	Chemical Concentration µg/ℓ	Hydrolysis Rate Constant	Reference
Chlordane		0/M-hr (alk)	Mabey et al., 1982
Chlordane		0/M-hr (acid)	Mabey et al., 1982
Chlordane		0/M-hr (neut)	Mabey et al., 1982
Chlorobenzene		0/M-hr (alk)	Mabey et al., 1982
Chlorobenzene		0/M-hr (acid)	Mabey et al., 1982
Chlorobenzene		0/M-hr (neut)	Mabey et al., 1982
Chloroethane		0/M-hr (acid)	Mabey et al., 1982
Chloroethane		7.2×10^{-4} (25°C) (neut)	Mabey et al., 1982
Chloroethene		0/M-hr (alk)	Mabey et al., 1982
Chloroethene		0/M-hr (acid)	Mabey et al., 1982
Chloroethene		0/M-hr (neut)	Mabey et al., 1982
Chloroform		4.928E-4/hr	Callahan, 1979, p. 40-4
Chloroform		5.76E-5/hr (neut)	Harris, 1982b
Chloroform		2.16E-1/M-hr (alk)	Harris, 1982b
Chloromethane		0/M-hr (acid)	Mabey et al., 1982
Chloromethane		6.8×10^{-5} (25°C) (neut)	Mabey et al., 1982
Chrysene		0/M-hr (alk)	Mabey et al., 1982
Chrysene		0/M-hr (acid)	Mabey et al., 1982
Chrysene		0/M-hr (neut)	Mabey et al., 1982
DDD		4.16E-7/hr	Callahan, 1979, p. 23-3
DDD		5.04/M-hr (alk)	Callahan, 1979, p. 23-3
DDD		5.0/M-hr (alk)	Mabey et al., 1982
DDD		0/M-hr (acid)	Mabey et al., 1982
DDD		4E-7/M-hr (neut)	Mabey et al., 1982
DDE		6.58E-7/hr	Callahan, 1979, p. 24-4
DDE		0/M-hr (alk)	Mabey et al., 1982
DDE		0/M-hr (acid)	Mabey et al., 1982
DDE		< 6.6E-7/M-hr (neut)	Mabey et al., 1982
DDT		3.564E+1/M-hr (alk)	Callahan, 1979, p. 25-9
DDT		6.84E-6/hr (acid)	Callahan, 1979, p. 25-9
DDT	0.003545	3.564E+1/M-hr (alk)	Harris, 1982b
DDT	0.003545	6.84E-6/hr (acid)	Wolfe, 1977b
DDT		3.6/M-hr (alk)	Wolfe, 1977b
Di-*n*-butyl phthalate		79.2 (30°C) (alk)	Mabey et al., 1982

TABLE A2 (continued)

Chemical	Chemical Concentration µg/ℓ	Hydrolysis Rate Constant	Reference
Di-n-butyl phthalate		7.92×10^{-3} (30°C)	Mabey et al., 1982
Di-n-butyl phthalate		0/M-hr (neut)	Mabey et al., 1982
Di-n-butyl phthalate		7.9E-6/hr	Callahan, 1979, p. 94-20
Di-n-octyl phthalate		79.2 (30°C) (alk)	Mabey et al., 1982
Di-n-octyl phthalate		7.92×10^{-3} (30°C) (acid)	Mabey et al., 1982
Di-n-octyl phthalate		0/M-hr (neut)	Mabey et al., 1982
Di-n-propyl nitrosamine		0/M-hr (alk)	Mabey et al., 1982
Di-n-propyl nitrosamine		0/M-hr (acid)	Mabey et al., 1982
Di-n-propyl nitrosamine		0/M-hr (neut)	Mabey et al., 1982
Diazinon	3.04	7.56E+1/M-hr (acid)	Harris, 1982b
Diazinon	3.04	1.548E-4/hr (neut)	Harris, 1982b
Diazinon	3.04	1.908E+1/M-hr (alk)	Harris, 1982b
Dibenzo(a,h)anthracene		0/M-hr (alk)	Mabey et al., 1982
Dibenzo(a,h)anthracene		0/M-hr (acid)	Mabey et al., 1982
Dibenzo(a,h)anthracene		0/M-hr (neut)	Mabey et al., 1982
Dibromochloromethane		2.88 (25°C) (alk)	Mabey et al., 1982
Dibromochloromethane		0/M-hr (acid)	Mabey et al., 1982
Dibromochloromethane		2.88×10^{-8} (25°C) (neut)	Mabey et al., 1982
Dibromochloromethane		2.88E-7/hr	Callahan, 1979, p. 60-2
Dichlorodifluoromethane		0/M-hr (alk)	Mabey et al., 1982
Dichlorodifluoromethane		0/M-hr (acid)	Mabey et al., 1982
Dichlorodifluoromethane		0/M-hr (neut)	Mabey et al., 1982
Dichloromethane		0/M-hr (acid)	Mabey et al., 1982
Dichloromethane		1.15×10^{-7} (25°C) (neut)	Mabey et al., 1982
Dieldrin		1.975E-5/hr	Callahan, 1979, p. 26-4
Dieldrin		0/M-hr (alk)	Mabey et al., 1982
Dieldrin		0/M-hr (acid)	Mabey et al., 1982
Dieldrin		0/M-hr (neut)	Mabey et al., 1982
Diethyl phthalate		43.2 (30°C) (alk)	Mabey et al., 1982
Diethyl phthalate		4.32×10^{-3} (30°C) (acid)	Mabey et al., 1982
Diethyl phthalate		0/M-hr (neut)	Mabey et al., 1982
Diethyl phthalate		4.31E-6/hr	Callahan, 1979, p. 94-19
Dimethyl nitrosamine		0/M-hr (alk)	Mabey et al., 1982
Dimethyl nitrosamine		0/M-hr (acid)	Mabey et al., 1982

TABLE A2 (continued)

Chemical	Chemical Concentration µg/ℓ	Hydrolysis Rate Constant	Reference
Dimethyl nitrosamine		0/M-hr (neut)	Mabey et al., 1982
Dimethyl phthalate		248 (30°C) (alk)	Mabey et al., 1982
Dimethyl phthalate		0.025 (30°C) (acid)	Mabey et al., 1982
Dimethyl phthalate		0/M-hr (neut)	Mabey et al., 1982
Dimethyl phthalate		2.47E-5/hr	Callahan, 1979, p.94-18
Diphenyl nitrosamine		0/M-hr (alk)	Mabey et al., 1982
Diphenyl nitrosamine		0/M-hr (acid)	Mabey et al., 1982
Diphenyl nitrosamine		0/M-hr (neut)	Mabey et al., 1982
Endosulfan		8.333E-4/hr (neut)	Callahan, 1979, p. 27-6
Endosulfan		1.917E-4/hr (acid)	Callahan, 1979, p. 27-6
Endosulfan		8.3E3 (alk)	Mabey et al., 1982
α-Endosulfan		8.3×10^{3} (20°C)	Mabey et al., 1982
α-Endosulfan		1.6×10^{-4} (20°C)	Mabey et al., 1982
β-Endosulfan		8.3×10^{3} (20°C)	Mabey et al., 1982
β-Endosulfan		1.3×10^{-4} (20°C)	Mabey et al., 1982
Endosulfan sulfate		8.3E3/M-hr (alk)	Mabey et al., 1982
Endosulfan sulfate		1.3E-4/M-hr (neut)	Mabey et al., 1982
Endrin		1.975E-5/hr	Callahan, 1979, p. 28-5
Endrin		0/M-hr (alk)	Mabey et al., 1982
Endrin		0/M-hr (acid)	Mabey et al., 1982
Endrin		0/M-hr (neut)	Mabey et al., 1982
Endrin aldehyde		0/M-hr (alk)	Mabey et al., 1982
Endrin aldehyde		0/M-hr (acid)	Mabey et al., 1982
Endrin aldehyde		0/M-hr (neut)	Mabey et al., 1982
Ethyl chloride		0.000722/hr	Callahan, 1979, p. 43-3
Ethylbenzene		0/M-hr (alk)	Mabey et al., 1982
Ethylbenzene		0/M-hr (acid)	Mabey et al., 1982
Ethylbenzene		0/M-hr (neut)	Mabey et al., 1982
Fluoranthene		0/M-hr (alk)	Mabey et al., 1982
Fluoranthene		0/M-hr (acid)	Mabey et al., 1982
Fluoranthene		0/M-hr (neut)	Mabey et al., 1982
Fluorene		0/M-hr (alk)	Mabey et al., 1982
Fluorene		0/M-hr (acid)	Mabey et al., 1982
Fluorene		0/M-hr (neut)	Mabey et al., 1982

TABLE A2 (continued)

Chemical	Chemical Concentration µg/ℓ	Hydrolysis Rate Constant	Reference
Heptachlor		3.00E-2/hr (neut)	Callahan, 1979, p. 29-4
Heptachlor epoxide		1.975E-5/hr	Callahan, 1979, p. 30-4
Heptachlor epoxide		0/M-hr (alk)	Mabey et al., 1982
Heptachlor epoxide		0/M-hr (acid)	Mabey et al., 1982
Heptachlor epoxide		0/M-hr (neut)	Mabey et al., 1982
Hexachlorobenzene		0/M-hr (alk)	Mabey et al., 1982
Hexachlorobenzene		0/M-hr (acid)	Mabey et al., 1982
Hexachlorobenzene		0/M-hr (neut)	Mabey et al., 1982
Hexachlorobutadiene		0/M-hr (alk)	Mabey et al., 1982
Hexachlorobutadiene		0/M-hr (acid)	Mabey et al., 1982
Hexachlorobutadiene		0/M-hr (neut)	Mabey et al., 1982
Hexachlorocyclohexane		6.12E+2/M-hr	Callahan, 1979, p. 31-4
Hexachlorocyclohexane		1.08E-2/M-hr	Callahan, 1979, p. 31-4
Hexachlorocyclohexane		0/M-hr (alk)	Mabey et al., 1982
Hexachlorocyclohexane		0/M-hr (acid)	Mabey et al., 1982
Hexachlorocyclohexane		0/M-hr (neut)	Mabey et al., 1982
Hexachlorocyclopentadiene		0/M-hr (acid)	Mabey et al., 1982
Hexachlorocyclopentadiene		2.0×10^{-3} (25°C) (neut)	Mabey et al., 1982
Hexachlorocyclopentadiene		2.016E-3/hr	Callahan, 1979, p. 57-3
Hexachlorocyclopentadiene	49	5.4E-3/hr	Wolfe, 1982
Hexachloroethane		0/M-hr (alk)	Mabey et al., 1982
Hexachloroethane		0/M-hr (acid)	Mabey et al., 1982
Hexachloroethane		0/M-hr (neut)	Mabey et al., 1982
Indeno(1,2,3-cd)pyrene		0/M-hr (alk)	Mabey et al., 1982
Indeno(1,2,3-cd)pyrene		0/M-hr (acid)	Mabey et al., 1982
Indeno(1,2,3-cd)pyrene		0/M-hr (neut)	Mabey et al., 1982
Isophorone		0/M-hr (alk)	Mabey et al., 1982
Isophorone		0/M-hr (acid)	Mabey et al., 1982
Isophorone		0/M-hr (neut)	Mabey et al., 1982
Lindane		3.0/M-hr	Callahan, 1979, p. 31-4
Malathion	33	2.77E-5/hr (neut)	Harris, 1982b
Malathion	33	1.728E-1/M-hr (acid)	Harris, 1982b
Malathion		1.728E-1/M-hr (acid)	Wolfe, 1977a
Malathion		1.98E+4/M-hr (alk)	Wolfe, 1977a

TABLE A2 (continued).

Chemical	Chemical Concentration µg/ℓ	Hydrolysis Rate Constant	Reference
Methoxychlor	0.003455	7.92E-5/hr (neut)	Harris, 1982b
Methoxychlor	0.003455	1.368/M-sec (alk)	Harris, 1982b
Methoxychlor	0.000003455	0.1368/hr (alk)	Wolfe, 1977b
Methoxychlor	0.000003455	5.4E-3/hr (neut)	Wolfe, 1977b
Methoxychlor	0.000003455	0.18/hr (acid)	Wolfe, 1977b
Methylene chloride		1.281E-3/hr	Callahan, 1979, p. 39-3
Naphthalene		0/M-hr (alk)	Mabey et al., 1982
Naphthalene		0/M-hr (acid)	Mabey et al., 1982
Naphthalene		0/M-hr (neut)	Mabey et al., 1982
Nitrobenzene		0/M-hr (alk)	Mabey et al., 1982
Nitrobenzene		0/M-hr (acid)	Mabey et al., 1982
Nitrobenzene		0/M-hr (neut)	Mabey et al., 1982
p-Chloro-m-cresol		0/M-hr (alk)	Mabey et al., 1982
p-Chloro-m-cresol		0/M-hr (acid)	Mabey et al., 1982
p-Chloro-m-cresol		0/M-hr (neut)	Mabey et al., 1982
Parathion	2.91	8.28E+1/M-hr (alk)	Harris, 1982b
Parathion	2.91	1.62E-4/hr (neut)	Harris, 1982b
Parathion	26,000	2.16E+11/hr	Mill, 1982
Pentachlorophenol		0/M-hr (alk)	Mabey et al., 1982
Pentachlorophenol		0/M-hr (acid)	Mabey et al., 1982
Pentachlorophenol		0/M-hr (neut)	Mabey et al., 1982
Phenanthrene		0/M-hr (alk)	Mabey et al., 1982
Phenanthrene		0/M-hr (acid)	Mabey et al., 1982
Phenanthrene		0/M-hr (neut)	Mabey et al., 1982
Phenol		0/M-hr (alk)	Mabey et al., 1982
Phenol		0/M-hr (acid)	Mabey et al., 1982
Phenol		0/M-hr (neut)	Mabey et al., 1982
Pyrene		0/M-hr (alk)	Mabey et al., 1982
Pyrene		0/M-hr (acid)	Mabey et al., 1982
Pyrene		0/M-hr (neut)	Mabey et al., 1982
TCDD		0/M-hr (alk)	Mabey et al., 1982
TCDD		0/M-hr (acid)	Mabey et al., 1982
TCDD		0/M-hr (neut)	Mabey et al., 1982
Tetrachloroethene		0/M-hr (alk)	Mabey et al., 1982

TABLE A2 (continued)

Chemical	Chemical Concentration µg/ℓ	Hydrolysis Rate Constant	Reference
Tetrachloroethene		0/M-hr (acid)	Mabey et al., 1982
Tetrachloroethene		0/M-hr (neut)	Mabey et al., 1982
Tetrachloroethene		1.082E-4/hr	Callahan, 1979, p. 53-4
Tetrachloroethylene		1.082E-4/hr	Callahan, 1979, p. 55-2
Tetrachloromethane		0/M-hr (acid)	Mabey et al., 1982
Toluene		0/M-hr (alk)	Mabey et al., 1982
Toluene		0/M-hr (acid)	Mabey et al., 1982
Toluene		0/M-hr (neut)	Mabey et al., 1982
Toxaphene		7.9E-6/hr	Callahan, 1979, p. 35-5
Toxaphene		0/M-hr (alk)	Mabey et al., 1982
Toxaphene		0/M-hr (acid)	Mabey et al., 1982
Toxaphene		0/M-hr (neut)	Mabey et al., 1982
Tribromomethane		1.15 (25°C) (alk)	Mabey et al., 1982
Tribromomethane		0/M-hr (acid)	Mabey et al., 1982
Tribromomethane		2.5×10^{-9} (25°C) (neut)	Mabey et al., 1982
Trichloroethene		0/M-hr (alk)	Mabey et al., 1982
Trichloroethene		0/M-hr (acid)	Mabey et al., 1982
Trichloroethene		0/M-hr (neut)	Mabey et al., 1982
Trichloroethene		8.87E-5/hr	Callahan, 1979, p. 52-4
Trichloroethylene		8.87E-5/hr	Callahan, 1979, p. 55-2
Trichlorofluoromethane		0/M-hr (alk)	Mabey et al., 1982
Trichlorofluoromethane		0/M-hr (acid)	Mabey et al., 1982
Trichlorofluoromethane		0/M-hr (neut)	Mabey et al., 1982
Trichloromethane		0.23 (25°C) (alk)	Mabey et al., 1982
Trichloromethane		0/M-hr (acid)	Mabey et al., 1982
Trichloromethane		2.5×10^{-9} (25°C) (neut)	Mabey et al., 1982

TABLE A3. OXIDATION

Chemical	Oxidation Reaction Rate	Radical Present	Reference
1,1,1-Trichloroethane	<0.463/hr		Callahan, et al, 1979, p. 46-3
1,1,1-Trichloroethane	<< 360	O_2	Mabey et al., 1982
1,1,1-Trichloroethane	1	RO_2	Mabey et al., 1982
1,1,2-Trichloroethane	1.986/hr		Callahan, et al, 1979, p. 46-3
1,1,2-Trichloroethane	<< 360	O_2	Mabey et al., 1982
1,1,2-Trichloroethane	3	RO_2	Mabey et al., 1982
1,1,2,2-Tetrachloroethane	<< 360	O_2	Mabey et al., 1982
1,1,2,2-Tetrachloroethane	2	RO_2	Mabey et al., 1982
1,1-Dichloroethane	<< 360	O_2	Mabey et al., 1982
1,1-Dichloroethane	1	RO_2	Mabey et al., 1982
1,1-Dichloroethane	$< 10^8$	O_2	Mabey et al., 1982
1,1-Dichloroethane	3	RO_2	Mabey et al., 1982
1,1-Diphenylhydrazine	104.25/hr	O_3	Fochtman & Eisenberg, 1979
1,2,4-Trichlorobenzene	<< 360	O_2	Mabey et al., 1982
1,2,4-Trichlorobenzene	<< 1	RO_2	Mabey et al., 1982
1,2-Dichlorobenzene	<< 360	O_2	Mabey et al., 1982
1,2-Dichlorobenzene	<< 1	RO_2	Mabey et al., 1982
1,2-Dichloroethane	< 360	O_2	Mabey et al., 1982
1,2-Dichloroethane	< 1	RO_2	Mabey et al., 1982
1,2-Dichloroethene-trans	$<10^5$	O_2	Mabey et al., 1982
1,2-Dichloroethene-trans	6	RO_2	Mabey et al., 1982
1,2-Dichloropropane	<< 360	O_2	Mabey et al., 1982
1,2-Dichloropropane	- 1	RO_2	Mabey et al., 1982
1,2-Diphenylhydrazine	36/hr	Cu^{4+}	Callahan, et al, 1979, p. 104-3
1,2-Diphenylhyrazine	7.2/hr		Callahan, et al, 1979, p. 104-3
1,2-Diphenylhydrazine	$< 4x10^7$	O_2	Mabey et al., 1982
1,2-Diphenylhydrazine	$1x10^9$	RO_2	Mabey et al., 1982
1,3-Dichlorobenzene	<< 360	O_2	Mabey et al., 1982
1,3-Dichlorobenzene	<< 1	RO_2	Mabey et al., 1982
1,3-Dichloropropene	$< 10^8$	O_2	Mabey et al., 1982
1,3-Dichloropropene	44	RO_2	Mabey et al., 1982
1,4-Dichlorobenzene	<< 360	O_2	Mabey et al., 1982
1,4-Dichlorobenzene	<< 1	RO_2	Mabey et al., 1982
2,4-Dichlorophenol	$< 7x10^5$	O_2	Mabey et al., 1982
2,4-Dichlorophenol	$1x10^7$	RO_2	Mabey et al., 1982
2,4-Dimethyl phenol	$< 4x10_6$	O_2	Mabey et al., 1982

TABLE A3 (continued)

Chemical	Oxidation Reaction Rate	Radical Present	Reference
2,4-Dimethyl phenol	$1.1x10^8$	RO_2	Mabey et al., 1982
2,4-Dinitrophenol	$3x10^4$	O_2	Mabey et al., 1982
2,4-Dinitrophenol	$5x10^5$	RO_2	Mabey et al., 1982
2,4-Dinitrotoluene	<< 360	O_2	Mabey et al., 1982
2,4-Dinitrotoluene	144	RO_2	Mabey et al., 1982
2,4,6-Trichlorophenol	$< 7x10^4$	O_2	Mabey et al., 1982
2,4,6-Trichlorophenol	$1x10^6$	RO_2	Mabey et al., 1982
2,6-Dinitrotoluene	<< 360	O_2	Mabey et al., 1982
2,6-Dinitrotoluene	144	RO_2	Mabey et al., 1982
2-Chloroethyl vinyl ether	$1x10^{10}$	O_2	Mabey et al., 1982
2-Chloroethyl vinyl ether	34	RO_2	Mabey et al., 1982
2-Chloronaphthalene	<<360	O_2	Mabey et al., 1982
2-Chloronaphthalene	<< 1	RO_2	Mabey et al., 1982
2-Chlorophenol	$< 7x10^5$	O_2	Mabey et al., 1982
2-Chlorophenol	$1x10^7$	RO_2	Mabey et al., 1982
2-Nitrophenol	$< 2x10^5$	O_2	Mabey et al., 1982
2-Nitrophenol	$2x10^6$	RO_2	Mabey et al., 1982
3,3'-Dichlorobenzidine	$< 4x10^7$	O_2	Mabey et al., 1982
3,3'-Dichlorobenzidine	$4x10^7$	RO_2	Mabey et al., 1982
4,6-Dinitro-o-cresol	$3x10^4$	O_2	Mabey et al., 1982
4,6-Dinitro-o-cresol	$5x10^5$	RO_2	Mabey et al., 1982
4-Bromophenyl phenyl ether	<< 360	O_2	Mabey et al., 1982
4-Bromophenyl phenyl ether	<< 1	RO_2	Mabey et al., 1982
4-Chlorophenyl phenyl ether	<< 360	O_2	Mabey et al., 1982
4-Chlorophenyl phenyl ether	<< 1	RO_2	Mabey et al., 1982
4-Nitrophenol	$< 2x10^5$	O_2	Mabey et al., 1982
4-Nitrophenol	$2x10^6$	RO_2	Mabey et al., 1982
Acenaphthene	< 3600	O_2	Mabey et al., 1982
Acenaphthene	$8x10^3$	RO_2	Mabey et al., 1982
Acenaphthylene	$- 4x10^7$	O_2	Mabey et al., 1982
Acenaphthylene	$5x10^3$	RO_2	Mabey et al., 1982
Acrolein	1E7	O_2	Mabey et al., 1982
Acrolein	3.4E3	RO_2	Mabey et al., 1982
Acrylonitrile	$< 1x10^8$	O_2	Mabey et al., 1982
Acrylonitrile	36	RO_2	Mabey et al., 1982
Aldrin	< 3600	O_2	Mabey et al., 1982

TABLE A3 (continued)

Chemical	Oxidation Reaction Rate	Radical Present	Reference
Aldrin	5E3	RO_2	Mabey et al., 1982
Anthracene	0.000018/hr	RO_2	Callahan, et al, 1979, p. 94-5
Anthracene	0.122/hr	Cu(II) acetate	Koshitani, et al, 1982
Anthracene	$5x10^8$	O_2	Mabey et al., 1982
Anthracene	$2.2x10^5$	RO_2	Mabey et al., 1982
Aroclor 1016	<< 360	O_2	Mabey et al., 1982
Aroclor 1016	<< 1	RO_2	Mabey et al., 1982
Aroclor 1221	<< 360	O_2	Mabey et al., 1982
Aroclor 1221	<< 1	RO_2	Mabey et al., 1982
Aroclor 1232	<< 360	O_2	Mabey et al., 1982
Aroclor 1232	<< 1	RO_2	Mabey et al., 1982
Aroclor 1242	<< 360	O_2	Mabey et al., 1982
Aroclor 1242	<< 1	RO_2	Mabey et al., 1982
Aroclor 1248	<< 360	O_2	Mabey et al., 1982
Aroclor 1248	<< 1	RO_2	Mabey et al., 1982
Aroclor 1254	<< 360	O_2	Mabey et al., 1982
Aroclor 1254	<< 1	RO_2	Mabey et al., 1982
Aroclor 1260	<< 360	O_2	Mabey et al., 1982
Aroclor 1260	<< 1	RO_2	Mabey et al., 1982
Benzene	43200/hr [ozone reaction rate, independent of benzene]	O_3	Kuo & Soong, 1984
Benzene	<< 360	O_2	Mabey et al., 1982
Benzene	<< 1	RO_2	Mabey et al., 1982
Benzidine	0.1738/hr	Me^+	Callahan, et al, 1979, p. 102-3
Benzidine	< $4x10^7$	O_2	Mabey et al., 1982
Benzidine	$1.1x10^8$	RO_2	Mabey et al., 1982
Benzo[a]anthracene	41.7/hr	O_3	Callahan, et al, 1979, p. 95-5
Benzo[a]anthracene	2.085/hr	Cl	Callahan, et al, 1979, p. 97-6
Benzo[a]anthracene	0.0183/hr	RO_2	Callahan, et al, 1979, p. 97-6
Benzo[a]anthracene	$5x10^8$	O_2	Mabey et al., 1982
Benzo[a]anthracene	$2x10^4$	RO_2	Mabey et al., 1982
Benzo[a]pyrene	4.17/hr	Cl	Callahan, et al, 1979, p. 95-5
Benzo[a]pyrene	0.0000029/hr	RO_2	Callahan, et al, 1979, p. 95-5
Benzo[a]pyrene	4.17/hr	O_3	Callahan, et al, 1979, p. 95-5
Benzo[a]pyrene	$5x10^8$	O_2	Mabey et al., 1982

TABLE A3 (continued)

Chemical	Oxidation Reaction Rate	Radical Present	Reference
Benzo[a]pyrene	$2x10^4$	RO_2	Mabey et al., 1982
Benzo[b]fluoranthene	$4x10^7$	O_2	Mabey et al., 1982
Benzo[b]fluoranthene	$5x10^3$	RO_2	Mabey et al., 1982
Benzo[ghi]perylene	2.78/hr	Cl	Callahan, et al, 1979, p. 98-7
Benzo[ghi]perylene	< 360	O_2	Mabey et al., 1982
Benzo[ghi]perylene	< 36	RO_2	Mabey et al., 1982
Bis(2-chloroethoxy)ether	<< 360	O_2	Mabey et al., 1982
Bis(2-chloroethoxy)ether	52	RO_2	Mabey et al., 1982
Bis(2-chloroethyl)ether	<< 360	O_2	Mabey et al., 1982
Bis(2-chloroethyl)ether	24	RO_2	Mabey et al., 1982
Bis(2-chloroisopropyl)ether	<< 360	O_2	Mabey et al., 1982
Bis(2-chloroisopropyl)ether	2	RO_2	Mabey et al., 1982
Bis(2-ethylhexyl)phthalate	<< 360	O_2	Mabey et al., 1982
Bis(2-ethylhexyl)phthalate	7.2	RO_2	Mabey et al., 1982
Bis(chloromethyl)ether	<0.00302/hr	OH^-	Callahan, et al, 1979, p. 64-2
Bis(chloromethyl)ether	<< 360	O_2	Mabey et al., 1982
Bis(chloromethyl)ether	3	RO_2	Mabey et al., 1982
Bromodichloromethane	<< 360	O_2	Mabey et al., 1982
Bromodichloromethane	0.2	RO_2	Mabey et al., 1982
Bromomethane	<< 360	O_2	Mabey et al., 1982
Bromomethane	0.1	RO_2	Mabey et al., 1982
Butyl benzyl phthalate	<< 360	O_2	Mabey et al., 1982
Butyl benzyl phthalate	280	RO_2	Mabey et al., 1982
Chlordane	< 3600	O_2	Mabey et al., 1982
Chlordane	~ 30	RO_2	Mabey et al., 1982
Chlorobenzene	<< 360	O_2	Mabey et al., 1982
Chlorobenzene	<< 1	RO_2	Mabey et al., 1982
Chloroethane	<< 360	O_2	Mabey et al., 1982
Chloroethane	<< 1	RO_2	Mabey et al., 1982
Chloroethene	$< 10^8$	O_2	Mabey et al., 1982
Chloroethene	3	RO_2	Mabey et al., 1982
Chloromethane	<< 360	O_2	Mabey et al., 1982
Chloromethane	0.05	RO_2	Mabey et al., 1982
Chrysens	$> 1x10^6$	O_2	Mabey et al., 1982
Chrysene	$1x10^3$	RO_2	Mabey et al., 1982
DDD	< 3600	O_2	Mabey et al., 1982

TABLE A3 (continued)

Chemical	Oxidation Reaction Rate	Radical Present	Reference
DDD	< 1600	RO_2	Mabey et al., 1982
DDE	< 3600	O_2	Mabey et al., 1982
DDE	1.2E5	RO_2	Mabey et al., 1982
DDT	< 3600	O_2	Mabey et al., 1982
DDT	3600	RO_2	Mabey et al., 1982
Di-n-butyl phthalate	<< 360	O_2	Mabey et al., 1982
Di-n-butyl phthalate	1.4	RO_2	Mabey et al., 1982
Di-n-octyl phthalate	<< 360	O_2	Mabey et al., 1982
Di-n-octyl phthalate	1.4	RO_2	Mabey et al., 1982
Di-n-propyl nitrosamine	< 3600	O_2	Mabey et al., 1982
Di-n-propyl nitrosamine	< 3600	RO_2	Mabey et al., 1982
Diazinon	31.1875/hr	Cl	Dennis, et al, 1979
Dibenzo[a,h]anthracene	$5x10^8$	O_2	Mabey et al., 1982
Dibenzo[a,h]anthracene	$1.5x10^4$	RO_2	Mabey et al., 1982
Dibromochloromethane	<< 360	O_2	Mabey et al., 1982
Dibromochloromethane	0.5	RO_2	Mabey et al., 1982
Dichlorodifluoromethane	0	O_2	Mabey et al., 1982
Dichlorodifluoromethane	0	RO_2	Mabey et al., 1982
Dichloromethane	<< 360	O_2	Mabey et al., 1982
Dichloromethane	0.2	RO_2	Mabey et al., 1982
Dieldrin	< 3600	O_2	Mabey et al., 1982
Dieldrin	30	RO_2	Mabey et al., 1982
Diethyl phthalate	<< 360	O_2	Mabey et al., 1982
Diethyl phthalate	1.4	RO_2	Mabey et al., 1982
Dimethyl nitrosamine	< 3600	O_2	Mabey et al., 1982
Dimethyl nitrosamine	< 3600	RO_2	Mabey et al., 1982
Dimethyl phthalate	<< 360	O_2	Mabey et al., 1982
Dimethyl phthalate	0.05	RO_2	Mabey et al., 1982
Dimethylnitrosamine	no reaction	O_3	Fochtman & Eisenberg, 1979
Diphenyl nitrosamine	< 3600	O_2	Mabey et al., 1982
Diphenyl nitrosamine	< 3600	RO_2	Mabey et al., 1982
α-Endosulfan	< 3600	O_2	Mabey et al., 1982
α-Endosulfan	$3.6x10^4$	RO_2	Mabey et al., 1982
β-Endosulfan	< 3600	O_2	Mabey et al., 1982
β-Endosulfan	$3.6x10^4$	RO_2	Mabey et al., 1982
Endosulfan-alpha	4.33E-4/hr		Callahan, et al, 1979, p. 27-5

TABLE A3 (continued)

Chemical	Oxidation Reaction Rate	Radical Present	Reference
Endosulfan-beta	4.04E-4/hr		Callahan, et al, 1979, p. 27-5
Endosulfan sulfate	< 3600	O_2	Mabey et al., 1982
Endosulfan sulfate	20	RO_2	Mabey et al., 1982
Endrin	< 3600	O_2	Mabey et al., 1982
Endrine	20	RO_2	Mabey et al., 1982
Endrine aldehyde	< 3600	O_2	Mabey et al., 1982
Endrine aldehyde	3100	RO_2	Mabey et al., 1982
Ethylbenzene	<< 360	O_2	Mabey et al., 1982
Ethylbenzene	720	RO_2	Mabey et al., 1982
Fluoranthene	< 3600	O_2	Mabey et al., 1982
Fluoranthene	< 360	RO_2	Mabey et al., 1982
Fluorene	< 360	O_2	Mabey et al., 1982
Fluorene	$3x10^3$	RO_2	Mabey et al., 1982
Heptachlor	$3x10^{10}$	O_2	Mabey et al., 1982
Heptachlor	2500	RO_2	Mabey et al., 1982
Heptachlor epoxide	< 3600	O_2	Mabey et al., 1982
Heptachlor epoxide	20	RO_2	Mabey et al., 1982
α-Hexachlorocyclohexane	< 3600	O_2	Mabey et al., 1982
α-Hexachlorocyclohexane	6	RO_2	Mabey et al., 1982
β-Hexachlorocyclohexane	< 3600	O_2	Mabey et al., 1982
β-Hexachlorocyclohexane	6	RO_2	Mabey et al., 1982
δ-Hexachlorocyclohexane	< 3600	O_2	Mabey et al., 1982
δ-Hexachlorocyclohexane	6	RO_2	Mabey et al., 1982
γ-Hexachlorocyclohexane	< 3600	O_2	Mabey et al., 1982
γ-Hexachlorocyclohexane	6	RO_2	Mabey et al., 1982
Hexachlorobenzene	<< 360	O_2	Mabey et al., 1982
Hexachlorobenzene	<< 1	RO_2	Mabey et al., 1982
Hexachlorobutadiene	$< 10^3$	O_2	Mabey et al., 1982
Hexachlorobutadiene	6	RO_2	Mabey et al., 1982
Hexachlorocyclopentadiene	$< 10^3$	O_2	Mabey et al., 1982
Hexachlorocyclopentadiene	12	RO_2	Mabey et al., 1982
Hexachloroethane	0	O_2	Mabey et al., 1982
Hexachloroethane	0	RO_2	Mabey et al., 1982
Indeno[1,2,3-cd]pyrene	$5x10^8$	O_2	Mabey et al., 1982
Indeno[1,2,3-cd]pyrene	$2x10^4$	RO_2	Mabey et al., 1982
Isophorone	$< 1x10^7$	O_2	Mabey et al., 1982

TABLE A3 (continued)

Chemical	Oxidation Reaction Rate	Radical Present	Reference
Isophorone	225	RO_2	Mabey et al., 1982
Naphthalene	fast	O_3	Fochtman & Eisenberg, 1979
Naphthalene	< 360	O_2	Mabey et al., 1982
Naphthalene	< 1	RO_2	Mabey et al., 1982
Nitrobenzene	<< 360	O_2	Mabey et al., 1982
Nitrobenzene	<< 1	RO_2	Mabey et al., 1982
Pentachlorophenol	< $7x10^3$	O_2	Mabey et al., 1982
Pentachlorophenol	$1x10^5$	RO_2	Mabey et al., 1982
Perylene	0.000018/hr	RO_2	Callahan, et al, 1979, p. 95-5
Phenanthrene	3.61E-9/hr	RO_2	Callahan, et al, 1979, p. 97-6
Phenanthrene	< 360	O_2	Mabey et al., 1982
Phenanthrene	< 36	RO_2	Mabey et al., 1982
Phenol	< $7x10^5$	O_2	Mabey et al., 1982
Phenol	$1x10^7$	RO_2	Mabey et al., 1982
Pyrene	41.7/hr	O_3	Callahan, et al, 1979, p. 95-5
Pyrene	2.085/hr	Cl	Callahan, et al, 1979, p. 97-6
Pyrene	$5x10^8$	O_2	Mabey et al., 1982
Pyrene	$2.2x10^4$	RO_2	Mabey et al., 1982
TCDD	< 3600	O_2	Mabey et al., 1982
TCDD	< 1	RO_2	Mabey et al., 1982
Tetrachloroethene	<< 100	O_2	Mabey et al., 1982
Tetrachloroethene	6	RO_2	Mabey et al., 1982
Tetrachloromethane	<< 360	O_2	Mabey et al., 1982
Tetrachloromethane	<< 1	RO_2	Mabey et al., 1982
Toluene	<< 360	O_2	Mabey et al., 1982
Toluene	144	RO_2	Mabey et al., 1982
Toxaphene	< 3600	O_2	Mabey et al., 1982
Toxaphene	3	RO_2	Mabey et al., 1982
Tribromomethane	<< 360	O_2	Mabey et al., 1982
Tribromomethane	0.5	RO_2	Mabey et al., 1982
Trichloroethene	< 10^3	O_2	Mabey et al., 1982
Trichloroethene	6	RO_2	Mabey et al., 1982
Trichlorofluoromethane	0	O_2	Mabey et al., 1982
Trichlorofluoromethane	0	RO_2	Mabey et al., 1982
Trichloromethane	<< 360	O_2	Mabey et al., 1982
Trichloromethane	0.7	RO_2	Mabey et al., 1982

TABLE A3 (continued)

Chemical	Oxidation Reaction Rate	Radical Present	Reference
p-Chloro-m-cresol	$< 7 \times 10^5$	O_2	Mabey et al., 1982
p-Chloro-m-cresol	1×10^7	RO_2	Mabey et al., 1982

TABLE A4. PHOTOLYSIS

Chemical	Chemical Concentration ug/l	Photolysis Reaction Rate (surface)	Quantum Yield	Wavelength (nm)	Reference
2,4-D	88.4	0.000466/hr	0.06		Hautala, 1978
2,4-D butoxyethyl ester		0.00222/hr		sunlight	Callahan, 1979, p. 35-4
2,4-D butyl ester		0.00222/hr		295-335	Que Hee & Sutherland, 1979
2,4-D methyl ester		0.000466/hr			Harris, 1982a
2,4-D methyl ester			0.06		Harris, 1982a
2,4-Dinitrotoluene		0.016/hr			Mabey et.al., 1982
3,3'-Dichlorobenzidine		2.1E-6/hr			Mabey et al., 1982
Acrolein			0.003	313	Callahan, 1979, p. 20-3
Anthracene		1.188/hr			Callahan, 1979, p. 96-14
Anthracene		0.924/hr			Harris, 1982a
Anthracene			0.003		Harris, 1982a
Anthracene		0.15/hr			Mabey et al., 1982
Benzidine		11.09/hr		254	Lu, 1977
Benzo[a]anthracene		0.21/hr			Harris, 1982a
Benzo[a]anthracene		0.216/hr			Callahan, 1979, p. 97-15
Benzo[a]anthracene			0.0033		Harris, 1982a
Benzo(a)anthracene		1.39/hr			Mabey et al., 1982
Benzo[a]pyrene		1.008/hr			Callahan, 1979, p. 98-21
Benzo[a]pyrene		0.694/hr			Harris, 1982a
Benzo[a]pyrene		1.386/hr			Mill, 1982
Benzo[a]pyrene	2.5	0.348/hr		254	Lu, 1977
Benzo[a]pyrene			0.00089		Harris, 1982a
Benzo(a)pyrene		0.58/hr			Mabey et al., 1982
Butylbenzylphthalate	9.73	<0.00029/hr			Gledhill, 1980
Carbaryl		0.00262/hr		sunlight	Harris, 1982a
Carbaryl	2.01			sunlight	Harris, 1982b
Carbaryl		0.00438/hr	0.0055		Wolfe, Zepp & Paris, 1978
Carbaryl			0.01	sunlight	Harris, 1982a
Carbaryl	70.35	0.00262/hr	0.01	sunlight	Hautala, 1978
Chrysene		0.158/hr			Harris, 1982a
Chrysene			0.003		Harris, 1982a
DDD			0.04	254	Callahan, 1979, p. 23-2
DDD		< 5E-7/hr			Mabey et al., 1982
DDE			0.26	254	Callahan, 1979, p. 24-3
DDE	1	0.0206/hr	0.3		Zepp, 1977

TABLE A4 (continued)

Chemical	Chemical Concentration ug/l	Photolysis Reaction Rate (surface)	Quantum Yield	Wavelength (nm)	Reference
DDE			0.30	313	Callahan, 1979, p. 24-2
DDT			0.16	254	Callahan, 1979, p. 23-2
DDT			0.16	254	Callahan, 1979, p. 25-6
DDT		< 5E-7/hr			Mabey et al., 1982
Dieldrin		0.00048/hr			Callahan, 1979, p. 26-3
Fluoranthene		0.033/hr			Harris, 1982a
Fluoranthene			0.0002		Harris, 1982a
Heptachlor			0.025	254	Callahan, 1979, p. 29-3
Hexachlorocyclopentadiene	49.1	3.9/hr			Wolfe, 1982
Malathion		0.0433/hr			Wolfe, 1977a
Malathion		0.007/hr			Wolfe, 1977a
Malathion		0.0462/hr			Harris, 1982a
Methoxychlor		0.000996/hr			Harris, 1982a
Methoxychlor			0.3		Harris, 1982a
Methylene chloride		<0.0028/hr			Callahan, 1979, p. 39-2
Naphthalene		0.0099/hr			Harris, 1982a
Naphthalene			0.015		Harris, 1982a
Parathion	26,000	0.0024/hr			Mill, 1982
Parathion		0.00314/hr			Harris, 1982a
Parathion			<0.001	>280	Harris, 1982a
Parathion	14.55	0.00314/hr	0.0002		Hautala, 1978
Pentachlorophenol	10,000	1.224/hr		290-330	Callahan, 1979, p. 87-3
Pentachlorophenol		0.2296/hr			Pignatello, 1983
Phenanthrene		0.0825/hr		313	Harris, 1982a
Phenanthrene			0.01	313, 366	Harris, 1982a
Pyrene		1.0205/hr		313	Harris, 1982a
Pyrene			0.002	313	Harris, 1982a
Trifluralin			0.002		Harris, 1982a

TABLE A5. SOLUBILITY AND VOLATILIZATION

Chemical	Solubility (mg/ℓ)	Vapor Pressure	Henry's Constant ($atm\text{-}m^3/M$)	Reference
1,1,1-Trichloroethane	4,400	96 mm Hg		Callahan, 1979, p. 45-2
1,1,1-Trichloroethane		100 mm Hg		Gossett & Lincoff, 1981
1,1,1-Trichloroethane	950	100 mm Hg	0.018	Thomas, 1982
1,1,1-Trichloroethane	720(25°C)	123(25°C)	0.03	Mabey et al., 1982
1,1,2,2-Tetrachloroethane	2,900	5 mm Hg		Callahan, 1979, p. 47-2
1,1,2,2-Tetrachloroethane	2.9×10^3(25°C)	5(20°C)	3.8×10^{-4}	Mabey et al., 1982
1,1,2-Trichloroethane	4,500	19 mm Hg		Callahan, 1979, p. 46-2
1,1,2-Trichloroethane	4.5×10^3(20°C)	19(20°C)	7.42×10^{-4}	Mabey et al., 1982
1,1-Dichloroethane	5.5×10^3(20°C)	180(20°C)	4.26×10^{-3}	Mabey et al., 1982
1,1-Dichloroethane	400(20°C)	591(25°C)	0.190	Mabey et al., 1982
1,1-Dichloroethene	5,500	180 mm Hg		Callahan, 1979, p. 43-2
1,1-Dichloroethene	400	591 mm Hg		Callahan, 1979, p. 50-2
1,1-Dichloroethene	273			Lyman 1982b
1,1-Dichloroethylene			0.352	Matter-Muller, Gujer & Giger, 1981
1,2,4,5-Tetrachlorobenzene	6			Kenaga & Goring, 1980
1,2,4-Trichlorobenzene	30	0.42 mm Hg		Callahan, 1979, p. 76-
1,2,4-Trichlorobenzene	30			Kenaga & Goring, 1980
1,2,4-Trichlorobenzene	34			Yalkowski, Orr & Valvani, 1979
1,2,4-Trichlorobenzene	34			Yalkowsky, 1983
1,2,4-Trichlorobenzene	30(25°C)	0.29(25°C)	2.3×10^{-3}	Mabey et al., 1982
1,2,4-Trimethylbenzene			0.0058	Matter-Muller, Gujer & Giger, 1981
1,2-Dibromomethane	4,000	10.94 mm Hg	0.005	Mackay, 1982
1,2-Dichlorobenzene	145	1.5 mm Hg		Callahan, 1979, p. 73-2
1,2-Dichlorobenzene		1 mm Hg		Gossett & Lincoff, 1981
1,2-Dichlorobenzene	100	1 mm Hg	0.0018	Mackay, 1982
1,2-Dichlorobenzene	93			Yalkowski, Orr & Valvani, 1979
1,2-Dichlorobenzene	125			Yalkowsky, 1983
1,2-Dichlorobenzene	100(20°C)	1.0(20°C)	1.93×10^{-3}	Mabey et al., 1982
1,2-Dichloroethane	8,690	61 mm Hg		Callahan, 1979, p. 44-2
1,2-Dichloroethane	8,000	67 mm Hg	0.0011	Thomas, 1982
1,2-Dichloroethane	8.69×10^3	61(20°C)	9.14×10^{-4}	Mabey et al., 1982
1,2-Dichloroethene-trans	600	200 mm Hg		Callahan, 1979, p. 51-2
1,2-Dichloroethene-trans	600(20°C)	326(20°C)	0.067	Mabey et al., 1982
1,2-Dichloropropane	2,700	42 mm Hg		Callahan, 1979, p. 54-1
1,2-Dichloropropane	2825	39.52 mm Hg	0.00207	Mackay, 1982
1,2-Dichloropropane	2.7×10^3(20°C)	42(20°C)	2.31×10^{-3}	Mabey et al., 1982

TABLE A5 (continued)

Chemical	Solubility (mg/ℓ)	Vapor Pressure	Henry's Constant (atm-m^3/M)	Reference
1,2-Diphenylhydrazine	1.84×10^3	2.6×10^{-5}(25°C)	3.4×10^{-9}(25°C)	Mabey et al., 1982
1,3-Dibromopropane			0.0003	Mackay, 1982
1,3-Dichlorobenzene	123	2.28 mm Hg		Callahan, 1979, p. 74-2
1,3-Dichlorobenzene	119			Yalkowski, Orr & Valvani, 1979
1,3-Dichlorobenzene	125			Yalkowsky, 1983
1,3-Dichlorobenzene	123(25°C)	2.28(25°C)	3.61×10^{-3}	Mabey et al., 1982
1,3-Dichloropropene	2,700	25 mm Hg		Callahan, 1979, p. 55-2
1,3-Dichloropropene	2,700			Kenaga & Goring, 1980
1,3-Dichloropropene	2,700	25 mm Hg	0.00125	McCall, 1983
1,3-Dichloropropene	2.7×10^3/2.8×10^3(25°C)	25(20°C)	1.33×10^{-3}	Mabey et al., 1982
1,3-Dinitrotoluene	498			Lyman, 1982b
1,4-Dichlorobenzene	79			Callahan, 1979, p. 75-2
1,4-Dichlorobenzene	79			Kenaga & Goring, 1980
1,4-Dichlorobenzene			0.00314	Matter-Muller, Gujer & Giger, 1981
1,4-Dichlorobenzene	91			Yalkowski, Orr & Valvani, 1979
1,4-Dichlorobenzene	86			Yalkowsky, 1983
1,4-Dichlorobenzene	79(25°C)	1.18(25°C)	3.1×10^{-3}	Mabey et al., 1982
1,4-Nitrophenol	16,000	2.2 mm Hg	0.000029	Jaffe & Ferrara, 1983
1-Chloronaphthalene	39			Yalkowsky, 1983
2,2',3,3',4,4',5,5',6-PCB	0.00009			Yalkowsky, 1983
2,2',3,3',4,4',5,5'-PCB	0.00138			Yalkowsky, 1983
2,2',3,3',4,4'-PCB	0.00043			Yalkowsky, 1983
2,2',3,3',4,5-PCB	0.00083			Yalkowsky, 1983
2,2',3,3',5,5',6,6'-PCB	0.00017			Yalkowsky, 1983
2,2',3,3',5,6-PCB	0.00090			Yalkowsky, 1983
2,2',3,3'-PCB	0.02978			Yalkowsky, 1983
2,2',3,4,5'-PCB	0.01006			Yalkowsky, 1983
2,2',3,4,5,5',6-PCB	0.00047			Yalkowsky, 1983
2,2',3,4,6-PCB	0.01208			Yalkowsky, 1983
2,2',3,5'-PCB	0.17140			Yalkowsky, 1983
2,2',4,4',5,5'-PCB	0.001			Kenaga & Goring, 1980
2,2',4,4',5,5'-PCB	0.0013			Yalkowsky, 1983
2,2',4,4',6,6'-PCB	0.00090			Yalkowsky, 1983
2,2',4,4'-PCB	0.06687			Yalkowsky, 1983
2,2',4,5,5'-PCB	0.01296			Yalkowsky, 1983
2,2',4,5,5'-PCB	0.004			Swann, 1983

TABLE A5 (continued)

Chemical	Solubility (mg/ℓ)	Vapor Pressure	Henry's Constant (atm-m^3/M)	Reference
2,2',5,5'-PCB	0.01837			Yalkowsky, 1983
2,3',4',5-PCB	0.04117			Yalkowsky, 1983
2,3',4,4'-PCB	0.05957			Yalkowsky, 1983
2,3,4,5,6-PCB	0.00679			Yalkowsky, 1983
2,3,4,5-PCB	0.01924			Yalkowsky, 1983
2,4,6-Trichlorophenol	800	1 mm Hg		Callahan, 1979, p. 86-2
2,4,6-Trichlorophenol	800(25°C)	0.012(25°C)	$4x10^{-6}$	Mabey et al., 1982
2,4-D	9			Hautala, 1978
2,4-D	900			Kenaga & Goring, 1980
2,4-D	900	6.0E-7 mm Hg	1.72E-9	McCall, 1983
2,4-Dichlorophenol	4,500	0.12 mm Hg		Callahan, 1979, p. 85-2
2,4-Dichlorophenol	$4.6x10^3$(20°C)	0.059(20°C)	$2.8x10^{-6}$	Mabey et al., 1982
2,4-Dimethylphenol	4,200	0.0621 mm Hg		Callahan, 1979, p. 91-2
2,4-Dimethylphenol	590(25°C)	0.062(20°C)	$1.7x10^{-5}$	Mabey et al., 1982
2,4-Dinitrophenol	5,600			Callahan, 1979, p. 90-2
2,4-Dinitrophenol	$5.6x10^3$(18°C)	$1.49x10^{-5}$(18°C)	$6.45x10^{-10}$	Mabey et al., 1982
2,4-Dinitrotoluene	270	0.0013 mm Hg		Callahan, 1979, p. 81-2
2,4-Dinitrotoluene			0.000197	Smith, Mackay & Ng, 1983
2,4-Dinitrotoluene	270(22°C)	$5.1x10^{-3}$(20°C)	$4.5x10^{-6}$	Mabey et al., 1982
2,6-Dinitrotoluene	180(20°C)	0.018(20°C)	$7.9x10^{-6}$	Mabey et al., 1982
2-Chloroethyl vinyl ether	15,000	26.75 mm Hg		Callahan, 1979, p. 67-2
2-Chloroethyl vinyl ether	$1.5x10^4$(25°C)	26.75(20°C)	$2.50x10^{-7}$	Mabey et al., 1982
2-Chloronaphthalane	6.74	0.017 mm Hg		Callahan, 1979, p. 37-2
2-Chloronaphthalene	12.31			Yalkowsky, 1983
2-Chloronaphthalene	6.74(25°C)	0.017(20°C)	$5.4x10^{-4}$	Mabey et al., 1982
2-Chlorophenol	28,500	2.2 mm Hg		Callahan, 1979, p. 84-2
2-Chlorophenol			0.0000115	Smith, Mackay & Ng, 1983
2-Chlorophenol	$2.85x10^4$(20°C)	1.77(20°C)	$1.03x10^{-5}$	Mabey et al., 1982
2-Nitrophenol	2,100	1 mm Hg		Callahan, 1979, p. 88-2
2-Nitrophenol	$2.1x10^3$(20°C)	0.151(20°C)	$7.56x10^{-6}$	Mabey et al., 1982
3,3',4,4'-PCB	0.01133			Yalkowsky, 1983
3,3'-Dichlorobenzidine	4			Callahan, 1979, p. 103-2
3,3'-Dichlorobenzidine	4.0(22°C)	$1x10^{-5}$(22°C)	$8x10^{-7}$	Mabey et al., 1982
3,4-Benzopyrene	0.0038			Lyman, 1982b
4,4'-PCB	0.062			Kenaga & Goring, 1980
4,6-Dinitro-o-cresol	290(25°C)	$5x10^{-2}$(20°C)	$4x10^{-5}$	Mabey et al., 1982

TABLE A5 (continued)

Chemical	Solubility (mg/ℓ)	Vapor Pressure	Henry's Constant (atm-m^3/M)	Reference
4-Bromophenyl phenyl ether		0.0015 mm Hg		Callahan, 1979, p. 69-2
4-Bromophenyl phenyl ether	4.8(25°C)	$1.5x10^{-3}$(20°C)	$1.0x10^{-4}$	Mabey et al., 1982
4-Chlorobiphenyl	1.65			Kenaga & Goring, 1980
4-Chlorophenyl phenyl ether	3.3	0.0027 mm Hg		Callahan, 1979, p. 68-2
4-Chlorophenyl phenyl ether	3.3(25°C)	$2.7x10^{-3}$	$2.19x10^{-4}$	Mabey et al., 1982
4-Nitrophenol	16,000	2.2 mm Hg		Callahan, 1979, p. 89-2
4-Nitrophenol	$1.6x10^{4}$(25°C)	2.2(146°C)	$2.5x10^{-5}$	Mabey et al., 1982
Acenaphthene	3.42	0.01 mm Hg		Callahan, 1979, p. 95-3
Acenaphthene	3.9	2.8E-3 mm Hg	0.00015	Thomas, 1982
Acenaphthene	4.2			Yalkowsky, 1983
Acenaphthene	3.42(25°C)	$1.55x10^{-3}$(25°C)	$9.1x10^{-5}$	Mabey et al., 1982
Acenaphthylene	3.93	0.01 mm Hg		Callahan, 1979, p. 95-3
Acenaphthylene	3.93(25°C)	0.029(20°C)	$1.45x10^{-3}$	Mabey et al., 1982
Acrolein	208,000	220 mm Hg		Callahan, 1979, p. 20-2
Acrolein	$2.1x10^{5}$(20°C)	220 (20°C)	$5.66x10^{-5}$	Mabey et al., 1982
Acrylonitrile	73,500	100 mm Hg		Callahan, 1979, p. 105-2
Acrylonitrile	80,000			Lyman, 1982b
Acrylonitrile	$7.9x10^{-4}$(25°C)	100(22.8°C)	$8.8x10^{-5}$	Mabey et al., 1982
Alachlor	242			Kenaga & Goring, 1980
Aldicarb	7,800			Kenaga & Goring, 1980
Aldrin	0.2	2.31E-5 mm Hg		Callahan, 1979, p. 21-2
Aldrin	0.013			Kenaga & Goring, 1980
Aldrin	0.2	6E-6 mm Hg	0.000014	Thomas, 1982
Aldrin	0.18 (25°C)	$6x10^{-6}$(25°C)	$1.6x10^{-5}$	Mabey et al., 1982
Anthracene	0.045	1.95E-4 mm Hg		Callahan, 1979, p. 96-3
Anthracene	0.073			Kenaga & Goring, 1980
Anthracene			9.87E-7	Smith, Mackay & Ng, 1983
Anthracene	0.051			Swann, 1983
Anthracene	0.045			Wasik, 1983
Anthracene	0.049			Yalkowsky, 1983
Anthracene	0.045(25°C)	$1.7x10^{-5}$(25°C)	$8.6x10^{-5}$	Mabey et al., 1982
Aroclor 1016	0.42	4E-4 mm Hg		Callahan, 1979, p. 36-4
Aroclor 1016	0.42(25°C)	$4x10^{-4}$(25°C)	$3.3x10^{-4}$	Mabey et al., 1982
Aroclor 1016, 1242	0.085			Kenaga & Goring, 1980
Aroclor 1221	15	6.7E-3 mm Hg		Callahan, 1979, p. 36-4
Aroclor 1221	40.0(25°C)	$6.7x10^{-3}$(25°C)	$1.7x10^{-4}$	Mabey et al., 1982

TABLE A5 (continued)

Chemical	Solubility (mg/ℓ)	Vapor Pressure	Henry's Constant (atm-m^3/M)	Reference
Aroclor 1232	1.45	4.06E-3 mm Hg		Callahan, 1979, p. 36-4
Aroclor 1232	407(25°C)	4.06x10^{-3}(25°C)	1.13x10^{-5}	Mabey et al., 1982
Aroclor 1242	0.20	4.06E-4 mm Hg		Callahan, 1979, p. 36-4
Aroclor 1242	0.24	4.1E-4 mm Hg	0.0056	Thomas, 1982
Aroclor 1242	0.23(25°C)	1.3x10^{-3}(25°C)	1.98x10^{-3}	Mabey et al., 1982
Aroclor 1248	0.054	4.94E-4 mm Hg		Callahan, 1979, p. 36-4
Aroclor 1248	0.054	4.94E-4 mm Hg	0.00347	Jaffe & Ferrara, 1983
Aroclor 1248	0.017			Kenaga & Goring, 1980
Aroclor 1248	0.054	4.9E-4 mm Hg	0.0035	Thomas, 1982
Aroclor 1248	0.054(25°C)	4.94x10^{-4}(25°C)	3.6x10^{-3}	Mabey et al., 1982
Aroclor 1254	0.02	7.71E-5 mm Hg		Callahan, 1979, p. 36-4
Aroclor 1254	0.01			Kenaga & Goring, 1980
Aroclor 1254	0.012	7.7E-5 mm Hg	0.00027	Thomas, 1982
Aroclor 1254	0.031(25°C)	7.71x10^{-5}(25°C)	2.6x10^{-3}	Mabey et al., 1982
Aroclor 1260	.0027	4.05E-5 mm Hg		Callahan, 1979, p. 36-4
Aroclor 1260	0.0027	4.05E-5 mm Hg	0.00712	Jaffe & Ferrara, 1983
Aroclor 1260	0.0027	4.1E-5 mm Hg	0.0071	Thomas, 1982
Aroclor 1260	2.7x10^{-3}(25°C)	4.05x10^{-5}(25°C)	0.74	Mabey et al., 1982
Atrazine	33			Kenaga & Goring, 1980
Atrazine	33			Lyman, 1982b
Benzene		95.2 mm Hg		Callahan, 1979, p. 71-2
Benzene	1,780			Kenaga & Goring, 1980
Benzene	1,750	76 mm Hg	0.00439	Mackay, 1982
Benzene			0.005	Matter-Muller, Gujer & Giger, 1981
Benzene	1,780	95.2 mm Hg	0.0055	Thomas, 1982
Benzene	1,789			Wasik, 1983
Benzene	1,633			Yalkowski, Orr & Valvani, 1979
Benzene	1,789			Yalkowsky, 1983
Benzene	1.78x10^{3}(25°C)	95.2(25°C)	5.5x10^{-3}	Mabey et al., 1982
Benzidine	400			Callahan, 1979, p. 102-2
Benzidine	500			Lu, 1977
Benzidine	400(12°C)	5x10^{-4}	3x10^{-7}	Mabey et al., 1982
Benzo[a]anthracene	0.009	5E-9 mm Hg		Callahan, 1979, p. 97-3
Benzo[a]anthracene	5.7x10^{-3}(20°C)	2.2x10^{-8}(20°C)	1x10^{-6}	Mabey et al., 1982
Benzo[a]pyrene	0.0038	5E-9 mm Hg		Callahan, 1979, p. 98-3
Benzo[a]pyrene	0.00017			Lu, 1977

TABLE A5 (continued)

Chemical	Solubility (mg/ℓ)	Vapor Pressure	Henry's Constant (atm-m^3/M)	Reference
Benzo[a]pyrene	$3.8x10^{-3}$(25°C)	$5.6x10^{-9}$(25°C)	$4.9x10^{-7}$	Mabey et al., 1982
Benzo[b]fluoranthene	0.014(25°C)	$5x10^{-7}$(20°C)	$1.22x10^{-5}$	Mabey et al., 1982
Benzo[ghi]perylene	0.00026	E-10 mm Hg		Callahan, 1979, p. 98-3
Benzo[ghi]perylene	0.00026			Lyman, 1982b
Benzo[ghi]perylene	0.00025			Yalkowsky, 1983
Benzo[ghi]perylene	$2.6x10^{-4}$(25°C)	$1.63x10^{-10}$(25°C)	$1.44x10^{-7}$	Mabey et al., 1982
Benzo[k]fluoranthene		9.59E-11 mm Hg		Callahan, 1979, p. 97-3
Benzo[k]fluoranthene	$4.3x10^{-3}$(25°C)	$5x10^{-7}$(20°C)	$1.22x10^{-5}$	Mabey et al., 1982
Bis(2-chloroethoxy)methane	81,000	<0.1 mm Hg		Callahan, 1979, p. 70-2
Bis(2-chloroethoxy)methane	$8.1x10^{4}$(25°C)	< 0.1(20°C)	$2.8x10^{-7}$	Mabey et al., 1982
Bis(2-chloroethyl)ether	10,200	0.71 mm Hg		Callahan, 1979, p. 65-2
Bis(2-chloroethyl)ether	$1.02x10^{4}$	0.71(20°C)	$1.3x10^{-5}$	Mabey et al., 1982
Bis(2-chloroisopropyl)ether	1,700	0.85 mm Hg		Callahan, 1979, p. 66-2
Bis(2-chloroisopropyl)ether	$1.7x10^{3}$	0.85(20°C)	$1.1x10^{-4}$	Mabey et al., 1982
Bis(2-ethylhexyl)phthalate	0.4	<0.01 mm Hg		Callahan, 1979, p. 94-5
Bis(2-ethylhexyl)phthalate	0.4(25°C)	$2x10^{-7}$(20°C)	$3x10^{-7}$	Mabey et al., 1982
Bis(chloromethyl)ether	22,000	30 mm Hg		Callahan, 1979, p. 64-1
Bis(chloromethyl)ether	$2.2x10^{4}$(25°C)	30(22°C)	$2.1x10^{-4}$	Mabey et al., 1982
Bromobenzene	446			Kenaga & Goring, 1980
Bromobenzene			0.002	Mackay, 1982
Bromobenzene	413			Wasik, 1983
Bromodichloromethane		50 mm Hg		Callahan, 1979, p. 59-1
Bromodichloromethane	$4.5x10^{3}$	50(20°C)	$2.41x10^{-3}$	Mabey et al., 1982
Bromoform		4.56 mm Hg	0.0005	Mackay, 1982
Bromomethane	900	1420 mm Hg		Callahan, 1979, p. 58-2
Bromomethane	3,100	10 mm Hg		Callahan, 1979, p. 61-2
Bromomethane	13,000	1400 mm Hg	0.013	Thomas, 1982
Bromomethane	900(20°C)	$1.42x10^{3}$(20°C)	0.197	Mabey et al., 1982
Butylbenzylphthalate	2.90			Callahan, 1979, p. 94-5
Butylbenzylphthalate	2.9	8.6E-6 mm Hg		Gledhill, 1980
Butylbenzylphthalate	42.2			Lyman, 1982b
Butylbenzylphthalate	2.9	$6x10^{-5}$	$8.3x10^{-6}$	Mabey et al., 1982
Carbofuran	415			Kenaga & Goring, 1980
Carbofuran	415			Lyman, 1982b
Carbofuran	670			Swann, 1983
Carbon tetrachloride	785	90 mm Hg		Callahan, 1979, p. 41-2

TABLE A5 (continued)

Chemical	Solubility (mg/ℓ)	Vapor Pressure	Henry's Constant ($atm\text{-}m^3/M$)	Reference
Carbon tetrachloride	800			Kenaga & Goring, 1980
Carbon tetrachloride	800	90 mm Hg	0.023	Mackay, 1982
Carbon tetrachloride	800	91 mm Hg	0.023	Thomas, 1982
Chlordane	0.056	E-5 mm Hg		Callahan, 1979, p. 22-2
Chlordane	1.85	E-5 mm Hg	0.0000028	Jaffe & Ferrara, 1983
Chlordane	0.056			Kenaga & Goring, 1980
Chlordane	0.0156(25°C)	$1x10^{-5}$(25°C)	$9.4x10^{-5}$	Mabey et al., 1982
Chlorobenzene	448			Kenaga & Goring, 1980
Chlorobenzene	500	9.12 mm Hg	0.00261	Mackay, 1982
Chlorobenzene	472	11.8 mm Hg	0.0037	Thomas, 1982
Chlorobenzene	499			Wasik, 1983
Chlorobenzene	502			Yalkowski, Orr & Valvani, 1979
Chlorobenzene	507			Yalkowsky, 1983
Chlorobenzene	488(25°C)	11.7(20°C)	$3.58x10^{-3}$	Mabey et al., 1982
Chloroethane	$5.74x10^3$(20°C)	$1.0x10^3$(20°C)	0.148	Mabey et al., 1982
Chloroethene	$2.7x10^3$(25°C)	$2.66x10^3$(25°C)	$8.14x10^{-2}$	Mabey et al., 1982
Chloroform	8,200	150.5 mm Hg		Callahan, 1979, p. 40-2
Chloroform		200 mm Hg	0.0032	Gossett & Lincoff, 1981
Chloroform	9,600	150 mm Hg	0.002	Jaffe & Ferrara, 1983
Chloroform	8,000	246 mm Hg	0.0048	Thomas, 1982
Chloromethane	7,000	3765 mm Hg		Callahan, 1979, p. 38-2
Chloromethane	7,400	3600 mm Hg	0.024	Thomas, 1982
Chloromethane	$6.45x10^3$	$3.76x10^3$(20°C)	0.04	Mabey et al., 1982
Chlorpyrifos	1.2	1.9E-5 mm Hg	0.0000067	McCall, 1983
Chrysene	0.002			Callahan, 1979, p. 97-3
Chrysene	0.002			Yalkowsky, 1983
Chrysene	$1.8x10^{-3}$(25°C)	$6.3x10^{-9}$(25°C)	$1.05x10^{-6}$	Mabey et al., 1982
DDD	0.02	10.2E-7 mm Hg		Callahan, 1979, p. 23-2
DDD	0.005			Kenaga & Goring, 1980
DDD			$2.2x10^{-8}$	Mabey et al., 1982
DDE	0.014	6.5E-6 mm Hg		Callahan, 1979, p. 24-2
DDE	0.12	6.5E-6 mm Hg	0.000022	Jaffe & Ferrara, 1983
DDE	0.01			Kenaga & Goring, 1980
DDE	0.006			Swann, 1983
DDE	0.04(20°C)		$6.8x10^{-5}$	Mabey et al., 1982
DDT	0.0055	1.5E-7 mm Hg		Callahan, 1979, p. 25-3

TABLE A5 (continued)

Chemical	Solubility (mg/ℓ)	Vapor Pressure	Henry's Constant (atm-m^3/M)	Reference
DDT	0.0017			Kenaga & Goring, 1980
DDT	0.0017			Lyman, 1982b
DDT	0.0017	1.9E-7 mm Hg	0.000048	McCall, 1983
DDT	0.02			Swann, 1983
DDT	0.0012	E-7 mm Hg	0.000038	Thomas, 1982
DDT	5.5×10^{-3}(25°C)	1.9×10^{-7}(25°C)	1.58×10^{-5}	Mabey et al., 1982
Di-n-butyl phthalate	13	0.1 mm Hg		Callahan, 1979, p. 94-5
Di-n-butyl phthalate	13(25°C)	1.0×10^{-5}(25°C)	2.8×10^{-7}	Mabey et al., 1982
Di-n-octyl phthalate	3	<0.2 mm Hg		Callahan, 1979, p. 94-5
Di-n-octyl phthalate	3.0(25°C)	1.4×10^{-4}(25°C)	1.7×10^{-5}	Mabey et al., 1982
Di-n-propylnitrosamine	9,900			Callahan, 1979, p. 101-1
Di-n-propylnitrosamine	9900(25°C)	0.4(37°C)	6.3×10^{-6}	Mabey et al., 1982
Diazinon	40			Kenaga & Goring, 1980
Dibenzo[ah]anthracene	0.0005	E-10 mm Hg		Callahan, 1979, p. 98-3
Dibenzo[a,h]anthracene	5×10^{-4}(25°C)	1×10^{-10}(20°C)	7.3×10^{-8}	Mabey et al., 1982
Dibromochloromethane		15 mm Hg		Callahan, 1979, p. 60-1
Dibromochloromethane	4.0×10^{3}	76(20°C)	9.9×10^{-4}	Mabey et al., 1982
Dichlorodifluoromethane	280	4306 mm Hg		Callahan, 1979, p. 62-2
Dichlorodifluoromethane	280(25°C)	4.87×10^{3}(25°C)	2.98	Mabey et al., 1982
Dichloromethane	2.0×10^{4}(20°C)	362.4(20°C)	2.03×10^{-3}	Mabey et al., 1982
Dieldrin	0.2	1.78E-7 mm Hg		Callahan, 1979, p. 26-2
Dieldrin	0.022			Kenaga & Goring, 1980
Dieldrin	0.25	E-7 mm Hg	2.00E-07	Thomas, 1982
Dieldrin	0.195(25°C)	1.78×10^{-7}(2-°C)	4.57×10^{-10}	Mabey et al., 1982
Diethyl phthalate	896	0.05 mm Hg		Callahan, 1979, p. 94-5
Diethyl phthalate	7,040			Lyman, 1982b
Diethyl phthalate	896 (25°C)	3.5×10^{-3}(25°C)	1.2×10^{-6}	Mabey et al., 1982
Dimethyl phthalate	5,000	<0.01 mm Hg		Callahan, 1979, p. 94-5
Dimethyl phthalate	5.00×10^{3}(20°C)	4.19×10^{-3}(20°C)	2.15×10^{-6}	Mabey et al., 1982
Dimethylnitrosamine	miscible			Callahan, 1979, p. 99-2
Dimethylnitrosamine		8.1(25°C)	3.3×10^{-5}	Mabey et al., 1982
Dioxin	0.0002			Callahan, 1979, p. 34-2
Diphenylnitrosamine	40(25°C)	0.1(25°C)	6.6×10^{-4}	Mabey et al., 1982
α-Endosulfan	0.530(25°C)	1×10^{-5}(25°C)	1.0×10^{-5}	Mabey et al., 1982
β-Endosulfan	0.280(25°C)	1×10^{-5}(25°C)	1.91×10^{-5}	Mabey et al., 1982
Endosulfan	0.26	E-5 mm Hg		Callahan, 1979, p. 27-3

TABLE A5 (continued)

Chemical	Solubility (mg/ℓ)	Vapor Pressure	Henry's Constant (atm-m^3/M)	Reference
Endosulfan sulfate	0.117			Callahan, 1979, p. 27-3
Endosulfan sulfate	0.22	$1x10^{-5}$(25°C)	$2.6x10^{-5}$	Mabey et al., 1982
Endrin	0.25	2E-7 mm Hg		Callahan, 1979, p. 28-2
Endrin	0.024			Kenaga & Goring, 1980
Endrin	0.25(25°C)	$2x10^{-7}$(25°C)	$4.0x10^{-7}$	Mabey et al., 1982
Endrin aldehyde	50 (25°C)	$2.0x10^{-7}$(25°C)	$2x10^{-9}$	Mabey et al., 1982
Ethyl benzene	152	7 mm Hg		Callahan, 1979, p. 78-2
Ethyl benzene	152	9.5 mm Hg	0.0088	Thomas, 1982
Ethyl benzene	187			Wasik, 1983
Ethyl benzene	152(20°C)	7(20°C)	$6.6x10^{-3}$	Mabey et al., 1982
Ethyl chloride	5,740	1000 mm Hg		Callahan, 1979, p. 42-2
Fluoranthene	0.26	E-5 mm Hg		Callahan, 1979, p. 96-3
Fluoranthene	0.24			Yalkowsky, 1983
Fluroanthene	0.26(25°C)	$5.0x10^{-6}$(25°C)	$6.5x10^{-6}$	Mabey et al., 1982
Fluorene	1.98	0.01 mm Hg		Callahan, 1979, p. 95-3
Fluorene	1.98			Lyman, 1982b
Fluorene	1.17			Wasik, 1983
Fluorene	1.27			Yalkowsky, 1983
Fluorene	1.69(25°C)	$7.1x10^{-4}$	$6.4x10^{-5}$	Mabey et al., 1982
Heptachlor	0.18	3E-4 mm Hg		Callahan, 1979, p. 29-2
Heptachlor	0.03			Kenaga & Goring, 1980
Heptachlor	0.18(25°C)	$3.0x10^{-4}$(25°C)	$3.9x10^{-4}$	Mabey et al., 1982
Heptachlor epoxide	0.35			Callahan, 1979, p. 30-2
Heptachlor epoxide	0.350(25°C)	$3x10^{-4}$(25°C)	$3.9x10^{-4}$	Mabey et al., 1982
Hexachlorobenzene		1.089E-5 mm Hg		Callahan, 1979, p. 77-2
Hexachlorobenzene	0.006	1.09E-5 mm Hg	0.00065	Jaffe & Ferrara, 1983
Hexachlorobenzene	0.035			Kenaga & Goring, 1980
Hexachlorobenzene	0.008			Yalkowski, Orr & Valvani, 1979
Hexachlorobenzene	0.005			Yalkowsky, 1983
Hexachlorobenzene	$6x10^{-3}$(25°C)	$1.09x10^{-5}$(20°C)	$6.8x10^{-4}$	Mabey et al., 1982
Hexachlorobutadiene	2	0.15 mm Hg		Callahan, 1979, p. 56-2
Hexachlorobutadiene	2.0(20°C)	0.15(20°C)	0.0256	Mabey et al., 1982
α-Hexachlorocyclohexane	1.63(25°C)	$2.5x10^{-5}$(20°C)	$6.0x10^{-6}$	Mabey et al., 1982
Hexachlorocyclohexane(alpha)	2	2.5E-5 mm Hg		Callahan, 1979, p. 31-2
β-Hexachlorocyclohexane	0.24(25°C)	$2.8x10^{-7}$(20°C)	$4.5x10^{-7}$	Mabey et al., 1982
Hexachlorocyclohexane(beta)	0.2	2.8E-7 mm Hg		Callahan, 1979, p. 31-2

TABLE A5 (continued)

Chemical	Solubility (mg/ℓ)	Vapor Pressure	Henry's Constant (atm-m^3/M)	Reference
δ-Hexachlorocyclohexane	31.4(25°C)	1.7×10^{-5}(20°C)	2.07×10^{-7}	Mabey et al., 1982
Hexachlorocyclohexane(delta)	21	1.7E-5 mm Hg		Callahan, 1979, p. 31-2
γ-Hexachlorocyclohexane	7.8(25°C)	1.6×10^{-4}(20°C)	7.8×10^{-6}	Mabey et al., 1982
Hexachlorocyclopentadiene	1.8	0.81 mm Hg		Callahan, 1979, p. 57-2
Hexachlorocyclopentadiene	1.8		0.027	Wolfe, 1982
Hexachlorocyclopentadiene	1.8(25°C)	0.081(25°C)	0.016	Mabey et al., 1982
Hexachloroethane	50	0.4 mm Hg		Callahan, 1979, p. 48-1
Hexachloroethane	8	0.4 mm Hg	0.0178	Jaffe & Ferrara, 1983
Hexachloroethane	27.2			Lyman, 1982b
Hexachloroethane	50(22°C)	0.4(20°C)	2.49×10^{-3}	Mabey et al., 1982
Indeno[1,2,3-cd]pyrene		E-10 mm Hg		Callahan, 1979, p. 98-3
indeno[1,2,3-cd]pyrene	5.3×10^{-4}(25°C)	1.0×10^{-10}(20°C)	6.95×10^{-8}	Mabey et al., 1982
Isophorone	12,000	0.38 mm Hg		Callahan, 1979, p. 33-2
Isophorone	1.2×10^{4}	0.38(20°C)	5.75×10^{-6}	Mabey et al., 1982
Kepone	3			Kenaga & Goring, 1980
Lindane	7.52	2E-4 mm Hg		Callahan, 1979, p. 32-2
Lindane	0.15			Kenaga & Goring, 1980
Lindane	0.15	3.2E-5 mm Hg	0.000075	McCall, 1983
Lindane		0.326 mm Hg		Spencer & Cliath, 1983
Lindane	7.3	9.4E-6 mm Hg	4.80E-07	Thomas, 1982
Malathion	145			Kenaga & Goring, 1980
Malathion	145			Lyman, 1982b
Methoxychlor	0.003			Lyman, 1982b
Methyl parathion	57			Kenaga & Goring, 1980
Methyl parathion		1.72 mm Hg		Spencer & Cliath, 1983
Methylene chloride	13,200	362.4 mm Hg		Callahan, 1979, p. 39-2
Methylene chloride		400 mm Hg	0.0027	Gossett & Lincoff, 1981
Methylene chloride	13,000	349 mm Hg	0.003	Thomas, 1982
Naphthalene	34.3	0.0492 mm Hg		Callahan, 1979, p. 95-3
Naphthalene			1.97E-7	Smith, Mackay & Ng, 1983
Naphthalene	33	0.23 mm Hg	0.00115	Thomas, 1982
Naphthalene	31			Wasik, 1983
Naphthalene	31			Yalkowsky, 1983
Naphthalene	31.7			Kenaga & Goring, 1980
Naphthalene	31.7(25°C)	0.087(25°C)	4.6×10^{-4}	Mabey et al., 1982
Nitrapyrin	40	2.8E-5 mm Hg	0.0000195	McCall, 1983

TABLE A5 (continued)

Chemical	Solubility (mg/ℓ)	Vapor Pressure	Henry's Constant (atm-m^3/M)	Reference
Nitrobenzene	1,900	0.15 mm Hg		Callahan, 1979, p. 79-1
Nitrobenzene	1,900	0.15 mm Hg	0.0000123	Jaffe & Ferrara, 1983
Nitrobenzene	1,780			Lyman, 1982b
Nitrobenzene	2,000	0.27 mm Hg	0.000022	Thomas, 1982
Nitrobenzene	$1.9x10^3$(20°C)	0.15(20°C)	$1.31x10^{-5}$	Mabey et al., 1982
Parathion	24			Kenaga & Goring, 1980
Parathion	24			Lyman, 1982b
Pentachlorobenzene	0.135			Kenaga & Goring, 1980
Pentachlorobenzene	0.561			Lyman, 1982b
Pentachlorophenol	14	0.00011 mm Hg		Callahan, 1979, p. 87-2
Pentachlorophenol	14			Kenaga & Goring, 1980
Pentachlorophenol	14	1.4E-4 mm Hg	3.40E-06	Thomas, 1982
Pentachlorophenol	14(20°C)	$1.1x10^{-4}$(20°C)	$2.8x10^{-6}$	Mabey et al., 1982
Perchloroethylene	200	14 mm Hg		Callahan, 1979, p. 53-2
Perchloroethylene	400	14.3 mm Hg	0.0083	Thomas, 1982
Phenanthrene	1	6.8E-4 mm Hg		Callahan, 1979, p. 96-3
Phenanthrene	1.29			Kenaga & Goring, 1980
Phenanthrene			2.47E-6	Smith, Mackay & Ng, 1983
Phenanthrene	1.29	2.1E-4 mm Hg	0.000039	Thomas, 1982
Phenanthrene	1.0			Wasik, 1983
Phenanthrene	1.10			Yalkowsky, 1983
Phenanthrene	1.00(25°C)	$9.6x10^{-4}$(25°C)	$2.26x10^{-4}$	Mabey et al., 1982
Phenol	93,000	0.5293 mm Hg		Callahan, 1979, p. 83-2
Phenol	82,000			Kenaga & Goring, 1980
Phenol	$9.3x10^4$(25°C)	0.341(25°C)	$4.54x10^{-7}$	Mabey et al., 1982
Pyrene	0.132	6.85E-7 mm Hg		Callahan, 1979, p. 97-3
Pyrene	0.135			Kenaga & Goring, 1980
Pyrene	0.130			Yalkowsky, 1983
Pyrene	0.13(25°C)	$2.5x10^{-6}$(25°C)	$5.1x10^{-6}$	Mabey et al., 1982
TCDD	$2x10^{-4}$	$1x10^{-6}$	$2.1x10^{-3}$	Mabey et al., 1982
Terbufos	12			Kenaga & Goring, 19809
Tetrachlorobiphenyl	0.017	4.9E-4 mm Hg	0.0112	McCall, 1983
Tetrachloroethene	200(20°C)	14(20°C)	0.0153	Mabey et al., 1982
Tetrachloroethylene		20 mm Hg	0.012	Gossett & Lincoff, 1981
Tetrachloroethylene	200			Kenaga & Goring, 1980
Tetrachloroethylene			0.0237	Matter-Muller, Gujer & Giger, 1981

TABLE A5 (continued)

Chemical	Solubility (mg/ℓ)	Vapor Pressure	Henry's Constant (atm-m^3/M)	Reference
Tetrachloromethane	785(20°C)	90(20°C)	0.023	Mabey et al., 1982
Toluene	534.8	28.7 mm Hg		Callahan, 1979, p. 80-2
Toluene	497	22 mm Hg	0.00518	Mackay, 1982
Toluene			0.0056	Matter-Muller, Gujer & Giger, 1981
Toluene	515	28.4 mm Hg	0.0066	Thomas, 1982
Toluene	579			Wasik, 1983
Toluene	534.8(25°C)	28.7(20°C)	6.6×10^{-3}	Mabey et al., 1982
Toxaphene	0.5	0.2 mm Hg		Callahan, 1979, p. 35-4
Toxaphene	0.4			Kenaga & Goring, 1980
Toxaphene	0.50(25°C)	0.2-0.4(25°C)	0.21	Mabey et al., 1982
Tribromomethane	3.01×10^3(20°C)	5(20°C)	5.6×10^{-4}	Mabey et al., 1982
Trichloroethene	1,100	57.9 mm Hg		Callahan, 1979, p. 52-2
Trichloroethene	1.1×10^3(20°C)	57.9(20°C)	9.1×10^{-3}	Mabey et al., 1982
Trichloroethylene		60 mm Hg	0.0088	Gossett & Lincoff, 1981
Trichloroethylene	1,100	57.9 mm Hg	0.00876	Jaffe & Ferrara, 1983
Trichlorofluoromethane	1,100	667.4 mm Hg		Callahan, 1979, p. 63-2
Trichlorofluoromethane			5.0	Thomas, 1982
Trichlorofluoromethane	1.1×10^3(20°C)	667.4(20°C)	0.11	Mabey et al., 1982
Trichloromethane	8.2×10^3(20°C)	150.5(20°C)	2.88×10^{-3}	Mabey et al., 1982
Trifluralin	0.6			Kenaga & Goring, 1980
Trifluralin	0.7			Swann, 1983
Vinyl chloride	1.1	2,660 mm Hg		Callahan, 1979, p. 49-2
Vinyl chloride	90	2,580 mm Hg	2.4	Thomas, 1982
p-Chloro-m-cresol	3,850			Callahan, 1979, p. 92-2
p-Chloro-m-cresol	3.85×10^3(20°C)	0.05(20°C)	2.5×10^{-6}	Mabey et al., 1982
p-Cresol		<1 mm Hg		Gossett & Lincoff, 1981

TABLE A6. PARTITIONING

Chemical	K_{ow} log	Partition Coef (µg/kg)/(µg/ℓ)	Reference
1,1,1-Trichloroethane	2.17		Callahan, 1979, p. 45-2
1,1,1-Trichloroethane	2.47		Veith, 1980
1,1,1-Trichloroethane		104	Chiou, Peters & Freed, 1979
1,1,1-Trichloroethane	2.51		Mabey et al., 1982
1,1,2,2-Tetrachlorobenzene	2.39		Veith, 1980
1,1,2,2-Tetrachloroethane	2.56		Callahan, 1979, p. 47-2
1,1,2,2-Tetrachloroethane		46	Chiou, Peters & Freed, 1979
1,1,2,2-Tetrachloroethane	2.39		Mabey et al., 1982
1,1,2-Trichloroethane	2.17		Callahan, 1979, p. 46-2
1,1,2-Trichloroethane	2.07		Mabey et al., 1982
1,1,2-Trichloroethylene	2.42		Veith, 1980
1,1-Dichloroethane	1.79		Callahan, 1979, p. 43-2
1,1-Dichloroethane	1.80		Mabey et al., 1982
1,1-Dichloroethane	2.13		Mabey et al., 1982
1,1-Dichloroethene	1.48		Callahan, 1979, p. 50-2
1,2,3,4-Tetrachlorobenzene	4.72		Schwarzenbach & Wesfall, 1981
1,2,3,5-Tetrachlorobenzene	4.46		Veith, 1980
1,2,3-Trichlorobenzene	4.05		Schwarzenbach & Wesfall, 1981
1,2,4,5-Tetrachlorobenzene	4.67		Kenaga & Goring, 1980
1,2,4,5-Tetrachlorobenzene	4.72	37.9	Schwarzenbach & Wesfall, 1981
1,2,4-Trichlorobenzene	4.05	14.5	Schwarzenbach & Wesfall, 1981
1,2,4-Trichlorobenzene	4.18		Kenaga & Goring, 1980
1,2,4-Trichlorobenzene	4.26		Callahan, 1979, p. 76-2
1,2,4-Trichlorobenzene	4.27		Yalkowski, Orr & Valvani, 1979
1,2,4-Trichlorobenzene	4.27		Yalkowski, Valvani & Mackay, 1983
1,2,4-Trichlorobenzene	4.28		Mabey et al., 1982
1,2-Dichlorobenzene	3.38		Wasik, 1983
1,2-Dichlorobenzene	3.38		Callahan, 1979, p. 73-2
1,2-Dichlorobenzene	3.40		Veith, 1980
1,2-Dichlorobenzene	3.59		Yalkowski, Valvani & Mackay, 1983
1,2-Dichlorobenzene		180	Chiou, Peters & Freed, 1979
1,2-Dichlorobenzene	3.59		Yalkowski, Orr & Valvani, 1979
1,2-Dichlorobenzene	3.56		Mabey et al., 1982
1,2-Dichloroethane	1.45		Veith, 1980
1,2-Dichloroethane		19	Chiou, Peters & Freed, 1979
1,2-Dichloroethane	1.48		Callahan, 1979, p. 44-2

TABLE A6 (continued)

Chemical	K_{ow} log	Partition Coef (µg/kg)/(µg/ℓ)	Reference
1,2-Dichloroethane	1.48		Mabey et al., 1982
1,2-Dichloroethene-trans	1.48		Callahan, 1979, p. 51-2
1,2-Dichloroethene-trans	2.09		Mabey et al., 1982
1,2-Dichloropropane	2.28		Callahan, 1979, p. 54-2
1,2-Dichloropropane		27	Chiou, Peters & Freed, 1979
1,2-Dichloropropane	2.02		Mabey et al., 1982
1,2-Diphenylhydrazine	3.03		Callahan, 1979, p. 104-2
1,2-Diphenylhydrazine	2.94		Mabey et al., 1982
1,3-Dichlorobenzene	3.38		Callahan, 1979, p. 74-2
1,3-Dichlorobenzene	3.44		Veith, 1980
1,3-Dichlorobenzene	3.48		Wasik, 1983
1,3-Dichlorobenzene	3.59		Yalkowski, Valvani & Mackay, 1983
1,3-Dichlorobenzene	3.59		Yalkowski, Orr & Valvani, 1979
1,3-Dichlorobenzene	3.56		Mabey et al., 1982
1,3-Dichloropropene	1.36		Kenaga & Goring, 1980
1,3-Dichloropropene	1.83		McCall, 1983
1,3-Dichloropropene	1.98		Callahan, 1979, p. 55-2
1,3-Dichloropropene	2.00		Mabey et al., 1982
1,4-Dichlorobenzene	3.37		Veith, 1980
1,4-Dichlorobenzene	3.37		Wasik, 1983
1,4-Dichlorobenzene	3.38	4.4	Schwarzenbach & Wesfall, 1981
1,4-Dichlorobenzene	3.39		Kenaga & Goring, 1980
1,4-Dichlorobenzene	3.39		Callahan, 1979, p. 75-2
1,4-Dichlorobenzene	3.59		Yalkowski, Valvani & Mackay, 1983
1,4-Dichlorobenzene	3.59		Yalkowski, Orr & Valvani, 1979
1,4-Dichlorobenzene	3.56		Mabey et al., 1982
1,4-Nitrophenol	1.91		Lyman, 1982a
1,4-Nitrophenol	1.91	2.6	Jaffe & Ferrara, 1983
1-Chloronaphthalane	4.08		Yalkowski, Valvani & Mackay, 1983
2,2',3,3',4,4',5,5',6-PCB	10.44		Yalkowski, Valvani & Mackay, 1983
2,2',3,3',4,4',5,5'-PCB	9.69		Yalkowski, Valvani & Mackay, 1983
2,2',3,3',4,4'-PCB	8.18		Yalkowski, Valvani & Mackay, 1983
2,2',3,3'4,5-PCB	8.26		Yalkowski, Valvani & Mackay, 1983
2,2',3,3',5,5',6,6'-PCB	9.69		Yalkowski, Valvani & Mackay, 1983
2,2',3,3',5,6-PCB	8.18		Yalkowski, Valvani & Mackay, 1983

TABLE A6 (continued)

Chemical	K_{ow} log	Partition Coef (µg/kg)/(µg/ℓ)	Reference
2,2',3,3'-PCB	6.67		Yalkowski, Valvani & Mackay, 1983
2,2',3,4,5'-PCB	7.43		Yalkowski, Valvani & Mackay, 1983
2,2',3,4,5,5',6-PCB	8.94		Yalkowski, Valvani & Mackay, 1983
2,2',3,4,6-PCB	7.51		Yalkowski, Valvani & Mackay, 1983
2,2',3,5'-PCB	6.67		Yalkowski, Valvani & Mackay, 1983
2,2',4,4',5,5-PCB	6.57		Kenaga & Goring, 1980
2,2',4,4',5,5'-PCB	8.18		Yalkowski, Valvani & Mackay, 1983
2,2',4,4',5,5'-PCB		2350-5400	DiToro & Horzempa, 1982
2,2',4,4',5,5'-PCB	6.72		Schwarzenbach & Wesfall, 1981
2,2',4,4',5,5'-PCB		220,000	Chiou, Peters & Freed, 1979
2,2',4,4',6,6'-PCB	8.18		Yalkowski, Valvani & Mackay, 1983
2,2',4,4'-PCB	6.67		Yalkowski, Valvani & Mackay, 1983
2,2',4,5,5'-PCB	7.43		Yalkowski, Valvani & Mackay, 1983
2,2',4,5,5'-PCB	6.42		Swann, 1983
2,2',5,5'-PCB	6.67		Yalkowski, Valvani & Mackay, 1983
2,2',5,5'-PCB		47,000	Chiou, Peters & Freed, 1979
2,3',4',5-PCB	6.67		Yalkowski, Valvani & Mackay, 1983
2,3',4,4'-PCB	6.67		Yalkowski, Valvani & Mackay, 1983
2,3,4,5,6-PCB	7.49		Yalkowski, Valvani & Mackay, 1983
2,3,4,5-PCB	6.74		Yalkowski, Valvani & Mackay, 1983
2,4,5-Trichlorophenol	3.38		Callahan, 1979, p. 86-2
2,4,6-Trichlorophenol	3.61		Mabey et al., 1982
2,4-D	1.57		Kenaga & Goring, 1980
2,4-D	1.78		McCall, 1983
2,4-Dichlorophenol	2.75		Callahan, 1979, p. 85-2
2,4-Dichlorophenol	2.90		Mabey et al., 1982
2,4-Dimethylphenol	2.42		Veith, 1980
2,4-Dimethylphenol	2.50		Callahan, 1979, p. 91-2
2,4-Dimethyl phenol	2.30		Mabey et al., 1982
2,4-Dinitrophenol	1.53		Callahan, 1979, p. 90-2
2,4-Dinitrophenol	1.54		Mabey et al., 1982
2,4-Dinitrotoluene	2.01		Callahan, 1979, p. 81-2
2,4-Dinitrotoluene	1.98		Mabey et al., 1982
2,6-Dinitrotoluene	2.05		Callahan, 1979, p. 82-2
2,6-Dinitrotoluene	2.28		Mabey et al., 1982

TABLE A6 (continued)

Chemical	K_{ow} log	Partition Coef (µg/kg)/(µg/ℓ)	Reference
2-Chloroethyl vinyl ether	1.28		Callahan, 1979, p. 67-2
2-Chloroethyl vinyl eher	1.14		Mabey et al., 1982
2-Chloronaphthalene	4.08		Yalkowski, Valvani & Mackay, 1983
2-Chloronaphthalene	4.12		Callahan, 1979, p. 37-2
2-Chloronaphthalene	4.00		Mabey et al., 1982
2-Chlorophenol	2.16		Veith, 1980
2-Chlorophenol	2.17		Callahan, 1979, p. 84-2
2-Chlorophenol	2.18		Mabey et al., 1982
2-Nitrophenol	1.76		Callahan, 1979, p. 88-2
2-Nitrophenol	1.75		Mabey et al., 1982
3,3',4,4'-PCB	6.67		Yalkowski, Valvani & Mackay, 1983
3,3'-Dichlorobenzidine	3.02		Callahan, 1979, p. 103-2
3,3'-Dichlorobenzidine	3.51		Mabey et al., 1982
4,4'-PCB	5.58		Kenaga & Goring, 1980
4,6-Dinitro-o-cresol	2.85		Callahan, 1979, p. 93-2
4,6-Dinitro-o-cresol	2.70		Mabey et al., 1982
4-Bromophenyl phenyl ether	4.28		Callahan, 1979, p. 69-2
4-Bromophenyl phenyl ether	4.94		Mabey et al., 1982
4-Chlorobiphenyl	4.90		Kenaga & Goring, 1980
4-Chlorophenyl phenyl ether	4.08		Callahan, 1979, p. 68-2
4-Chlorophenyl phenyl ether	5.08		Mabey et al., 1982
4-Nitrophenol	1.91		Callahan, 1979, p. 89-2
4-Nitrophenol	1.97		Mabey et al., 1982
Acenaphthene	3.70		Yalkowski, Valvani & Mackay, 1983
Acenaphthene	4.33		Callahan, 1979, p. 95-3
Acenaphthene	-2.02		Mabey et al., 1982
Acenaphthylene	4.07		Callahan, 1979, p. 95-3
Acenaphthylene	3.72		Mabey et al., 1982
Acrolein	0.01		Mabey et al., 1982
Acrylonitrile	-0.14		Callahan, 1979, p.105-2
Acrylonitrile	0.25		Mabey et al., 1982
Alachlor	2.92		Kenaga & Goring, 1980
Aldrin	5.30		Mabey et al., 1982
Anthracene	4.34		Kenaga & Goring, 1980
Anthracene	4.45		Lyman, 1982a

TABLE A6 (continued)

Chemical	K_{ow} log	Partition Coef (μg/kg)/(μg/ℓ)	Reference
Anthracene	4.45		Callahan, 1979, p. 96-3
Anthracene	4.54		Karickhoff, Brown & Scott, 1979
Anthracene	4.63		Yalkowski, Valvani & Mackay, 1983
Anthracene	4.45		Mabey et al., 1982
Aroclor 1016	5.58		Callahan, 1979, p. 36-4
Aroclor 1016	5.58		Mabey et al., 1982
Aroclor 1016, 1242	5.58		Kenaga & Goring, 1980
Aroclor 1221	4.09		Callahan, 1979, p. 36-4
Aroclor 1221	4.0		Mabey et al., 1982
Aroclor 1232	4.54		Callahan, 1979, p. 36-4
Aroclor 1232	3.20		Mabey et al., 1982
Aroclor 1242	5.58		Callahan, 1979, p. 36-4
Aroclor 1242	4.11		Mabey et al., 1982
Aroclor 1248	5.75	11,703	Jaffe & Ferrara, 1983
Aroclor 1248	6.11		Kenaga & Goring, 1980
Aroclor 1248	6.11		Callahan, 1979, p. 36-4
Aroclor 1248	5.76		Mabey et al., 1982
Aroclor 1254	6.03		Callahan, 1979, p. 36-4
Aroclor 1254	6.30		Kenaga & Goring, 1980
Aroclor 1254	6.04		Mabey et al., 1982
Aroclor 1260	6.11		Callahan, 1979, p. 36-4
Aroclor 1260	7.14	287,000	Jaffe & Ferrara, 1983
Aroclor 1260	7.15		Mabey et al., 1982
Atrazine		0.9	DiToro & Horzempa, 1982
Atrazine	2.68		Kenaga & Goring, 1980
Benzene	2.11		Schwarzenbach & Wesfall, 1981
Benzene	2.11		Karickhoff, Brown & Scott, 1979
Benzene	2.13		Yalkowski, Orr & Valvani, 1979
Benzene	2.13		Yalkowski, Valvani & Mackay, 1983
Benzene	2.13		Kenaga & Goring, 1980
Benzene	2.48		Swann, 1983
Benzene	2.13		Mabey et al., 1982
Benzidine	1.36		Lu, 1977
Benzidine	1.66		Gossett & Lincoff, 1981
Benzidine	1.81		Callahan, 1979, p. 102-2

TABLE A6 (continued)

Chemical	K_{ow} log	Partition Coef (µg/kg)/(µg/ℓ)	Reference
Benzidine	1.34		Mabey et al., 1982
Benzo[a]anthracene	5.61		Callahan, 1979, p. 97-3
Benzo[a]anthracene	5.61		Mabey et al., 1982
Benzo[a]pyrene	4.05		Lu, 1977
Benzo[a]pyrene	6.04		Callahan, 1979, p. 98-3
Benzo[a]pyrene	6.06		Mabey et al., 1982
Benzo[b]fluoranthene	6.57		Callahan, 1979, p. 97-3
Benzo[b]fluoranthene	6.06		Mabey et al., 1982
Benzo[ghi]perylene	6.85		Yalkowski, Valvani & Mackay, 1983
Benzo[ghi]perylene	7.23		Callahan, 1979, p. 98-3
Benzo[ghi]perylene	6.51		Mabey et al., 1982
Benzo[k]fluoranthene	6.84		Callahan, 1979, p. 97-3
Benzo[k]fluoranthene	6.06		Mabey et al., 1982
Bis(2-chloroethoxy)methane	1.26		Callahan, 1979, p. 70-2
Bis(2-chloroethoxy)methane	1.03		Mabey et al., 1982
Bis(2-chloroethyl)ether	1.12		Veith, 1980
Bis(2-chloroethyl)ether	1.58		Callahan, 1979, p. 65-2
Bis(2-chloroethyl)ether	1.46		Mabey et al., 1982
Bis(2-chloroisopropyl)ether	2.58		Callahan, 1979, p. 66-2
Bis(2-chloroisopropyl)ether	2.10		Mabey et al., 1982
Bis(2-ethylhexyl)phthalate	8.73		Callahan, 1979, p. 94-5
Bis(2-ethylhexyl)phthalate	9.61		Mabey et al., 1982
Bis(chloromethyl)ether	-0.38		Callahan, 1979, p. 64-1
Bis(chloromethyl)ether	0.38		Mabey et al., 1982
Bromobenzene	2.95		Kenaga & Goring, 1980
Bromobenzene	2.97		Swann, 1983
Bromobenzene	2.98		Wasik, 1983
Bromodichloromethane	1.88		Callahan, 1979, p. 59-2
Bromodichloromethane	2.10		Mabey et al., 1982
Bromoform	2.30		Callahan, 1979, p. 61-2
Bromomethane	1.10		Callahan, 1979, p. 58-2
Bromomethane	1.09		Mabey et al., 1982
Butylbenzylphthalate	4.05		Veith, 1980
Butylbenzylphthalate	4.77		Gledhill, 1980
Butylbenzylphthalate	5.80		Callahan, 1979, p. 9405

TABLE A6 (continued)

Chemical	K_{ow} log	Partition Coef (µg/kg)/(µg/ℓ)	Reference
Butylbenzylphthalate	5.56		Mabey et al., 1982
Carbofuran	1.60		Kenaga & Goring, 1980
Carbon tetrachloride	2.64		Kenaga & Goring, 1980
Carbon tetrachloride	2.64		Callahan, 1979, p. 41-2
Carbon tetrachloride	2.73		Veith, 1980
Carbon tetrachloride	2.83		Lyman, 1982a
Chlordane	2.78	19	Jaffe & Ferrara, 1983
Chlordane	5.48		Mabey et al., 1982
Chlorobenzene	2.71	1.2	Schwarzenbach & Wesfall, 1981
Chlorobenzene	2.83		Yalkowski, Orr & Valvani, 1979
Chlorobenzene	2.83		Yalkowski, Valvani & Mackay, 1983
Chlorobenzene	2.84		Kenaga & Goring, 1980
Chlorobenzene	2.84		Callahan, 1979, p. 72-2
Chlorobenzene	2.98		Wasik, 1983
Chlorobenzene	2.84		Mabey et al., 1982
Chloroethane	1.49		Mabey et al., 1982
Chloroethene	1.23		Mabey et al., 1982
Chloroform	1.90		Veith, 1980
Chloroform	1.97	2.9	Jaffe & Ferrara, 1983
Chloroform	1.97		Callahan, 1979, p. 40-2
Chloromethane	0.91		Callahan, 1979, p. 38-2
Chloromethane (methyl chloride)	0.95		Mabey et al., 1982
Chlorpyrifos	3.79		McCall, 1983
Chrysene	5.61		Callahan, 1979, p. 97-3
Chrysene	5.91		Yalkowski, Valvani & Mackay, 1983
Chrysene	5.61		Mabey et al., 1982
DDD	6.02		Kenaga & Goring, 1980
DDD	6.20		Mabey et al., 1982
DDE	5.63		Swann, 1983
DDE	5.69	10,193	Jaffe & Ferrara, 1983
DDE	5.77		Kenaga & Goring, 1980
DDE	6.96		Mabey et al., 1982
DDT		10,000	O'Connor, 1980
DDT	4.89		Callahan, 1979, p. 25-3
DDT	4.90		Wolfe, 1977b

TABLE A6 (continued)

Chemical	K_{ow} log	Partition Coef (μg/kg)/(μg/ℓ)	Reference
DDT	5.18		McCall, 1983
DDT	5.98		Kenaga & Goring, 1980
DDT		140,000	Chiou, Peters & Freed, 1979
DDT	6.19		Schwarzenbach & Wesfall, 1981
DDT	6.91		Mabey et al., 1982
Di-n-butyl phthalate	5.20		Callahan, 1979, p. 94-5
Di-n-butyl phthalate	5.56		Mabey et al., 1982
Di-n-octyl phthalate	9.20		Callahan, 1979, p. 94-5
Di-n-octyl phthalate	9.87		Mabey et al., 1982
Di-n-propylnitrosamine	1.31		Callahan, 1979, p. 101-1
Di-n-propylnitrosamine	1.49		Mabey et al., 1982
Dibenzo[ah]anthracene	5.97		Callahan, 1979, p. 98-3
Dibenzo[ah]anthracene	6.50		Gossett & Lincoff, 1981
Dibenzo[a,h]anthracene	6.84		Mabey et al., 1982
Dibromochloromethane	2.09		Callahan, 1979, p. 60-2
Dibromochloromethane	2.24		Mabey et al., 1982
Dichlorodifluoromethane	2.16		Callahan, 1979, p. 6202
Dichlorodifluoromethane	2.08		Mabey et al., 1982
Dichloromethane	1.26		Mabey et al., 1982
Dieldrin		100	O'Connor, 1980
Dieldrin	3.54		Mabey et al., 1982
Diethyl phthalate	1.40		Veith, 1980
Diethyl phthalate	3.22		Callahan, 1979, p. 94-5
Diethyl phthalate	2.47		Mabey et al., 1982
Dimethyl phthalate	1.61		Veith, 1980
Dimethyl phthalate	2.12		Callahan, 1979, p. 94-5
Dimethyl phthalate	1.56		Mabey et al., 1982
Dimethylnitrosamine	0.06		Callahan, 1979, p. 99-2
Dimethylnitrosamine	-0.68		Mabey et al., 1982
Diphenylnitrosamine	2.57		Callahan, 1979, p. 100-1
Diphenylnitrosamine	3.13		Veith, 1980
Diphenylnitrosamine	3.13		Mabey et al., 1982
α-Endosulfan	-1.70		Mabey et al., 1982
β-Endosulfan	-1.70		Mabey et al., 1982
Endosulfan sulfate	-1.30		Mabey et al., 1982

TABLE A6 (continued)

Chemical	K_{ow} log	Partition Coef (µg/kg)/(µg/ℓ)	Reference
Endrin	5.34		Kenaga & Goring, 1980
Endrin	5.60		Callahan, 1979, p. 28-2
Endrin	3.54		Mabey et al., 1982
Endrin aldehyde	3.15		Mabey et al., 1982
Ethyl benzene	3.13		Wasik, 1983
Ethyl benzene	3.15		Callahan, 1979, p. 78-2
Ethyl benzene	3.34		Mabey et al., 1982
Ethyl chloride	1.54		Callahan, 1979, p. 42-2
Fluoranthene	5.22		Yalkowski, Valvani & Mackay, 1983
Fluoranthene	5.33		Callahan, 1979, p. 96-3
Fluoranthene	4.90		Mabey et al., 1982
Fluorene	3.99		Yalkowski, Valvani & Mackay, 1983
Fluorene	4.12		Lyman, 1982a
Fluorene	4.18		Callahan, 1979, p. 95-3
Fluorene	4.18		Mabey et al., 1982
Heptachlor		2,000	O'Connor, 1980
Heptachlor	4.41		Mabey et al., 1982
Heptachlor epoxide	2.65		Mabey et al., 1982
Hexachlorobenzene	5.23		Kenaga & Goring, 1980
Hexachlorobenzene	6.18	47,677	Jaffe & Ferrara, 1983
Hexachlorobenzene	6.18		Callahan, 1979, p. 77-2
Hexachlorobenzene	6.53		Yalkowski, Valvani & Mackay, 1983
Hexachlorobenzene	6.53		Yalkowski, Orr & Valvani, 1979
Hexachlorobenzene	6.41		Mabey et al., 1982
Hexachlorobiphenyl	6.34		Karickhoff, Brown & Scott, 1979
Hexachlorobutadiene	3.74		Callahan, 1979, p. 56-2
Hexachlorobutadiene	4.78		Mabey et al., 1982
α-Hexachlorocyclohexane	3.89		Mabey et al., 1982
β-Hexachlorocyclohexane	3.89		Mabey et al., 1982
δ-Hexachlorocyclohexane	4.15		Mabey et al., 1982
γ-Hexachlorocyclohexane (lindane)	3.89		Mabey et al., 1982
Hexachlorocyclohexane (alpha)	3.81		Callahan, 1979, p. 31-2
Hexachlorocyclohexane (beta)	3.80		Callahan, 1979, p. 31-2
Hexachlorocyclohexane (delta)	4.14		Callahan, 1979, p. 31-2
Hexachlorocyclopentadiene	3.99		Callahan, 1979, p. 57-2

TABLE A6 (continued)

Chemical	K_{ow} log	Partition Coef (µg/kg)/(µg/ℓ)	Reference
Hexachlorocyclopentadiene	5.04		Wolfe, 1982
Hexachlorocyclopentadiene	4.00		Mabey et al., 1982
Hexachloroethane	3.34		Callahan, 1979, p. 48-1
Hexachloroethane	3.34	68.9	Jaffe & Ferrara, 1983
Hexachloroethane	3.93		Veith, 1980
Hexachloroethane	4.62		Mabey et al., 1982
Indeno[1,2,3-cd]pyrene	7.66		Callahan, 1979, p. 98-3
Indeno[1,2,3-cd]pyrene	6.51		Mabey et al., 1982
Isophorone	1.67		Veith, 1980
Isophorone	1.70		Callahan, 1979, p. 33-2
Isophorone	2.26		Mabey et al., 1982
Kepone		1,000	O'Connor, 1980
Lindane		400	O'Connor, 1980
Lindane	3.11		McCall, 1983
Lindane	3.72		Callahan, 1979, p. 32-2
Lindane		1,730	Chiou, Peters & Freed, 1979
Malathion	2.89		Kenaga & Goring, 1980
Methoxychlor	3.40		Wolfe, 1977b
Methoxychlor	5.08	1,100	Karickhoff, Brown & Scott, 1979
Methyl parathion	1.91		Kenaga & Goring, 1980
Methylene chloride	1.25		Callahan, 1979, p. 39-2
Naphthalene	3.35		Wasik, 1983
Naphthalene	3.35		Yalkowski, Valvani & Mackay, 1983
Naphthalene	3.36		Karickhoff, Brown & Scott, 1979
Naphthalene	3.37		Callahan, 1979, p. 95-3
Naphthalene	3.31		Kenaga & Goring, 1980
Naphthalene	3.36		Schwarzenbach & Wesfall, 1981
Naphthalene	3.29		Mabey et al., 1982
Nitrapyrin	2.75		McCall, 1983
Nitrobenzene	1.85	2.2	Jaffe & Ferrara, 1983
Nitrobenzene	1.85		Callahan, 1979, p. 79-1
Nitrobenzene	1.87		Mabey et al., 1982
PCB		9.63	DiToro, 1982
Parathion	3.81		Kenaga & Goring, 1980
Parathion	3.81		Schwarzenbach & Wesfall, 1981

TABLE A6 (continued)

Chemical	K_{ow} log	Partition Coef (μg/kg)/(μg/ℓ)	Reference
Parathion		1,160	Chiou, Peters & Freed, 1979
Pentachlorobenzene	4.94		Veith, 1980
Pentachlorobenzene	5.19		Kenaga & Goring, 1980
Pentachloroethane	2.89		Veith, 1980
Pentachlorophenol	5.01		Kenaga & Goring, 1980
Pentachlorophenol	5.01		Callahan, 1979, p. 87-2
Pentachlorophenol	5.04		Mabey et al., 1982
Phenanthrene	4.46		Callahan, 1979, p. 96-3
Phenanthrene	4.52		Kenaga & Goring, 1980
Phenanthrene	4.56		Karickhoff, Brown & Scott, 1979
Phenanthrene	4.63		Yalkowski, Valvani & Mackay, 1983
Phenanthrene	4.45		Mabey et al., 1982
Phenol	1.46		Callahan, 1979, p. 83-2
Phenol	1.48		Mabey et al., 1982
Pyrene	4.88		Lyman, 1982a
Pyrene	5.09		Gossett & Lincoff, 1981
Pyrene	5.18	2,100	Karickhoff, Brown & Scott, 1979
Pyrene	5.18		Kenaga & Goring, 1980
Pyrene	5.18		Schwarzenbach & Wesfall, 1981
Pyrene	5.22		Yalkowski, Valvani & Mackay, 1983
Pyrene	5.32		Callahan, 1979, p. 97-3
Pyrene	4.90		Mabey et al., 1982
TCDD	6.84		Mabey et al., 1982
Tetrachlorobiphenyl	4.51		McCall, 1983
Tetrachloroethene	2.88		Callahan, 1979, p. 53-2
Tetrachloroethene		210	Chiou, Peters & Freed, 1979
Tetrachloroethene	2.88		Mabey et al., 1982
Tetrachloroethylene	2.53		Veith, 1980
Tetrachloroethylene	2.60		Schwarzenbach & Wesfall, 1981
Tetrachloroethylene	2.88		Kenaga & Goring, 1980
Tetrachloromethane	2.96		Mabey et al., 1982
Toluene	2.65		Wasik, 1983
Toluene	2.69		Callahan, 1979, p. 80-2
Toluene	2.69		Schwarzenbach & Wesfall, 1981
Toluene	2.79		Mabey et al., 1982

TABLE A6 (continued)

Chemical	K_{ow} log	Partition Coef (µg/kg)/(µg/ℓ)	Reference
Toxaphene	3.30		Callahan, 1979, p. 35-4
Toxaphene	3.30		Mabey et al., 1982
Tribromomethane	2.38		Mabey et al., 1982
Trichloroethene	2.29		Callahan, 1979, p. 52-2
Trichloroethene	2.42		Mabey et al., 1982
Trichloroethylene	2.29	6.14	Jaffe & Ferrara, 1983
Trichlorofluoromethane	2.53		Callahan, 1979, p. 63-2
Trichlorofluoromethane	2.52		Mabey et al., 1982
Trichloromethane	1.96		Mabey et al., 1982
Trifluralin	5.34		Kenaga & Goring, 1980
Vinyl chloride	0.60		Callahan, 1979, p. 49-2
p-Chloro-m-cresol	2.95		Callahan, 1979, p. 92-2
p-Chloro-m-cresol	3.10		Mabey et al., 1982

TABLE A7. BIOCONCENTRATION FACTORS

Chemical	Chemical Concentration µg/ℓ	Bioconcentration Factor	Organism	Reference
1,1,1-Trichloroethane	73.4	9	Lepomis macrochirus	Veith, 1980
1,1,2,2-Tetrachlorobenzene	9.62	8	Lepomis macrochirus	Veith, 1980
1,1,2,3,4,4-Hexachloro-1,3-butadiene	0.00003	5,800	Salmo gairdneri	Oliver & Niimi, 1983
1,1,2,3,4,4-Hexachloro-1,3-butadiene	0.0034	17,000	Salmo gairdneri	Oliver & Niimi, 1983
1,1,2-Trichloroethylene	8.23	17	Lepomis macrochirus	Veith, 1980
1,2,3,4-Tetrachlorobenzene	0.026	12,000	Salmo gairdneri	Oliver & Niimi, 1983
1,2,3,4-Tetrachlorobenzene	0.0003	5,200	Salmo gairdneri	Oliver & Niimi, 1983
1,2,3,4-Tetrachlorobenzene		5,000	Salmo gairdneri	Banerjee, Sugatt & O'Grady, 1984
1,2,3,5-Tetrachlorobenzene	7.72	1,800	Lepomis macrochirus	Veith, 1980
1,2,3,5-Tetrachlorobenzene		2,900	Lepomis macrchirus	Banerjee, Sugatt & O'Grady, 1984
1,2,3-Trichlorobenzene	0.0007	1,200	Salmo gairdneri	Oliver & Niimi, 1983
1,2,3-Trichlorobenzene	0.072	2,600	Salmo gairdneri	Oliver & Niimi, 1983
1,2,4,5-Tetrachlorobenzene		4,500	fish	Kenaga & Goring, 1980
1,2,4,5-Tetrachlorobenzene	0.21	13,000	Salmo gairdneri	Oliver & Niimi, 1983
1,2,4,5-Tetrachlorobenzene	0.0002	5,300	Salmo gairdneri	Oliver & Niimi, 1983
1,2,4-Trichlorobenzene		491	fish	Kenaga & Goring, 1980
1,2,4-Trichlorobenzene	0.052	3,200	Salmo gairdneri	Oliver & Niimi, 1983
1,2,4-Trichlorobenzene	0.0005	1,300	Salmo gairdneri	Oliver & Niimi, 1983
1,2,4-Trichlorobenzene	2.9	182	bluegill	Callahan, 1979, p. 76-4
1,2,4-Trichlorobenzene	3.1	142	daphnids	Callahan, 1979, p. 76-4
1,2-Dichlorobenzene	7.89	89	Lepomis macrochirus	Veith, 1980
1,2-Dichlorobenzene	0.009	270	Salmo gairdneri	Oliver & Niimi, 1983
1,2-Dichlorobenzene	0.94	560	Salmo gairdneri	Oliver & Niimi, 1983
1,2-Dichloroethane	95.7	2	Lepomis macrochirus	Veith, 1980
1,3,5-Trichlorobenzene	0.045	4,100	Salmo gairdneri	Oliver & Niimi, 1983
1,3,5-Trichlorobenzene	0.0003	1,800	Salmo gairdneri	Oliver & Niimi, 1983
1,3-Dichlorobenzene	107	66	Lepomis macrochirus	Veith, 1980
1,3-Dichlorobenzene	0.69	740	Salmo gairdneri	Oliver & Niimi, 1983
1,3-Dichlorobenzene	0.004	420	Salmo gairdneri	Oliver & Niimi, 1983
1,3-Dichloropropene		3		McCall, 1983
1,4-Dichlorobenzene		215	fish	Kenaga & Goring, 1980
1,4-Dichlorobenzene	10.1	60	Lepomis macrochirus	Veith, 1980
1,4-Dichlorobenzene	0.004	370	Salmo gairdneri	Oliver & Niimi, 1983
1,4-Dichlorobenzene	0.67	720	Salmo gairdneri	Oliver & Niimi, 1983
2,2',4,4',5,5'-PCB		46,000	fish	Kenaga & Goring, 1980

TABLE A7 (continued)

Chemical	Chemical Concentration µg/ℓ	Bioconcentration Factor	Organism	Reference
2,4,6-Trichlorophenol	0.47	1,000	Echinodorus	Virtanen & Hattula
2,4,6-Trichlorophenol	0.47	4,460	Elodea	Virtanen & Hattula
2,4,6-Trichlorophenol	0.47	1,720	algae	Virtanen & Hattula
2,4,6-Trichlorophenol	0.47	10,000	guppy	Virtanen & Hattula
2,4,6-Trichlorophenol	0.47	3,020	snail	Virtanen & Hattula
2,4-D		0	fish	Kenaga & Goring, 1980
2,4-D		3		McCall, 1983
2,4-Dimethylphenol	10.1	150	Lepomis macrochirus	Veith, 1980
2-Chlorophenol	9.18	214	Lepomis macrochirus	Veith, 1980
4,4'-PCB		215	fish	Kenaga & Goring, 1980
4-Chlorobiphenyl		590	fish	Kenaga & Goring, 1980
4-Chlorophenyl phenyl ether		736	rainbow trout	Callahan, 1979, p. 68-4
Alachlor		0	fish	Kenaga & Goring, 1980
Alachlor		6	Pimephales promelas	Call, 1984
Aldicarb		42	fish	Kenaga & Goring, 1980
Aldrin		3,140	fish	Kenaga & Goring, 1980
Aldrin		1800-9100	Daphnia	Callahan, 1979, p. 21-7
Aldrin		39,000	alga	Callahan, 1979, p. 21-7
Aldrin		1,000	blue-green algae	Callahan, 1979, p. 21-7
Aldrin		3,100	fish	Callahan, 1979, p. 21-7
Aldrin		970-1100	mosquito larvae	Callahan, 1979, p. 21-7
Aldrin		45,000	snail	Callahan, 1979, p. 21-7
Anthracene		917	Daphnia pulex	Bysshe, 1982
Aroclor 1016		15,000	fishes	Bysshe, 1982
Aroclor 1016, 1242		48,980	fish	Kenaga & Goring, 1980
Aroclor 1248		72,950	fish	Kenaga & Goring, 1980
Aroclor 1254		45,600	fish	Kenaga & Goring, 1980
Aroclor 1254		>220	carp	Bysshe, 1982
Atrazine		0	fish	Kenaga & Goring, 1980
Benzidine	3.1	456	Culex pipiens	Lu, 1977
Benzidine	3.1	293	Daphnia magna	Lu, 1977
Benzidine	3.1	55	Gambusia affinis	Lu, 1977
Benzidine	3.1	2,617	Oedogonium cardiacum	Lu, 1977
Benzidine	3.1	645	Physa sp.	Lu, 1977
Benzo[a]anthracene		10,100	Daphnia pulex	Bysshe, 1982

TABLE A7 (continued)

Chemical	Chemical Concentration µg/ℓ	Bioconcentration Factor	Organism	Reference
Benzo[a]pyrene		11,536	Culex pipiens	Lu, 1977
Benzo[a]pyrene		134,248	Daphnia	Callahan, 1979, p. 98-13
Benzo[a]pyrene	2.5	134,248	Daphnia magna	Lu, 1977
Benzo[a]pyrene	2.5	930	Gambusia affinis	Lu, 1977
Benzo[a]pyrene	2.5	5,258	Oedogonium cardiacum	Lu, 1977
Benzo[a]pyrene	2.5	82,231	Physa sp.	Lu, 1977
Benzo[a]pyrene		5,258	algae	Callahan, 1979, p. 98-13
Benzo[a]pyrene		930	fish	Callahan, 1979, p. 98-13
Benzo[a]pyrene		11,536	mosquito	Callahan, 1979, p. 98-13
Benzo[a]pyrene		82,231	snail	Callahan, 1979, p. 98-13
Bis(2-chloroethyl)ether	9.91	11	Lepomis macrochirus	Veith, 1980
Bis(2-ethylhexyl)phthalate	1.9	80	Asellus brevicaudus	Callahan, 1979, p. 94-10
Bis(2-ethylhexyl)phthalate	62.3	20	Asellus brevicaudus	Callahan, 1979, p. 94-10
Bis(2-ethylhexyl)phthalate	0.3	3,100	Chironomus plumosus	Callahan, 1979, p. 94-10
Bis(2-ethylhexyl)phthalate	0.3	5,200	Daphnia magna	Callahan, 1979, p. 94-10
Bis(2-ethylhexyl)phthalate	62.8	116	Gammarus pseudolimnaeus	Callahan, 1979, p. 94-10
Bis(2-ethylhexyl)phthalate	0.1	13,600	Gammarus pseudolimnaeus	Callahan, 1979, p. 94-10
Bis(2-ethylhexyl)phthalate	0.1	2,300	Hexagenia bilineata	Callahan, 1979, p. 94-10
Butylbenzylphthalate	9.73	772	Lepomis macrochirus	Veith, 1980
Butylbenzylphthalate	9.73	663	bluegills	Gledhill, 1980
Carbofuran		0	fish	Kenaga & Goring, 1980
Carbon tetrachloride		18	fish	Kenaga & Goring, 1980
Carbon tetrachloride	52.3	30	Lepomis macrochirus	Veith, 1980
Chlordane		11,400	fish	Kenaga & Goring, 1980
Chlordane	0.002	1,002,493	fish	Schnoor, 1982
Chlordane (cis)		16,000	daphnids	Callahan, 1979, p. 22-7
Chlordane (cis)		5,500	redhorse & white suckers	Callahan, 1979, p. 22-7
Chlordane (trans)		20,000	daphnids	Callahan, 1979, p. 22-7
Chlorobenzene		12	fish	Kenaga & Goring, 1980
Chlorobenzene	10-100	2,789	Daphnia	Callahan, 1979, p. 72-5
Chlorobenzene	10-100	4,185	alga	Callahan, 1979, p. 72-5
Chlorobenzene	10-100	645	fish	Callahan, 1979, p. 72-5
Chlorobenzene	10-100	1,292	mosquito larvae	Callahan, 1979, p. 72-5
Chlorobenzene	10-100	1,313	snail	Callahan, 1979, p. 72-5
Chloroform	110	6	Lepomis macrochirus	Veith, 1980

TABLE A7 (continued)

Chemical	Chemical Concentration µg/ℓ	Bioconcentration Factor	Organism	Reference
Chlorpyrifos		470		McCall, 1983
DDD		63,830	fish	Kenaga & Goring, 1980
DDE		27,400	fish	Kenaga & Goring, 1980
DDE		12,000	alewife	Bysse, 1982
DDE		11,000	algae	Callahan, 1979, p. 24-7
DDE		110,000	bluegill	Callahan, 1979, p. 24-7
DDE	0.001	796,275	fish	Schnoor, 1982
DDE		30,000	mosquito fish	Callahan, 1979, p. 24-7
DDE		30,000	mosquito larvae	Callahan, 1979, p. 24-7
DDE		25,000	sculpin	Bysshe, 1982
DDE		36,000	smelt	Bysshe, 1982
DDE		20,000	snail	Callahan, 1979, p. 24-7
DDE		180,000	trout	Callahan, 1979, p. 24-7
DDE		50,000	zooplankton	Callahan, 1979, p. 24-7
DDT		61,600		McCall, 1983
DDT		61,600	fish	Kenaga & Goring, 1980
DDT		6,200	Daphnia	Callahan, 1979, p. 25-16
DDT		31,000	alewife	Bysshe, 1982
DDT		5,900	algae	Callahan, 1979, p. 25-16
DDT		26,000	fish	Callahan, 1979, p. 25-16
DDT		85,000	mosquito fish	Callahan, 1979, p. 25-16
DDT		8,200	mosquito larvae	Callahan, 1979, p. 25-16
DDT		51,000	smelt	Bysshe, 1982
DDT		34,000	snail	Callahan, 1979, p. 25-16
Di-n-butyl phthalate	0.18	6,600	Chironomus plumosus	Callahan, 1979, p. 94-10
Di-n-butyl phthalate	0.08	5,000	Daphnia magna	Callahan, 1979, p. 94-10
Di-n-butyl phthalate	0.1	6,500	Gammarus pseudolimnaeus	Callahan, 1979, p. 94-10
Di-n-butyl phthalate	0.08	1,900	Hexagenia bilineata	Callahan, 1979, p. 94-10
Di-n-butyl phthalate	0.1	2,700	Ischnura verticalis	Callahan, 1979, p. 94-10
Di-n-butyl phthalate	0.08	5,000	Palaemonetes kadiakensis	Callahan, 1979, p. 94-10
Diazinon		35	fish	Kenaga & Goring, 1980
Dieldrin		5,800	fish	Kenaga & Goring, 1980
Dieldrin		13,000	alewife	Bysshe, 1982
Dieldrin		7,500	alga	Callahan, 1979, p. 26-6
Dieldrin		6,100	fish	Callahan, 1979, p. 26-6

TABLE A7 (continued)

Chemical	Chemical Concentration µg/ℓ	Bioconcentration Factor	Organism	Reference
Dieldrin	0.0045	502,374	fish	Schnoor, 1982
Dieldrin		110,000	snail	Callahan, 1979, p. 26-6
Diethyl phthalate	9.42	117	Lepomis macrochirus	Veith, 1980
Dimethyl phthalate	8.73	57	Lepomis macrochirus	Veith, 1980
Dioxin		4000-9000	algae	Callahan, 1979, p. 34-4
Dioxin		4000-9000	catfish	Callahan, 1979, p. 34-4
Dioxin		20,000	daphnids	Callahan, 1979, p. 34-4
Dioxin		4000-9000	duckweed	Callahan, 1979, p. 34-4
Dioxin		20,000	mosquito fish	Callahan, 1979, p. 34-4
Dioxin		20,000	snails	Callahan, 1979, p. 34-4
Diphenylnitrosamine	9.21	217	Lepomis macrochirus	Veith, 1980
Endrin		4,050	fish	Kenaga & Goring, 1980
Endrin		330	Daphnia	Callahan, 1979, p. 28-6
Endrin		680	fish	Callahan, 1979, p. 28-6
Endrin		310	mosquito	Callahan, 1979, p. 28-6
Endrin		1,900	mussel	Callahan, 1979, p. 28-5
Heptachlor		17,400	fish	Kenaga & Goring, 1980
Heptachlor		21,000	alga	Callahan, 1979, p. 29-6
Heptachlor		3,800	mosquito fish	Callahan, 1979, p. 29-6
Heptachlor		31,000	mosquito larvae	Callahan, 1979, p. 29-6
Heptachlor		37,000	snail	Callahan, 1979, p. 29-6
Heptachlor epoxide		2,000	alga	Callahan, 1979, p. 30-4
Heptachlor epoxide	0.001	632,478	fish	Schnoor, 1984
Heptachlor epoxide		6,000	mosquito fish	Callahan, 1979, p. 30-4
Heptachlor epoxide		1,700	mussel	Callahan, 1979, p. 30-5
Heptachlor epoxide		80,000	snail	Callahan, 1979, p. 30-4
Hexachlorobenzene		8,600	fish	Kenaga & Goring, 1980
Hexachlorobenzene	2.98	143	Culex quinquifasciatus	Callahan, 1979, p. 77-6
Hexachlorobenzene	9.34	2,622	Culex quinquifasciatus	Callahan, 1979, p. 77-6
Hexachlorobenzene	0.22	770	Daphnia magna	Callahan, 1979, p. 77-6
Hexachlorobenzene	1.72	940	Daphnia magna	Callahan, 1979, p. 77-6
Hexachlorobenzene	9.34	1,129	Daphnia magna	Callahan, 1979, p. 77-6
Hexachlorobenzene	0.03	1,030	Daphnia magna	Callahan, 1979, p. 77-6
Hexachlorobenzene	2.98	200	Daphnia magna	Callahan, 1979, p. 77-6
Hexachlorobenzene	0.03	1,360	Helisoma sp.	Callahan, 1979, p. 77-6

TABLE A7 (continued)

Chemical	Chemical Concentration µg/ℓ	Bioconcentration Factor	Organism	Reference
Hexachlorobenzene	0.22	1,510	Helisoma sp.	Callahan, 1979, p. 77-6
Hexachlorobenzene	1.72	1,630	Helisoma sp.	Callahan, 1979, p. 77-6
Hexachlorobenzene	0.22	9,830	Ictalurus punctatus	Callahan, 1979, p. 77-6
Hexachlorobenzene	0.03	6,160	Ictalurus punctatus	Callahan, 1979, p. 77-6
Hexachlorobenzene	1.72	15,850	Ictalurus punctatus	Callahan, 1979, p. 77-6
Hexachlorobenzene	1.72	910	Oedogonium cardiacum	Callahan, 1979, p. 77-6
Hexachlorobenzene	0.03	610	Oedogonium cardiacum	Callahan, 1979, p. 77-6
Hexachlorobenzene	2.98	522	Oedogonium cardiacum	Callahan, 1979, p. 77-6
Hexachlorobenzene	0.22	710	Oedogonium cardiacum	Callahan, 1979, p. 77-6
Hexachlorobenzene	9.34	3,969	Oedogonium cardiacum	Callahan, 1979, p. 77-6
Hexachlorobenzene	2.98	1,248	Physa sp.	Callahan, 1979, p. 77-6
Hexachlorobenzene	9.34	2,672	Physa sp.	Callahan, 1979, p. 77-6
Hexachlorobenzene	0.0001	12,000	Salmo gairdneri	Oliver & Niimi, 1983
Hexachlorobenzene	0.008	20,000	Salmo gairdneri	Oliver & Niimi, 1983
Hexachlorobenzene	0.03	1,260	Tambusia affinis	Callahan, 1979, p. 77-6
Hexachlorobenzene	0.22	1,530	Tambusia affinis	Callahan, 1979, p. 77-6
Hexachlorobenzene	1.72	2,040	Tambusia affinis	Callahan, 1979, p. 77-6
Hexachlorobenzene	2.98	287	Tambusia affinis	Callahan, 1979, p. 77-6
Hexachlorobenzene	9.34	1,166	Tambusia affinis	Callahan, 1979, p. 77-6
Hexachlorobutadiene		7.8-300	crayfish	Callahan, 1979, p. 57-4
Hexachlorocyclopentadiene		340	algae	Callahan, 1979, p. 57-4
Hexachlorocyclopentadiene		488	fish	Callahan, 1979, p. 57-4
Hexachlorocyclopentadiene		1,634	mosquito	Callahan, 1979, p. 57-4
Hexachlorocyclopentadiene		929	snail	Callahan, 1979, p. 57-4
Hexachloroethane	6.17	139	Lepomis macrochirus	Veith, 1980
Hexachloroethane	0.0071	1,200	Salmo gairdneri	Oliver & Niimi, 1983
Hexachloroethane	0.00003	510	Salmo gairdneri	Oliver & Niimi, 1983
Isophorone	92.4	7	Lepomis macrochirus	Veith, 1980
Kepone		8,400	fish	Kenaga & Goring, 1980
Lindane		325	fish	Kenaga & Goring, 1980
Lindane		325		McCall, 1983
Lindane		768	bluegill	Callahan, 1979, p. 32-6
Lindane		1,050	trout	Bysshe, 1982
Lindane		170-448	zooplankton	Callahan, 1979, p. 32-6
Malathion		0	fish	Kenaga & Goring, 1980

TABLE A7 (continued)

Chemical	Chemical Concentration µg/ℓ	Bioconcentration Factor	Organism	Reference
Methyl parathion		95	fish	Kenaga & Goring, 1980
Napthalene		131	Daphnia pulex	Bysshe, 1982
Nitrapyrin		82		McCall, 1983
Parathion		335	fish	Kenaga & Goring, 1980
PCB	0.005	20,000	phytoplankton	Thomann & Connolly, 1984
PCB	0.005	50,000	Mysis relicta	Thomann & Connolly, 1984
PCB	0.005	100,000	Alosa pseudohareengus	Thomann & Connolly, 1984
PCB	0.005	100,000	Salvelinus namycush	Thomann & Connolly, 1984
Pentachlorobenzene		5,000	fish	Kenaga & Goring, 1980
Pentachlorobenzene	5.15	3,400	Lepomis macrochirus	Veith, 1980
Pentachlorobenzene	0.0001	13,000	Salmo gairdneri	Oliver & Niimi, 1983
Pentachlorobenzene	0.0093	20,000	Salmo gairdneri	Oliver & Niimi, 1983
Pentachloroethane	7.93	67	Lepomis macrochirus	Veith, 1980
Pentachlorobenzene		5,100	Lepomis macrochirus	Banerjee, Sugatt & O'Grady, 1984
Pentachlorobenzene		7,300	Poecilia reticulata	Banerjee, Sugatt & O'Grady, 1984
Pentachlorobenzene	0.625	4,000	Salmo gairdneri	Banerjee, Sugatt & O'Grady, 1984
Pentachlorobenzene	7.64	4,300	Salmo gairdneri	Banerjee, Sugatt & O'Grady, 1984
Pentachlorobenzene	32.8	6,900	Salmo gairdneri	Banerjee, Sugatt & O'Grady, 1984
Pentachlorobenzene	70.8	5,800	Salmo gairdneri	Banerjee, Sugatt & O'Grady, 1984
Pentachlorobenzene	106	5,500	Salmo gairdneri	Banerjee, Sugatt & O'Grady, 1984
Pentachlorophenol		16	fish	Kenaga & Goring, 1980
Pentachlorophenol	100	900	Carassius auratus	Callahan, 1979, p. 87-5
Perylene		7,190	Daphnia pulex	Bysshe, 1982
Phenanthrene		325	Daphnia pulex	Bysshe, 1982
Pyrene		2,700	Daphnia pulex	Bysshe, 1982
Terbufos		535	fish	Kenaga & Goring, 1980
Tetrachlorobiphenyl		72,950		McCall, 1983
Tetrachloroethylene		39	fish	Kenaga & Goring, 1980
Tetrachloroethylene	3.43	49	Lepomis macrochirus	Veith, 1980
Toxaphene		26,400	fish	Kenaga & Goring, 1980
Toxaphene		6,900	alga	Callahan, 1979, p. 35-6
Toxaphene		500	aquatic plants	Callahan, 1979, p. 35-6
Toxaphene		4,200	fish	Callahan, 1979, p. 35-6
Toxaphene		8,900	mosquito larvae	Callahan, 1979, p. 35-6
Toxaphene		10,000	rainbow trout	Callahan, 1979, p. 35-6

TABLE A7 (continued)

Chemical	Chemical Concentration µg/ℓ	Bioconcentration Factor	Organism	Reference
Toxaphene		9,600	snail	Callahan, 1979, p. 35-6
Trifluralin		4,570	fish	Kenaga & Goring, 1980

TABLE B1. TOXIWASP INPUTS

(1). Exchange coefficients, segment volume and flow.

- Exchange coefficient between segments.
- Dispersion coefficient for the interface between segments.
- Interfacial cross-sectional area between segments.
- Length of segments.
- Volumes of segments.
- Flow between segments.

(2). Boundary conditions, forcing functions.

- Boundary conditions (concentrations) of segments.
- Sources (loads) or sinks of the toxic chemical.
- Segment depth.

(3). Environmental characteristics.

- Average temperature for segment.
- Depth of segment.
- Average veloity of water in segment.
- Average wind velocity 10 cm above the water surface.
- Bacterial population density in segment.
- Proportion of bacterial population that actively degrades the chemical.
- Total actively sorbing biomass in segment.
- Biotemperature in segment.
- Molar concentration of environmental oxidants in segment.
- Organic carbon content of sediments as fraction of dry weight.
- Percent water in benthic sediments, expressed as fresh/dry weight.
- Fraction of sediment volume that mixes.
- Hydrogen ion activity in segment.
- Single-valued zenith light extinction coefficients.
- Total first order decay rates calculated externally.

(4). Chemical characteristics (constants).

- Arrhenius activation energy of specific-base-catalyzed hydrolysis of the chemical.
- Arrhenius activation energy of neutral hydrolysis of the chemical.
- Arrhenius activation energy of specific-acid-catalyzed hydrolysis of the chemical.
- Second order rate constants for specific-base-catalyzed hydrolysis of the chemical.
- Second order rate constants for specific-acid-catalyzed hydrolysis of chemical.

- First order rate constants for neutral hydrolysis of the chemical.
- Arrhenius activation energy of oxidative transformation of the chemical.
- Second order rate constants for water column bacterial biolysis of the chemical.
- Q-10 values for bacterial transformation rate in the water column.
- Second order rate constants for benthic sediment bacterial biolysis of the chemical.
- Q-10 values for bacterial transformation of organic chemical in benthic sediments.
- Organic carbon partition coefficient.
- Octanol water partition coefficient.
- Organic carbon content of the compartment biomass as a fraction of dry weight.
- The molecular weight of the chemical.
- Henry's Law constant of the chemical.
- Vapor pressure of compound.
- Measured experimental value for volatilization (liquid-phase transport resistance, expressed as a ratio to the reaeration rate.
- Aqueous solubility of toxicant chemical species.
- Exponential term for describing solubility of the toxicant as a function of temperature.
- Molar heat of vaporization for vapor pressure described as a function of temperature.
- Constant used to compute the Henry's Law constants for volatilization as a function of environmental temperature.
- A near-surface photolytic rate constant for the chemical.
- Reference latitude for corresponding direct photolysis rate constant.
- Average cloudness in tenths of full sky cover.
- Geographic latitude of ecosystem.
- Distribution function (ratio of optical path length to vertical depth).
- Reaction quantum yield in photolytic transformation of chemical.
- Trigger concentration that define a peak event.

TABLE B2. EXAMS II INPUTS

(1) Chemical data and rate constants

- Gram molecular weight of the toxic chemical.
- Aqueous solubility of toxicant chemical species.
- Enthalpy term for describing solubility of the toxicant as a function of temperature.

- Refrence latitude for corresponding direct photolysis rate constant.
- Measured experimental value for (volatilization) liquid-phase transport resistance, expressed as a ratio to the reaeration rate.
- Henry's Law constant of the toxic chemical.
- Vapor pressure of toxic chemical.
- Molar heat of vaporization for vapor pressure described as function of temperature.
- Partition coefficients for computing sorption of toxicant on compartment sediments.
- Partition coefficient for computing sorption of toxicant with compartment biomass (BIOMS).
- Multiplication of KOC (partition coefficient corrected for organic carbon) by the fractional organic carbon content of each system sediment yields the partition coefficient for sorption of unionized compound to the sediment.
- Octanol-water partition coefficient of toxicant.
- Near-surface photolysis rate constant for the chemical species of the toxicant.
- Reaction quantum yield in photolytic transformation of toxic chemical.
- Second-order rate constants for specific-acid-catalyzed hydrolysis of toxicant.
- Second-order rate constants for specific-base-catalyzed hydrolysis of toxicant.
- Arrhenius activation energy of specific-acid-catalyzed hydrolysis of he toxicant.
- Arrhenius activation energy of specific-base-catalyzed hydrolysis of the toxicant.
- Rate constant for neutral hydrolysis of organic toxicant.
- Second-order rate constants for oxidation transformation of toxicant.
- Arrhenius activation energy of neutral hydrolysis of the toxicant.
- Arrhenius activation energy of oxidative transformation of the toxicant.
- Second-order rate constants for water column bacterial biolysis of the organic toxicant.
- Q-10 values for bacterial transformation of toxicant in the water column of the system.
- Second-order rate constants for benthic sediment bacterial biolysis of the organic toxicant.
- Q-10 values for bacterial transformation of organic toxicant in benthic sediments.
- Absorption spectrum (molar extinction coefficients) for each chemical species of the toxicant.

(2) Global parameters

- Average rainfall in geographic of the system.
- Average cloudiness in tenths of full sky cover.

- Geographic latitude of the ecosystem

(3) Biological parameters

- Total actively sorbing biomass in each ecosystem compartment.
- Fraction of total biomass in each compartment that is planktonic, i.e., subject to passive transport via entrainment in advective or turbulent motions.
- Biotemperature in each ecosystem compartment, i.e., temperature to be used in conjunction with Q-10 expressions for biolysis rate constants.
- Bacterial population density in each compartment.
- Proportion of total bacterial population that actively degrades toxicant.
- Concentration of chlorophyll and chlorophyll-like pigments in water column compartments.

(4) Depth and inflows

- Average depth of each compartment.
- Stream flow entering ecosystem compartments.
- Stream-borne sediment load entering ecosystem compartments.
- Non-point-source water flow entering ecosystem compartments.
- Non-point-source sediment loading entering ecosystem compartments.
- Interflow (subsurface water flow, flow seepage) entering each compartment.

(5) Sediment characteristics

- Percent water in bottom sediments as fraction of dry weight.
- Organic carbon content of compartments as fraction of dry weight.
- Cation exchange capacity of sediments in each compartment.
- Dissolved organic carbon concentration in water column compartments.

(6) Aeration, light and others

- Reaeration parameter at 20 degrees C in each ecosystem compartment.
- Average wind velocity at a reference height of 10 cm above the water surface.
- Single-valued zenith light extinction coefficient for water columns, dummy variable for benthic compartments.
- Distribution function (ratio of optical path length to vertical depth) for each compartment.
- Evaporative water losses from ecosystem compartments.
- Area of ecosystem elements (compartments).

TABLE B3. HSPF INPUTS

INPUTS TO PERLND

(1) Inputs to correct air temperature for elevation difference.

- Difference in elevation between the temperature gage and the pervious land segment.
- Air temperature over the pervious land segment.

(2) Inputs to simulate accumulation and melting of snow and ice.

- Latitude of the pervious land segment.
- Mean elevation of the pervious land segment.
- Fraction of the pervious land segment which is shaded from solar radiation by, for example, trees.
- Maximum pack (water equivalent) at which the entire pervious land segment will be covered with snow.
- Density of cold, new snow relative to water.
- Air temperature below which precipitation will be snow, under saturated conditions.
- A parameter which adapts the snow evaporation equation to field conditions.
- A parameter which adapts the snow condensation/convection melt equation to field conditions.
- Maximum water content of the snow pack, in depth water per depth water equivalent.
- Maximum rate of snowmelt by ground heat, in depth of water equivalent per day.
- Quantities of snow, ice and liquid water in the pack (water equivalent).
- Density of the frozen contents (snow + ice) of pack, relative to water.
- Mean temperature of the frozen contents of the pack.
- Current pack (water equivalent) required to obtain complete areal coverage of the pervious land segment.
- Current remaining possible increment to ice storage in the pack.
- Fraction of sky which is assumed to be clear at the present time.

(3) Inputs to simulate water budget for pervious land segment.

- Fraction of the pervious land segment which is covered by forest which will continue to transpire in winter.
- Lower zone nominal storage
- Length and slope of the assumed overland flow plane
- Basic groundwater recession rate.
- Air temperature below which evapotranspiration will arbitrarily be reduced below the value obtained from the input time series.

- Temperature below which evapotranspiration will be zero regardless of the value in the input time series.
- Exponent in the infiltration equation.
- Ratio between the max and mean infiltration capacities over the pervious land segment.
- Fraction of groundwater inflow which will enter deep (inactive) groundwater and, thus, be lost from the system.
- Fraction of remaining potential evapotranspiration which can be satisfied from baseflow (groundwater outflow), if enough is available.
- Fraction of remaining potential evapotranspiration which can be satisfied from active groundwater storage if enough is available.
- Interception storage capacity.
- Upper zone nominal storage.
- Manning's n for the assumed overland flow plane.
- Interflow inflow and recession parameters.
- Lower zone evapotranspiration parameter.
- Monthly interception storage capacity.
- Monthly upper zone storage.
- Monthly Manning's n values.
- Monthly interflow parameters.
- Monthly interflow recession constants.
- Monthly lower zone evapotranspiratino parameter.
- Interception storage.
- Surface (overland flow) storage.
- Storages of upper, lower and interflow zones.
- Active groundwater storage.
- Surface storage (upper zone and interflow).

(4) Inputs to produce and remove sediment.

- Supporting management practice factor. It is used to simulate the reduction in erosion achieved by use of erosion control practices.
- Coefficient in the soil detachment equation.
- Exponent in the soil detachment equation.
- Fraction by which detached sediment storage decreases eaach day, as a result of soil compaction.
- Fraction of land surface which is shielded from erosion by rainfall.
- Rate at which sediment enters detached storage from the atmosphere.
- Coefficient and exponent in the detached sediment washoff equation.
- Coefficient and exponent in the matrix soil scour equation.
- Monthly erosion related cover values.
- Monthly net vertical sediment input.
- Initial storage of detached sediment.

(5) Inputs to estimate soil temperature.

- Surface layer temperature, when the air temperature is 32 degrees F (ASLT).
- Slope of the surface layer temperature regression equation (BSLT).
- Smoothing factor in upper layer temperature calculation (ULTP1).
- Mean difference between upper layer soil temperature and air temperature (ULTP2).
- Smoothing factor for calculating lower layer/groundwater soil temperature (UGTP1).
- Mean departure from air temperature for calculating lower layer/groundwater soil temperature (UGTP2).
- Intercept in the upper layer soil temperature regression equation.
- Slope in the upper layer soil temperature regression equation.
- Monthly values for ASLT, BSLT, ULTP1, ULTP2, LGTP1, and LGTP2.
- Initial air temperature.
- Initial surface layer soil temperature.
- Initial upper layer soil temperature.
- Initial layer/groundwater layer soil temperature.

(6) Inputs to estimate water temperature and dissolved gas concentrations.

- Elevation of the pervious land segment above seal level.
- Concentration of dissolved oxygen nd CO2 in interflow outflow, and in active groundwater flow.
- Monthly interflow DO and CO2 concentrations.
- Monthly groundwater DO and CO2 concentrations.
- Initial surface and interflow outflow temperature.
- Initial active groundwater outflow temperature.
- Initial DO and CO2 concentrations in surface outflow, interflow outflow, and active groundwater outflow.

(7) Inputs to simulate quality constituents using simple relationships with sediment and water yield.

- Washoff potency factor.
- Scour potency factor.
  Note: A potency factor is the ratio of constituent yield to sediment (washoff or scour) outflow.
- Initial storage of constituent on the surface of the pervious land segment.
- Rate of accumulation of constituent.
- Maximum storage of constituent.
- Rate of surface runoff which will remove 90 percent of stored constituent per hour.
- Concentration of the constituent in interflow outflow.
- Concentration of the constituent in active groundwater outflow.
- Monthly washoff and scour potency factors.
- Monthly accumulation rates of constituent.
- Monthly limiting storage of constituent.

- Monthy concentrations of constituent in interflow and groundwater.

(8) Inputs to estimate the moisture and fractions of solutes being transported in the soil layers.

- Nominal upper and lower zones storage.
- Initial surface detention storage.
- Initial surface detention storage on each block of the pervious land segment.
- Initial moisture content in the surface storage, in the upper principal storage, and in the upper transitory (interflow) storage.
- Initial moisture storages in the lower layer, and in the active groundwater layer.

(9) Inputs to simulate pesticide behavior in detail.

- Chemical first-order reaction temperature correction parameters which is used to adjust the desorption and adsorption rates.
- Desorption and adsorption rates (first-order) at 35°C.
- Maximum solubility of the pesticide in water.
- Maximum concentration (on the soil) of pesticide which is permanently fixed to the soil.
- Coefficient and exponent parameters for the Freundlich adsorption-desorption equation.
- Pesticides degradation rates in the surface, upper, and active groundwater layers.
- Initial storage of pesticide in crystalline adsorbed and solution forms in surface, upper, lower or groundwater layer.
- Initial storage of pesticide in the upper layer transitory (interflow) storage.

(10) Inputs to simulate nitrogen behavior in detail.

- Plant nitrogen uptake reaction rate parameters for the surface layer, upper layer, lower layer, and active groundwater layer.
- Monthly plant uptake parameters for nitrogen, for the surface, upper, lower or groundwater layer.
- Parameters intended to designate which fraction of nitrogen uptake comes from nitrite and ammonium.
- Temperature coefficients for plant uptake, ammonium desorption, ammonium adsorption, nitrate immobilization, organic N ammonification, NO3 denitrification, Nitrification, and ammonium immobilization.
- Maximum solubility of ammonium in water.
- Initial storage of N in organic N, adsorbed ammonium, nitrate, and plants.
- Initial storages of ammonium and nitrate in the upper layer transitory (interflow) storage.

(11) Inputs to simulate phosphorus behavior in detail.

- Plant phosphorus uptake reaction rate parameters for the surface layer, upper layer, lower layer, and active groundwater layer.
- Monthly plant uptake parameters for phosphorus, for the surface, upper, lower or groundwater layer.
- Temperature correction parameters for phosphorus plant uptake, phosphate desorption, phosphate immobilization, and organic P mineralization.
- First-order reaction rates for phosphate desorption, phosphate adsorption, phosphate immobilization, and organic P mineralization.
- Maximum solubility of phosphorus in water.
- Initial phosphorus storage (in organic P, adsorbed P, solution P, and P stored in plants) in the surface, upper, lower or groundwater layer.
- Initial storage of phosphate in upper layer transitory (interflow) storage.

(12) Inputs to simulate the movement of a tracer (conservative).

- Initial storage of tracer (conservative) in the surface storage, upper principal storage, upper transitory storage, lower groundwater layer, and active groundwater layers.

INPUTS TO IMPLND

(1) Inputs to correct air temperature for elevation difference.

- See temperature inputs in the PERLAND section.

(2) Inputs to simulate the accumulation and melting of snow and ice.

- See snow inputs in the PERLND section.

(3) Inputs to simulate water budget for impervious land segment.

- Length and slope of the assumed overland flow plane.
- Manning's n for the overland flow plane.
- Retention (interception) storage capacity of the surface.
- Air temperature below which evapotranspiration will arbitrarily be reduced below the value obtained from the input time series.
- Temperature below which evapotranspiration will be zero regardless of the value in the input time series.
- Monthly retention storage capacity.
- Monthly Manning's n values.
- Initial retention storage.
- Initial surface (overland flow) storage.

(4) Inputs to estimate accumulation and removal of solids.

- Coefficient in the solids washoff equation.

- Exponent in the solids washoff equation.
- Rate at which solids are placed on the land surface.
- Fraction of solids storaage which is removed each day; when there is no runoff, for example, because of street sweeping.
- Monthly solids accumulation rates.
- Monthly solids unit removal rates.
- Initial storage of solids.

(5) Inputs to estimate water temperature and dissolved gas concentrations.

- Elevation of the impervious land segment above sea level.
- Surface water temperature, when the air temperature is 32°F (AWTF).
- Slope of the surface water temperature regression equation (BWTF).
- Monthly values for AWTF and BWTF.
- Initial values for the temperature, DO and CO2.

(6) Inputs to simulate quality constituents using simple relationships with solids and/or water yield.

- Washoff potency factor.
- Initial storage of constituent on the surface of the impervious land segment.
- Rate of accumulation of constituent.
- Maximum storage of constituent.
- Rate of surface runoff which will remove 90 percent of stored constituent per hour.

INPUT TO RCHRES

(1) Inputs to simulate hydraulic behavior.

- Length of the receiving water body (RCHRES).
- Drop in water elevation from the upstream to the downstream extremities of the RCHRES.
- Correction to the RCHRES depth to calculate stage.
- Weighting factor for hydraulic routing.
- Median diameter of the bed sediment (assumed constant throughout the run).
- Initial volume of water in the RCHRES.

(2) Inputs to prepare to simulate advection of entrained constituents.

- Ration of maximum velocity to mean velocity in the RCHRES cross section under typical flow conditions.
- Volume of water in the RCHRES at the start of the simulation.

(3) Inputs to simulate behavior of conservative constituents.

- Initial concentration of the conservative.

(4) Inputs to simulate heat exchange and water temperature.

- Mean RCHRES elevation.
- Difference in elevation between the RCHRES and the air temperature gage.
- Correction factor for solar radiation.
- Longwave radiation coefficient.
- Conduction-convection heat transport coefficient.
- Evaporation coefficient.
- Water temperature at the RCHRES.
- Air temperature at the RCHRES.

(5) Inputs to simulate behavior of inorganic sediment.

- Width of the cross-section over which HSPF will assume bed sediment is deposited regardless of stage, top-width, etc.
- Bed depth.
- Porosity of the bed (volume voids/total volume).
- Effective diameter of the transported sand, silt and clay particles.
- Fall velocity of the sand, silt and clay particles in still water.
- Density of the sand, silt and clay particles.
- Critical bed shear stresses for deposition and scour.
- Erodibility coefficient of the sediment.
- Initial concentrations (in suspension) of sand, silt, and clay.
- Initial total depth (thickness) of the bed.
- Initial fractions (by weight) of sand, silt and clay in the bed material.

(6) Inputs to simulate behavior of a generalized quality constituent.

- Latitude of the RCHRES.
- Initial concentration of constituent.
- Second order acid and base rate constants for hydrolysis.
- First order rate constant of neutral reaction with water.
- Temperature correction coefficient for hydrolysis.
- Second order rate constant for oxidation by free radical oxygen.
- Temperature correction coefficient for oxidation by free radical oxygen.
- Molar absorption coefficients for constituent for 18 wavelength ranges of light.
- Quantum yield for the constituent in air-saturated pure water.
- Temperature correction coefficient for photolysis.
- Ratio of volatilization rate to oxygen reaeration rate.
- Second order rate constant for biomass concentration causing biodegradatino of constituent.
- Temperature correction coefficient for biodegradation of constituent.
- Concentration of biomass causing biodegradation of constituent.
- Monthly concentration of biomass causing biodegradation of constituent.

- First order decay rate for constituent.
- Temperature correction coefficient for first order decay of constituent.
- Decay rate for constituent adsorbed to suspended sediment.
- Temperature correction coefficient for decay of constituent on suspended sediment.
- Decay rate for constituent adsorbed to bed sediment.
- Temperature correction coefficient for decay of constituent on bed sediment.
- Partition coefficient - distribution coefficients for constituent with: suspended sand, suspended silt, suspended clay, bed sand, bed silt, bed clay.
- Transfer rate between adsorbed and desorbed states for constituent with: suspended sand, suspended silt, suspended clay, bed sand, bed silt, bed clay.
- Temperature correction coefficients for adsorbtion-desorbtion on: suspended sand, suspended silt, suspended clay, bed sand, bed silt, bed clay.
- Initial concentration of constituent on: suspended sand, suspended silt, suspended clay, bed sand, bed silt, bed clay.
- Initial values for water temperature, pH, free radical oxygen concnetration, cloud cover, and total suspended sediment concentration.
- Phytoplankton concentration (as biomass).
- Monthly values of water temperature, pH, and free radical oxygen.
- Base adsorption coefficients for 18 wavelengths of light passing through clear water.
- Increments to base absorbance coefficient for light passing through sediment-laden water.
- Increments to the base absorption coefficient for light passing through plankton-laden water.
- Light extenction efficiency of cloud cover for each of 18 wavelengths.
- Monthly values of average cloud cover.
- Monthly average suspended sediment concentration values.
- Monthly values of phytoplankton concentration.

(7) Inputs to simulate behavior of constituents involved in biochemical transformations.

- Velocity above which effects of scouring on benthal release rates is considered.

(a) Inputs to simulate primary DO, BOD balances.

- Unit BOD decay at 20 °C.
- Temperature correction coefficient for BOD decay.
- Rate of BOD settling.
- Allowable dissolved oxygen supersaturation.
- RCHRES elevation above sea level.
- Benthal oxygen demand at 20°C.

- Temperature correction coefficient for benthal oxygen demand.
- Benthal release of BOD at high oxygen concentration.
- Increment to benthal release of BOD under anaerobic conditions.
- A correction factor in the lake reaeration equation to account for good or poor circulation characteristics.
- Empirical constant in Tsivoglou's equation for reaeration.
- Temperature coefficient for surface gas invasion.
- Length of the RCHRES.
- Energy drop over its length.
- Temperature correction coefficient for surface gas invasion.
- Empirical constnat for equation used to calculate reaeration coefficient.
- Exponent to depth used in calculation of reaeration coefficient.
- Exponent to velocity used in calculation of reaeration coefficient.
- Dissolved oxygen.
- Biochemical oxygen demand.
- Dissolved oxygen saturation concentration.

(b) Inputs to determine primary inorganic nitrogen and phosphorous balances.

- Benthal release of inorganic nitrogen, and orthophosphate.
- Concentration of dissolved oxygen below which anerobic conditions exist.
- Unit oxidation rate of ammonia and nitrite at 20°C.
- Initial concentration of nitrate (as N), ammonia (as N), and nitrite (as N).
- Concentration of ortho-phosphorus (as phosphorus).
- Concentration of denitrifying bacteria.

(c) Inputs to simulate behavior of plankton populations and associated reactions.

- Ratio of chlorophyll "A" content of biomass to phosphorus content.
- Nonrefractory fraction of algae and zooplankton biomass.
- Fraction of nitrogen requirements for phytoplankton growth satisfied by nitrate.
- Base extinction coefficient for light.
- Maximal unit algal growth rate.
- Michaelis-Menten constant for light limited growth.
- Nitrate Michaelis-Menten constant for nigrogen limited growth.
- Nitrate Michaelis-Menten constant for phosphorus limited growth.
- Phosphate Michaelis-Menten constant for phosphorus limited growth.

- Temperatures above and below which algal growth ceases.
- Temperature below which algal growth is retarded.
- Algal unit respiration rate at 20°C.
- High algal unit death rate.
- Low algal unit death rate.
- Inorganic nitrogen concentration below which high algal death rate occurs (as phosphorus).
- Minimum concentration of plankton not subject to advection (SEED).
- Concentration of plankton not subject to advection at very low flow (MISTAY).
- Outflow at which concentration of plankton not subject to advection is midway between SEED and MXSTAY.
- Chlorophyll "A" concentration above which high algal death rate occurs.
- Rate of phytoplankton settling.
- Rate of settling for dead refractory organics.
- Maximum zooplankton filtering rate at 20°C.
- Zooplankton filtering rate at 20°C (MZOEAT).
- Natural zooplankton unit death rate.
- Increment to unit zooplankton death rate due to anaerobic conditions.
- Temperature correction coefficient for filtering.
- Temperature correction coefficient for respiration.
- The fraction of nonrefractory zooplankton excretion which is immediately decomposed when ingestion rate is greater than MZOEAT.
- Average weight of a zooplankton organism.
- Maximum benthic algae density (as biomass).
- Ratio of benthic algal to phytoplankton respiration rate.
- Ratio of benthic algal to phytoplankton growth rate.
- Initial conditions for phystoplankton (as iomass), zooplankton algae (as biomass), benthic algae (as biomass), dead refractory organic nitrogen, dead refractory organic phosphorus, and dead refractory organic carbon.

(d) Inputs to simulate pH and carbon species.

- Ratio of carbon dioxide invasion rate to oxygen reaeration rate.
- Benthal release of CO_2 (as C) for aerobic and anaerobic conditions.
- Initial total inorganic carbon for pH simulation.
- Initial carbon dioxide (as C) for pH simulation.
- Initial pH.

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