



Project Summary

Case Studies and Model Testing of the Metals Exposure Analysis Modeling System (MEXAMS)

A. J. Medine and B. R. Bicknell

In the EPA's wasteload allocation/total maximum daily load (WLA/TMDL) program, the agency must establish more stringent effluent limitations and guidelines for toxic chemicals (including metals) if previous limitations are not adequate to attain or maintain acceptable water quality levels. The Metals Exposure Analysis Modeling System (MEXAMS) was recently developed to assist in this effort. This model, linking a complex speciation model with an aquatic transport/fate model, should help discriminate between the fraction of metal that is dissolved and in bio-available form, and the fraction that is complexed and rendered relatively nontoxic.

The MEXAMS model has been tested with data from three rivers to determine its ability to simulate fate, transport, and speciation of heavy metals in river systems. The rivers selected for study were the Naugatuck River in Connecticut and the Ten Mile River in Massachusetts, both of which receive electroplating and metal finishing wastes; and the White River in Utah, which receives metal loadings from natural sources. This report documents the tests as case studies to guide future users in application of the model. In addition, the program has been enhanced by addition of sediment settling/resuspension to the aquatic transport submodel EXAMS.

This Project Summary was developed by EPA's Environmental Research Laboratory, Athens, GA, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Transport processes, environmental distributions, and biological effects of heavy metals in our aquatic environments have been the focus of increasing concern. Direct toxicity to aquatic organisms and indirect toxicity to humans and other higher organisms are at the center of this concern. Although heavy metals are natural constituents of aquatic environments, additional quantities introduced by man's presence may result in an altered chemical composition of the aqueous and sediment phases, often with detrimental impacts on the environment. In an effort to reduce these impacts, environmental transport/fate models of heavy metals in aquatic ecosystems are being developed.

One of these models is the Metals Exposure Analysis Modeling System (MEXAMS). This program links MINTEQ, a geochemical model, with EXAMS, an aquatic exposure assessment model. MEXAMS was developed to allow assessment of the impacts of "priority pollutant" metals (As, Cd, Cu, Pb, Ni, Ag and Zn). This report presents a case study and tutorial for MEXAMS.

The first evaluation consisted of calibrating, testing, and assessing the model response for an actual site application on the Naugatuck River, located in the Housatonic River Basin in western Connecticut.

The second evaluation addressed the use of the MINTEQ geochemical model for the White River (Utah), a dynamic lotic system. Water quality parameter input, laboratory adsorption experiments, chemical analysis, MINTEQ utilization, and prediction of laboratory results are described.

The third evaluation addressed application of MEXAMS to the Ten Mile River, a small stream located in southeastern Massachusetts, that receives inorganic metal waste from numerous industries along its banks. The evaluation involved data analysis, preparation of detailed MEXAMS input, and description of the model simulation for a wasteload allocation study of the river.

A second purpose of this work was to incorporate simple sediment settling and resuspension into MEXAMS. Consideration of metal losses from the water column due to steady-state sediment settling will add an important process to MEXAMS, allowing more accurate calibration and simulation of many systems.

Model Descriptions

The Exposure Analysis Model System (EXAMS) describes the fate, transport and impacts of organic contaminants in aquatic systems. The program is a deterministic simulation model, based on a core of mechanistic process equations derived from fundamental theoretical concepts.

The model estimates exposure, fate, and persistence of organic pollutant discharges, using conservation of mass to balance loadings, transport, and transformation of the compound. EXAMS simulates three transport processes: advection, dispersion, and volatilization. Advective and dispersive transport are possible for dissolved species, sediment sorbed material and bio-sorbed materials. Transport through the ecosystem compartments may be represented by whole sediment bed loads, suspended sediment washloads, exchanges with fixed volume sediment beds, and ground water infiltration.

EXAMS is capable of simulating both lotic and lentic aquatic systems. These systems are initially compartmentalized and classified as littoral, epilimnion, hypolimnion, or benthic. Each compartment is assumed to be completely mixed. The computer then develops single differential equations for each compartment.

MINTEQ, a computer program for calculating aqueous geochemical equilibria, was developed for incorporation into MEXAMS. MINTEQ is used to predict metal speciation including sorption, precipitation and ion exchange of "priority pollutant" metals in aquatic environments. This chemical equilibrium problem is described as a set of mass balance equations, one for each component, and a set of mass action equations, one for

each species. The equilibrium constant approach is utilized to solve the equilibrium problem, solving nonlinear mass action expressions using linear mass balance equations. The equilibrium composition of an aquatic environment is determined by minimization of Gibbs free energy of the system within the mass balance constraints. This chemical equilibrium will determine aqueous metal speciation in addition to the effects of precipitation/dissolution and sorption, and is used in EXAMS to determine fate and migration of a metal.

Solid phases are dealt with using the "transformation of basis" method. This method reduces the number of independent variables to be determined and allows the solution of a wider range of chemical equilibrium problems.

MINTEQ also is capable of modeling adsorption in a number of ways. Six different algorithms are accessible through the use of MINTEQ for describing sorption phenomena - "activity" K_d , "activity" Langmuir equation, "activity" Freundlich equation, ion exchange, constant capacitance surface complexation, and triple layer surface complexation.

EXAMS and MINTEQ are the two individual models linked to form MEXAMS. The MEXAMS program provides three different modes of operation. The first mode is the MINTEQ only, which allows the operator to determine how changes in water chemistry will affect metal speciation and solid phase interactions without regard to transport processes. The second mode is EXAMS only, which deals with the ionization, sorption, transport, and transformation of a given pollutant. Finally, the third mode links EXAMS and MINTEQ, allowing the user to determine the effect of transport processes and chemical interactions on priority pollutant concentration. To use the coupled mode, the first step is to create an EXAMS input file that describes the characteristics of the aquatic environment being assessed. The user then enters the MEXAMS Interactive Software Package (MISP). MISP will call for a MINTEQ file for each compartment that contains different water quality data. The user will also input run-specific information that controls the number of times MINTEQ updates metal concentrations. MEXAMS is now set to simulate metal behavior, migration, and fate.

Naugatuck River Case Study

The Naugatuck River has a long history of industrialization along its length. Currently approximately 30 to 300 cubic

meters/day of treated electroplating waste is being discharged into the Naugatuck River. Most industrial discharges on the river currently adhere to Best Available Technology (BAT) guidelines. Both long-term biological monitoring and recent toxicity testing, however, have shown toxic impacts of metals. The data set available was used to illustrate how to apply MEXAMS to field conditions such as in the Naugatuck River.

The main issue surrounding model calibration and verification is obtaining estimates for model parameters and comparing predicted concentrations with actual observed data. Ideally, several data sets are available for independent calibration and verification. In the case of the Naugatuck River data, limited data permitted only the calibration of the model.

Subjective variation of parameter values and a qualitative comparison of model solution and observation is the most common approach to model calibration. Through this procedure, the calibration process attempts to account for (1) spatial variations not represented by the model formulation; (2) functional dependencies of parameters that are either non-quantifiable, unknown and/or not included in the model algorithms; or (3) extrapolation of laboratory measurements of parameters to natural field conditions. During calibration, the analyst may choose to adjust some of the parameters to improve model predictions or to alter the structure of the relationships (or system physical representation) between the variables in the model.

The first step in the calibration was to determine which model inputs have the least reliability. These are the parameters that will be adjusted to perform a sensitivity analysis. Any sensitivity analysis is system dependent because certain input parameters may be more or less sensitive depending on the system being modeled. The first decision to be made in the utilization of MEXAMS was to select a system configuration. There are many possible configurations due to the range of advective and dispersive pathways. Two initial configurations, containing three water column and three benthic compartments, were tested. Originally, both of these configurations had the entire groundflow routed through the benthic compartments. This caused a considerable problem because the sediment residence time within the benthic compartments was so low that the metal was being flushed out of the system. This problem was corrected by routing a portion of the groundwater into the water

column compartments, increasing the sediment residence time and thus increasing the concentration of adsorbed pollutant within the bed sediments.

The parameters that were manipulated during the calibration process included the advective pathway for groundwater accrual, the benthic K_d 's, and the benthic dispersion coefficient. Varying the percent groundwater flow into the benthic compartments between 0.01% and 1% allowed adjustment of the benthic particulate metal concentration. Next, varying the benthic-water column dispersion coefficient from 5.00×10^{-5} to 5.00×10^{-8} (m^2/hr) gave another relationship between dispersion coefficient and adsorbed benthic metal concentrations. Finally, the benthic partition coefficient was increased from field-determined values, which were considered inaccurate. It is very difficult to obtain a benthic sediment sample without entrainment of water from the water column. This water dilutes sediment interstitial concentrations, resulting in low K_d values.

To obtain greater spatial accuracy in water column concentrations, a ten-compartment configuration was developed (Figure 1). The final configuration was calibrated by adjusting the percent ground water flow into the benthic compartments, the advective flow between compartments, and the K_d value for the benthic compartments.

The calibration results obtained from the final configuration are presented in Table 1. As stated previously, three parameters were adjusted to achieve a calibrated model. Table 2 displays the original log K_d 's and the final log K_d 's used to obtain the ten compartment calibration. The advective flow paths for the new compartmentalizations were presented in Figure 1, and the percent ground water routed into benthic compartments eight and ten were changed from 0.01% to 0.1% and 0.13%, respectively. The final calibration obtained for the ten-compartment model was reasonable, and the concentrations predicted by the model were well within the error bars of the field data.

The most important aspect of this model calibration was the compartmentalization of the river reach. Initially calibrated for a six-compartment configuration, the model did not predict adequately the total and dissolved concentrations in the downstream water column compartment due to its length of 6.7 miles. As a result, a ten-compartment configuration was used to obtain the final calibration. This final configuration accurately calculated total,

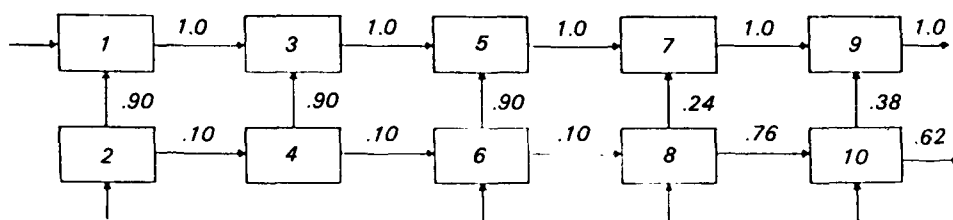


Figure 1. Final calibration configuration, compartments 1 through 10. Values are advective proportions.

Table 1. MEXAMS Model Results, Naugatuck River

Location	Model Compartment	Total Copper		% Diff.	Dissolved Copper		% Diff.
		Field	Model		Field	Model	
Water Column ($\mu g/l$)							
Palmer Br. Rd.	1	12.	11.5	-4.1	9.5	9.1	-4.7
Bogue Rd.	3	----- No Segment Data -----			----- No Segment Data -----		
Rte. 118	5	24.	24.6	+2.5	17.	16.8	-1.2
Campville Rd.	7	16.	16.6	+3.8	14.	14.	0.0
Br. Abutment	9	14.	12.6	-10.0	11.	10.6	3.6
Benthic Region (mg/l)							
		Particulate Copper					
Palmer Br. Rd.	2	140.	138.	-1.5	140.	138.	-1.5
Bogue Rd.	4	62.	59.	-4.8	62.	59.	-5.0
Rte. 118	6	73.	74.	+1.4	72.	73.	+1.4
Campville Rd.	8	177.	179.	+1.1	176.	178.	+0.6
Br. Abutment and Campville Rd.	10	154.*	150.	-2.6	154.*	150.	-2.6

* The average copper concentration measured at Campville Rd. and the Bridge Abutment was used for comparison (based on model compartmentalization).

Table 2. Comparative K_d Data, Naugatuck River

Compartment #	Original log K_d	Calibrated log K_d
1	0.30	0.30
2	3.72	5.02
3	-0.25	-0.25
4	2.95	4.20
5	-0.05	-0.05
6	2.67	4.42
7	-0.05	-0.05
8	2.67	5.30
9	-0.05	-0.05
10	2.67	5.17

dissolved, and particulate concentrations for all water column and benthic compartments. The calibration of this model is only the initial phase of accurately modeling this river reach, however, and model validation to another data set is required.

White River Case Study

Natural loadings of heavy metals into the White River system associated with tributary discharge from periodic storm events can result in dissolved metal con-

centrations that exceed the toxicity thresholds. Dissolved copper concentrations increased from $4 \mu g/l$ to $340 \mu g/l$ associated with an increase of river flow from $500 ft^3/sec$ to $1100 ft^3/sec$ due to a storm event in March 1975. Elevated dissolved concentrations for Zn, Pb, and Cr also have been observed.

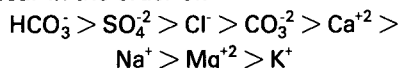
The White River is not extensively developed, although deposits of oil shale are presently being mined. The target metals chosen to exercise the MINTEQ adsorption model in this study (Zn, Pb, Ni, Cu) are associated with potential contamination to the lotic system from retorted waste shale leaching into groundwater and surface waters, retort processing waters, and mine dewatering activities. If leachate through groundwater or accidental discharge into the White River occurred, water quality standards established by the State of Utah could be exceeded, thus resulting in varying degrees of metal stress to the aquatic communities.

The upper basin of the White River originates in the Flat Tops Wilderness Area in northwestern Colorado, which contributes the majority of the flow. The lower basin drainage area extends from

northwestern Colorado to the confluence of the Green River in northeastern Utah. The lower basin area is characterized by a semiarid climate. The watershed contains surficial deposits of lacustrine sediments containing calcite and dolomite deposited by Lake Unita (Palocene Epoch). The physical-chemical processes associated with the geologic weathering and erosional transport causes drastic changes to water quality and gives the White River a strong carbonate system. The area of study on the White River is located in the lower drainage basin area in eastern Utah, near federal oil shale lease tracts.

Because of the land morphology, the study area has various perennial washes and one ephemeral stream, Evacuation Creek. For several months, the flow of this creek is low and contains very high levels of total dissolved solids. The watershed contains anthropogenic metal sources that are eroded and transported during storm events. This overland runoff can cause significant water quality changes to the White River by heavy metal and solids loading.

The flows of the White River are correlated to three flow regimes — upper basin runoff, lower basin runoff, and baseline. Concentrations of major anions and cations found in the White River occur in the order of:



Upper basin runoff provides the best water quality conditions, with low dissolved constituent concentrations but high total suspended solids concentrations. Lower basin runoff shows intermediate dissolved concentrations, where the baseline regime shows the highest concentration of dissolved substances and lowest total suspended solids values.

The chemical matrix (major anions/cations) of the water system had to be determined for subsequent input into MINTEQ as Type I components. This matrix can be determined by a full water quality analysis on field samples, from historical data, or from correlation graphs that show the relationship of the major anions and cations to a physical parameter (TDS). At least two years of constant monitoring of the system should be used to formulate the correlations, to encompass possible seasonal fluctuations. Redox chemistries were not considered in the water quality matrix because of the high dissolved oxygen concentrations, the relative concentrations of ammonia, nitrate and nitrite, and the low levels of

ferrous ion observed. It was assumed that these conditions would reflect a high pe with sulfide being rapidly converted to sulfate. High sulfide levels were reported in alluvial groundwater of Evacuation Creek and Asphalt Wash.

To best utilize the capabilities of MINTEQ and MEXAMS for describing metal fate and transport, data are required to describe the solid phase partitioning of any potential metal loadings. In most cases, limited data are available for suitable descriptions of sorption/desorption and chemical precipitation. A certain degree of caution must be exercised in using literature data to estimate metal partitioning to suspended solids and/or bed sediments, because natural sediments are a mixed population of solid types (oxides, clays, detritus, hydroxides, silicates, etc.). Site-specific data may often be necessary for successful model application.

To illustrate how basic data may be acquired for site-specific application, adsorption experiments have been performed and the details reported. These laboratory reactor studies quantify equilibrium concentrations of dissolved and particulate metals under controlled conditions. These equilibrium concentrations can be determined for variable conditions of pH, total metal concentrations, TSS concentrations, ionic strengths and matrix concentrations. By varying parameters, adsorption relationships can be analyzed and formulated for MINTEQ input.

Two reactor techniques were used for determining adsorption behavior for target metals — small volume reactors and large volume. Both of these techniques used ambient solids concentrations and ionic strengths. The parameters that were varied were total metal and pH.

In implementing MINTEQ, the user must first determine chemical activity by developing an input file without considering adsorption and chemical precipitation. Execution of this file creates output characterizing, among other things, the dissolved metal ion activity, the charge balance, and the saturation indices for solids. For the charge balance computations, two values should be noted, unspicated and spicated. An unspicated charge imbalance of greater than 30% can indicate that one or more ionic constituent may be missing. The more reliable indicator, however, is the charge balance after speciation. If this charge balance is greater than 20%, then it is very likely that an ionic component is absent. If environmental data are lacking, an ion

concentration adjustment may be required on a conservative Type I component.

An output section giving saturation indices (SI) for all minerals and solids can indicate what solids will precipitate for the full MINTEQ model run. The SI values for diasporite, argonite, calcite and fluorite were all positive, indicating the solid is oversaturated in the system. Because of kinetic factors, however, the solids may not actually obtain equilibrium in the time frame considered, or may not actually form due to the constraints placed on the system, such as no fixed partial pressure (open to atmosphere). Some of these solids form under high partial pressures of CO₂ (groundwater environment) and if used in a system with no fixed partial pressure, a Gibbs Phase Rule Violation will occur. General guidelines for selecting solid phases are given in the MINTEQ Technical Manual.

To determine which MINTEQ adsorption model can be implemented for the White River, data obtained from the metal addition reactor studies and MINTEQ were plotted. The first approach was to plot particulate metal concentration (moles/l) versus dissolved metal ion activity concentration (moles/l) obtained from MINTEQ for various total metal concentrations for a specific pH. A linear regression was performed and the slope of the line (activity K_d) was determined. The log value of the K_d was then utilized as an input parameter when implementing the MINTEQ adsorption model.

In utilizing the activity K_d approach to model metal-sediment adsorption, a new MINTEQ input file had to be developed. The component for surface sites (ID 990) was added as a Type I component and its activity fixed as a Type III species. Four Type V species (calcite, dolomite, diasporite, tenorite) were inserted. These species are allowed to precipitate in the system if their saturation indices are exceeded during chemical speciation. The last addition involved a Type II modification (insertion of species not in data base) to incorporate the adsorption "reaction" between Zn and the surface sites (SOH).

These new MINTEQ files were developed and executed for all Zn reactor experiments involving four total metal levels (0.124 mg/l, 0.224 mg/l, 0.524 mg/l, and 1.024 mg/l) at two specific pH conditions that conformed to the activity K_d approach (pH 7.50 and 8.39). In order to evaluate how well MINTEQ predicted the laboratory adsorption results, the predicted molar values of the sorbed mass (particulate) and aqueous

(dissolved) masses were compared with the actual experimental results from the pH = 8.39 data set that conformed to the linear Kd approach. Figures 2 and 3 show the comparison plots of the MINTEQ prediction versus actual laboratory results for both dissolved and particulate Zn.

If the system being modeled has a relatively constant pH and the metal variation is not too great ($< 2x$), the activity Kd approach would give satisfactory results. If pH, metal level, SS and other parameters change dramatically, however, then one of the other adsorption routines should be selected. For example, zinc adsorption in White River samples exhibited a curvilinear relationship more characteristic of Langmuir behavior. In most situations, however, the metal level is low enough that the linear portion could be used to calculate a Kd. Lead adsorption was linear in all pH ranges tested (6.40, 6.80, 7.30, 8.12, and 8.90) and nickel adsorption also appeared to show a linear relation between $1/(Ni^{+2})$ and particulate Ni. A summary of the log Kd's as a function of pH for the White River are shown in Figure 4.

The Langmuir model can often be used to predict metal sorption in natural systems. At low (Cu^{+2}), the equation is linear; whereas at very high (Cu^{+2}), the equation represents a saturation of surface sites ($CuS = ST$). The equation could be used over a wide range of (Cu^{+2})'s and could account for different site availability by variation of ST (maximum surface coverage). This equation would be very useful on the White River where large fluctuations in suspended solids and ambient dissolved copper are observed. Metal partitioning to solids is more significant in the water column, as opposed to bed sediments and thus, dissolved metal should be related to suspended sediment (and responsive to ST in the Langmuir equation). As metal partitioning becomes more dominated by bed sediment interaction, the usefulness of the Langmuir decreases and the activity Kd might be entirely appropriate.

An experiment using the White River with pH = 7.5 and SS = 200 mg/l illustrated the lower section of a Langmuir type fit. Attempts to increase the range of the plot by Cu addition only resulted in malachite precipitation. A plot of the linearized equation showed a curvilinear relation when a straight line would be anticipated if data fit a Langmuir model.

At this point, it is emphasized that the MINTEQ input files were only considering inorganic speciation of the metal. No

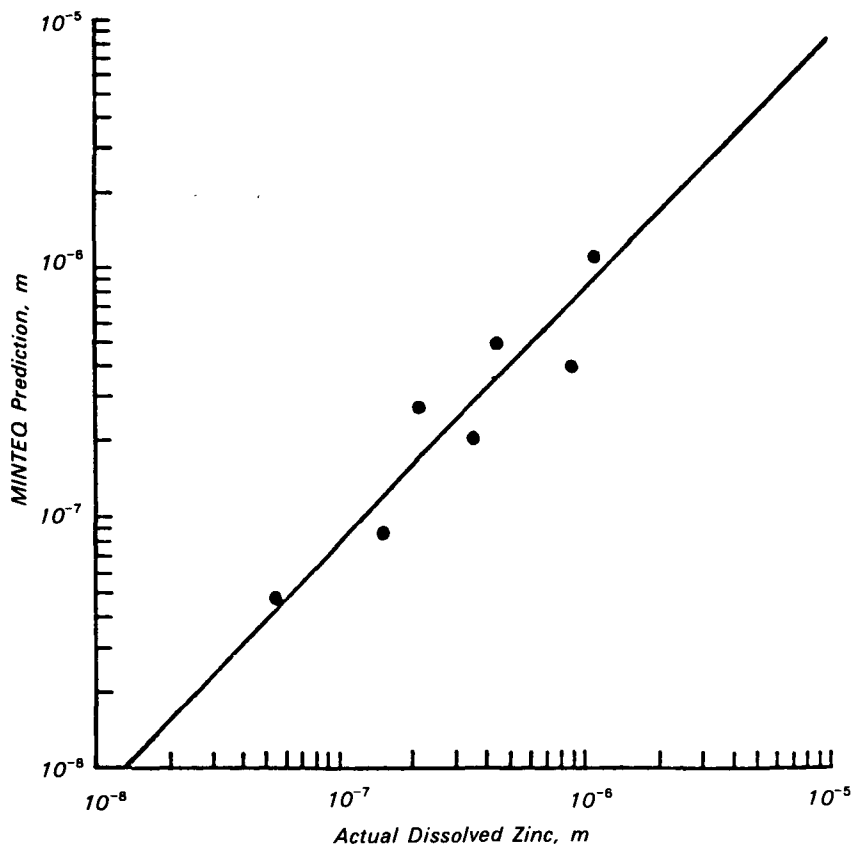


Figure 2. Actual dissolved zinc versus MINTEQ prediction.

organics were used even though the White River contains 5 to 7 mg/l of dissolved organic carbon (DOC, see Table 3). The curvilinear relation could result from omission of organic complexation, an effect that would be most pronounced at low (Cu^{+2}). Addition of EDTA simulates the effect of natural organic complexation on the (Cu^{+2}) calculation by MINTEQ.

The optimum fit (linear) was obtained with 55 $\mu g/l$ of EDTA ($10^{-6.66} M$). Using this organic level for two other experiments at pH = 6.7 and 8.3 gave linear plots indicating that this artificial specification of an organic complexing agent (EDTA) might be a reasonable substitute for actual complexing organics in the test water. The curvilinear nature observed in these experiments (without EDTA) is not due to lack of consideration of desorbed ions in the equilibrium solution. Under the conditions of the experiment (addition of > 1 mg/l of metal), background concentrations of Ca^{+2} , Mg^{+2} , Na^{+} , etc. would appear essentially unchanged in the White River matrix by release due to an ion exchange phenomenon.

The slope of the lines for pH = 6.7, 7.5 and 8.3 and estimates for ST from the

experiments allowed a determination of the Langmuir Constant, KL. The results (Table 4) indicate that the metal adsorption phenomena in the White River can be adequately described using kinetics based on the mass of solids, the dissolved (free) metal, the available sites and pH, and, that equilibrium metal experiments can be fit to an "activity" Langmuir Isotherm. The experiments at pH = 6.7 and 8.3 did not have sufficient data to permit precise estimates of ST and KL and the values in the table should be regarded as estimates. It is essential that continued development of methods for determining dissolved metal species be encouraged and that organic speciation of metals be considered in modeling systems highly transitory in flow and water quality, such as that observed in the White River.

Ten Mile River Case Study

This case study of MEXAMS involves application to a wasteload allocation program on the Ten Mile River in Massachusetts. This river receives metal wastes, treated municipal wastewater, and urban runoff at a number of points

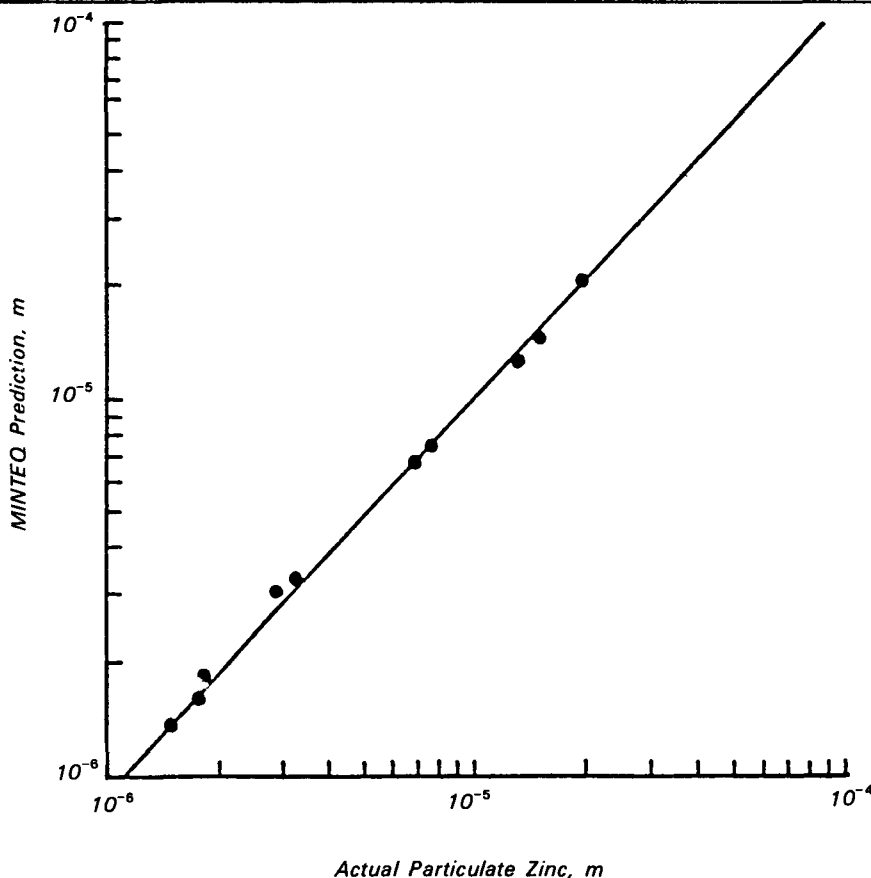


Figure 3. Actual particulate zinc versus MINTEQ prediction.

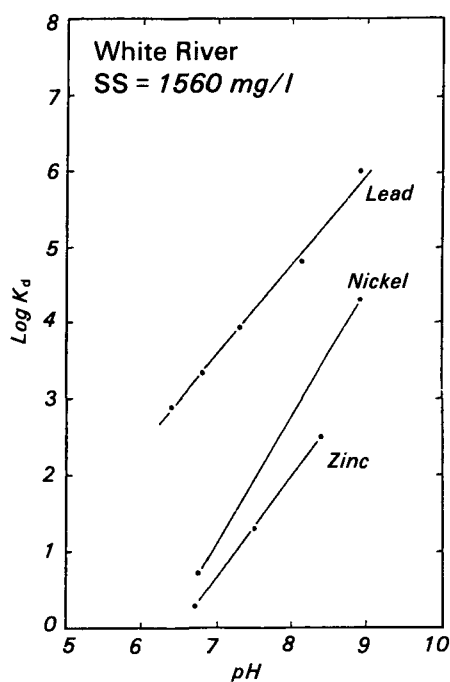


Figure 4. Log K_d s versus pH for Zn, Ni, and Pb.

River and tributary flow measurements at eight stations were available for several dates in the summer of 1984. Because heavy rainfall had occurred prior to the surveys, all flows were significantly higher than base flows for the basin. In addition, the flows were steadily decreasing during the surveys; consequently, they do not represent steady-state conditions. Channel depths and widths were measured at the flow stations. Additional data to characterize the channel geometry also were collected at several cross sections in the 1984 surveys. Impoundment dimensions (depth and surface area) were obtained from previous model estimates. Chemical concentrations and water quality parameters were measured at river monitoring stations and impoundments on several dates during the 1984 surveys. Table 5 lists the concentrations at various monitoring stations used in this application. Metal loadings data (concentrations and discharge rates) from industrial and municipal point sources represent averages of the data collected during separate surveys in July 1984.

Available data for this study contained problems that limited the scope of the application and the reliability of the model results. Primary among them is the lack of steady-state hydraulic conditions — a crucial requirement of MEXANS — which existed during the data collection surveys. Metal concentrations were imprecise due to the analytical methods. The flame atomic adsorption method provided an accuracy of 0.01 mg/l for most metals, which generally resulted in reported concentrations of one significant figure and many dissolved concentrations of 0. Calibration of MEXANS in Ten Mile River requires metal concentration measurements accurate to 0.001 mg/l. A related problem was the lack of metal adsorption data for Ten Mile River. MINTEQ adsorption models require precise measurements of dissolved and adsorbed concentrations using native water and sediments, as well as detailed chemical analyses of the samples. Major cationic species such as Ca^{2+} , Mg^{2+} , Na^+ , and K^+ , were not determined individually; consequently, ionic strength computations in MINTEQ were inaccurate. Conductivity measurements, from which ionic strength can be estimated, were available.

Copper speciation and adsorption was simulated in a 15-mile stretch of the river from the Fuller Pond outlet downstream to Ten Mile Reservation Pond. The EXAMS input was based on flow data of July 24, 1984. Segmentation of the river generally followed the gross channel morphology,

along its 22-mile length, and estimates of metal speciation within the river would be useful for determination of acceptable effluent limits to the basin.

In recent years, the question has been raised as to whether current inorganic industrial discharge limitations on Ten Mile River are adequate to attain or maintain acceptable water quality levels with regard to heavy metals. Also, the long history of metal waste discharges has resulted in extremely high concentrations of heavy metals in the sediments of impoundments along the river. These sediments now act as additional sources of metals to the river during high flow periods.

The basic data required to execute MEXANS for a system such as Ten Mile River are 1) detailed descriptions of the hydraulics, including flows and channel geometry; 2) dissolved and adsorbed concentrations of all major chemical species; and 3) loading rates of metals. The 1984 data that are described are preliminary; the data had not been completely analyzed and verified at the time this project was completed.

Table 3. Water Quality Data, White River

Selected Parameters	White River Surface Water Quality (11/1974-9/1976)														
	Baseflow					Lower Basin Runoff					Upper Basin Runoff				
	Mean	±	S. E.	Max	Min	Mean	±	S. E.	Max	Min	Mean	±	S. E.	Max	Min
Total Alkalinity (mgCaCO ₃ /l)	199	±	1.7	242	147	177	±	11.2	221	144	134	±	3.9	204	107
Dissolved Solids (mg/l)	526	±	5.7	717	449	588	±	8.8	676	513	293	±	13.7	536	212
Total Hardness (mg/l)	289	±	3.3	460	240	301	±	4.8	340	220	184	±	6.9	280	140
pH (units)	8.1	±	0.05	8.8	7.0	8.2	±	0.12	9.4	6.8	7.8	±	0.11	8.8	6.5
Conductance (μohms/cm)	813	±	12.7	1650	625	874	±	13.7	1010	700	473	±	23.3	810	320
Calcium (mg/l)	70	±	1.1	120	61	70	±	0.96	76	56	46	±	1.6	67	35
Magnesium (mg/l)	27	±	0.4	39	22	30	±	0.6	35	20	16	±	0.9	28	11
Sodium (mg/l)	71	±	1.9	180	34	82	±	1.9	110	65	32	±	2.5	75	17
Potassium (mg/l)	2.3	±	0.09	6.1	.9	2.3	±	0.28	4.0	2.0	1.7	±	0.07	3.0	1.3
Chloride (mg/l)	40	±	1.3	120	24	41	±	1.2	58	25	15.5	±	1.5	42	3
Sulfate (mg/l)	176	±	2.2	230	140	209	±	3.8	260	180	88	±	6.9	190	69
Sulfide (mg/l)	0.2	±		2.5	0	0.2	±		1.3	0	0.1	±		2	0
DOC (mg/l)	6.8	±	1.18	14.0	2.5	5.8	±	1.39	12	3.0	5.8	±	0.53	8.6	4.4
Orthophosphate (mgP/l)	.02	±	.01	.87	.00	.01	±	.002	.04	.00	.02	±	.004	.06	.00
Ammonia (mgN/l)	.03	±	.004	.19	.00	.05	±	.013	.29	.00	.02	±	.004	.04	.00
Nitrate (mgN/l)	12	±	.02	1.10	.00	.14	±	.029	.52	.00	.16	±	.02	.38	.01
Cu (μg/l)	6.0	±	3.08	160	0	41	±	18.8	340	2	4	±	1.2	60	1
2N (μg/l)	21	±	5.07	180	0	12	±	3.7	60	0	4	±	1.5	20	0
Cd (μg/l)	0			1	0	1			2	0	0			1	0
Cr (μg/l)	2			20	0	2			10	0	0			0	0
Pb (μg/l)	2			7	0	4			37	0	1			4	0
Ni (μg/l)	5			16	0	2			4	0	3			6	0
Fe (μg/l)	28	±	5.4	270	0	33	±	4.8	80	10	38	±	5.6	90	0
Ba (μg/l)	48	±	15.8	140	0	38	±	10.2	100	0	27	±	14.5	130	0
Al (μg/l)	17	±	2.2	80	0	30	±	5.7	90	0	30	±	4.4	80	0
Mn (μg/l)	4			20	0	9			30	0	2			10	0

Table 4. Summary of Adsorption Modeling In The White River-Langmuir Constants and Activity K_d For Copper Partitioning

SS, mg/l	pH	Activity Langmuir Model			Activity K _d
		K _L S _T	S _T , M/L	K _L , L/M	
220	6.70	14.3	—	—	—
220	7.50	243	3.3 E-05	7.36 E+06	—
220	8.30	6.090	—	—	—
1590	6.80	186	—	—	8.29
1590	7.46	800	—	—	575
1590	8.31	19.300	—	—	17.000
1590	8.95	136.000	—	—	933.000

Table 5. Water Quality Data, Ten Mile River

River Station	pH	Alkalinity	Hardness	Cl ₁	SO ₄ ²⁻	NO ₃ -N	NH ₃ -N	PO ₄ -P	SS
TM01	7.2	39.	100	17	6.0	2.2	0.06	0.03	1.5
TM02	6.8	27	71	21	3.9	2.6	0.05	0.03	6.5
TM03	6.9	26.	55.	22	3.3	1.3	0.07	0.24	12.
TM04	7.1	28	52	26.	3.4	1.8	0.29	0.61	5.0
TM05	7.1	23	42.	22	2.4	0.0	0.06	0.34	5.5
TM06	7.2	27.	44	21.	2.2	0.9	0.07	0.34	2.0
TM07	7.2	34.	50.	34.	3.0	4.4	0.12	1.2	4.5
TM07A	7.0	28.	39	31	2.2	2.2	0.16	0.61	5.5
TM08	7.1	29.	39	67	2.2	2.7	0.11	0.43	9.0
TM08A	7.2	32	42	35.	2.4	2.7	0.14	0.61	6.0
TM09	7.1	30	42.	35.	2.7	3.1	0.14	0.55	7.5
TM10	7.1	30	38.	32	2.4	2.7	0.12	0.61	6.0
TM11	7.2	30.	38	29.	2.7	2.2	0.08	0.49	10
TM12	7.1	29	36	27.	1.8	2.2	0.05	0.37	7.0
TM13	6.9	25.	38.	28.	2.2	2.2	0.08	0.40	3.5
TM14	7.3	33.	46	30	2.1	7.1	0.10	0.89	4.0

with impoundments and intervening channel sections forming the segments. Fifteen segments or 30 EXAMS compartments were delineated and divided into three sets of ten compartments, because MEXAMS is limited to ten compartments per run. A complete Ten Mile River simulation required three successive model runs, with simulated metal outflow from the downstream end of one run providing the input loading to the upstream end of the next run.

MINTEQ input was developed based on the water chemical survey data of July 2, 1984, and mean copper loadings from three July 1984 dates. Each EXAMS compartment requires an associated MINTEQ input set. Because many of the chemical constituent concentrations exhibited little spatial variation, all *channel* water column and benthic compartments in each ten-compartment section were assigned the same MINTEQ input file. Also, several ionic species were omitted from the final MINTEQ input, because they are unlikely to form complexes with metals or to affect the equilibrium calculation significantly. The species omitted were Cl⁻, NO₃⁻, PO₄³⁻, Na⁺, K⁺, and NH₄⁺.

The adsorption model selected was activity K_d. Extensive data requirements of other MINTEQ adsorption models

precluded their use in this study. The available data were inadequate for reliable application of the activity Kd model. Preliminary MINTEQ runs were performed to determine the activity Kd coefficients for copper under different conditions of water chemistry and sediment concentration. These Kd's were subsequently used in the MEXAMS simulation.

The activity Kd model is defined in terms of the activity of uncomplexed metal as opposed to the total dissolved metal concentration. This assumes that only free (uncomplexed) metal adsorbs. Thus, in order to obtain an activity Kd coefficient applicable to a specific water sample, one must have "measurements" of this activity. Analytical techniques measure the dissolved metal concentration, which includes uncomplexed metal plus aqueous complexes. To obtain the activity of the metal, preliminary MINTEQ runs were performed on the water analyses used in this application. The activity of uncomplexed metal computed by MINTEQ in these runs was combined with the corresponding measured concentration of adsorbed metal to obtain the activity Kd for each water sample. The activity of the uncomplexed metal is affected by the total ionic composition of the water as well as competition with complexes; consequently, a complete water analysis is necessary to develop the MINTEQ input.

MEXAMS was executed using the available input data. Calibration of MEXAMS was not performed in this study due largely to the non-steady-state conditions exhibited in the 1984 survey data and lack of critical adsorption and metal concentration data. It is instructive, however, to examine the results of the simulation to suggest further data collection and modeling efforts. In Table 6, simulated copper concentrations in all water column compartments and impoundment benthic compartments of the first ten-compartment section of Ten Mile River are compared with observed concentrations. As was noted previously, the MINTEQ input for channel benthic compartments was not differentiated from the overlying water column because channel sediments were not sampled, and impoundment sediments were judged to be more significant in transport/fate of metals.

The results show a definite over-prediction of both dissolved and total copper in the water column while the benthic results are slightly low. Since the river flow rates used in this study were higher than average, the likely cause of the discrepancies is either non-representative metal loading rates (i.e., higher than the

Table 6. Comparison of Predicted and Observed Copper Concentrations

Station		Observed		Compartment	Mexams	
		Dissolved (mg/l)	Total (mg/l)*		Dissolved (mg/l)	Total (mg/l)*
TM01		0.	0.47	1	0.15	0.47
Wetherells Pond	WC	0.	0.07	3	0.15	0.44
	B	—	1000.*	4	0.15	684.*
TM03, TM04		0.02	0.04	5	0.11	0.34
Falls Pond	WC	0.02	0.06	7	0.088	0.27
	B	—	850.*	8	0.088	418.*
TM06		0.02	0.02	9	0.075	0.23

WC - Water column

B - benthos

* Benthic total concentration units are mg/kg

historical average) or an incorrect model configuration such as not considering all transport processes from the water column to the benthic sediment. It is likely that this system could be calibrated by varying one or more processes so that more metal is present in the sediment (particularly the impoundments), and less in the water column. This would be done by further increasing benthic adsorption relative to the water column and/or increasing the dispersive transfer rates. The resulting calibration would be difficult to defend, however, given the uncertainties in hydraulics, metal loading, and observed metal concentrations.

The detailed MINTEQ speciation for the metal of interest (Cu) is shown in Table 7 for water column and benthic environments. As expected for a natural system of this type, sorption dominates copper fate, and uncomplexed copper probably represents a small fraction of the metal.

The factors that most affect metal fate in Ten Mile River are adsorption and transport within and through the impoundments, including settling of adsorbed metal during high flow. Insufficient knowledge of these factors as well as uncertainty regarding typical flow conditions, impoundment hydraulics, and metal concentrations limited the scope of this study.

Based on these conclusions, several recommendations would facilitate a

quantitative application. Data collection should be performed during low flow steady-state conditions, and all data should be collected concurrently when ever possible. Because of their importance, impoundments should be well characterized with regard to hydraulics including dimensions, flows, and estimated sediment trapping efficiencies. Metal concentration data should be accurate to at least 1 µg/l, and routine chemical analyses should include the following: H⁺, Na⁺, K⁺, Ca⁺², Mg⁺², SO₄⁻², Cl⁻, PO₄⁻³, NO₃⁻, NH₄⁺, alkalinity Eh, and suspended sediment.

A thorough equilibrium adsorption analysis should be performed for each metal, including precise metal determinations under varying conditions of sediment concentration and total metal to allow application of the Langmuir isotherm adsorption model. Composite sampling of metal discharges should be performed to limit the effect of variable flow and concentration. MEXAMS should be applied in a manner similar to that described here with a refined compartmental configuration and consideration of sediment settling.

Calibration of the system could be performed by varying settling rates, water-sediment dispersion, and adsorption coefficients to vary the water column-benthic interaction. Alternately, one could use a dynamic transport model that includes adsorption and sediment transport to characterize dissolved and particulate metal transport. Subsequent MINTEQ simulations would be performed to obtain more detailed information of metal speciation in selected critical reaches of Ten Mile River, such as near a large point source or in an impoundment.

Sediment Settling and Resuspension In MEXAMS

Sediment transport is likely to be important in the transport of highly adsorbed

Table 7. Typical Speciation of Copper In Ten Mile River

Species	Water Column %	Benthic %
Cu ⁺² (aq)	6	—
Cu-SOH	67	100
CuCO ₃ (aq)	12	—
Cu(OH) ₂ (aq)	13	—
CuHCO ₃ (aq)	2	—

and precipitated chemicals in rivers. The significant transport processes include advection and dispersion within the water column, deposition (settling), and scour (resuspension). In many rivers, net deposition over time can lead to effective burial of chemicals within the benthic sediments. EXAMS' steady-state hydraulic simulation does not explicitly consider the processes of sediment settling and resuspension. Currently, river sediment washloads are represented in EXAMS by advective and dispersive sediment transport between water column compartments. Also, bedload transport is represented by flows between benthic compartments which are horizontally adjacent. However, net sedimentation and resulting burial of chemicals must be represented by an artificial first-order degradation rate of the chemical in the benthic sediments.

A simple settling/resuspension algorithm was added to MEXAMS to improve the model's steady-state sediment transport capabilities. This algorithm allows the user to specify steady-state, vertical settling from the water column to benthic compartments and corresponding resuspension. Net deposition of sediment to the benthic compartment is considered; however, net erosion is not permitted. This section in the report documents the incorporation of these new capabilities in MEXAMS including computations added to the code, input, output, and limitations.

Allen J. Medine is with Ecosystem Research Institute, Logan, UT 84321; and Brian R. Bicknell is with AQUA TERRA Consultants, Mountain View, CA 94043.

Lee A. Mulkey is the EPA Project Officer (see below).

The complete report, entitled "Case Studies and Model Testing of the Metals Exposure Analysis Modeling System (MEXAMS)," (Order No. PB 87-141 081/AS; Cost: \$24.95, subject to change) will be available only from:

National Technical Information Service

5285 Port Royal Road

Springfield, VA 22161

Telephone: 703-487-4650

The EPA Project Officer can be contacted at:

Environmental Research Laboratory

U.S. Environmental Protection Agency

Athens, GA 30613

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Project Summary

Modeling the Benthos-Water Column Exchange of Hydrophobic Chemicals

P. M. Gschwend, S-C. Wu, O. S. Madsen, J. L. Wilkin, R. B. Ambrose, Jr.,
and S. C. McCutcheon

An analysis and modeling framework was developed to simulate and predict the transfer of hydrophobic organic chemicals between bed sediments and overlying waters. This approach entails coupling a description of the microscopic scale process of sorption kinetics with models of the exposure of bed particles to adjacent waters of varying composition (i.e., due to diffusion of solutes in interstitial fluids or pore water advection, due to biological mixing of surficial sediments, due to suspension of bed solids for a period into the overlying water column.) Numerical simulation routines are developed both for sorption kinetics and to demonstrate coupling of this particle-water exchange to particle movements in the case of a biologically mixed bed. These routines were used to assess the sensitivity of sorption kinetics and the overall transport to chemical and sediment properties. Similar computer programs can be used as subroutines in global chemical fate models. Also a formulation of bed-load transport and of sediment resuspension was developed which yields the contact time of bed particles with the overlying water column. This model result is then combined with the sorption kinetics subroutine to estimate bed-water exchange in instances where these processes greatly facilitate bed particle-water column contact.

This Project Summary was developed by EPA's Environmental Research Laboratory, Athens, GA, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Several models have been recently devised to describe the fate and transport of pollutants in bodies of water. However, these models are based on incomplete descriptions of the processes that control the exchange of chemicals between the bed and water column. In the current project, the authors describe the important processes and develop mathematical descriptions that should be useful in updating existing models and devising new models. In addition, the final project report will be a useful reference in describing the conceptual framework and relationships between direct sorption or desorption, diffusion, advection; bioturbation and sediment transport.

Figure 1 gives the conceptual framework for describing the benthic exchange processes. For the purpose of this study, the aquatic environment was envisioned as consisting of a water column, an active, moving bed load transport layer and an immobile bed where sediment is stored. The definition of the active bed layer is taken to be two grain diameters in thickness for sediment transport, and about 5 to 20 cm thick for bioturbation; however these definitions are arbitrary because thickness is difficult to forecast. The depth of the immobile layer is to be governed by burial, compaction, and erosion processes. The water column may be described with more than one layer if significant chemical gradients exist and are necessary to describe benthic exchange.

Figure 1 also ranks the processes in terms of process energy requirements and expected contact time between bed particles and the dissolved phase of a

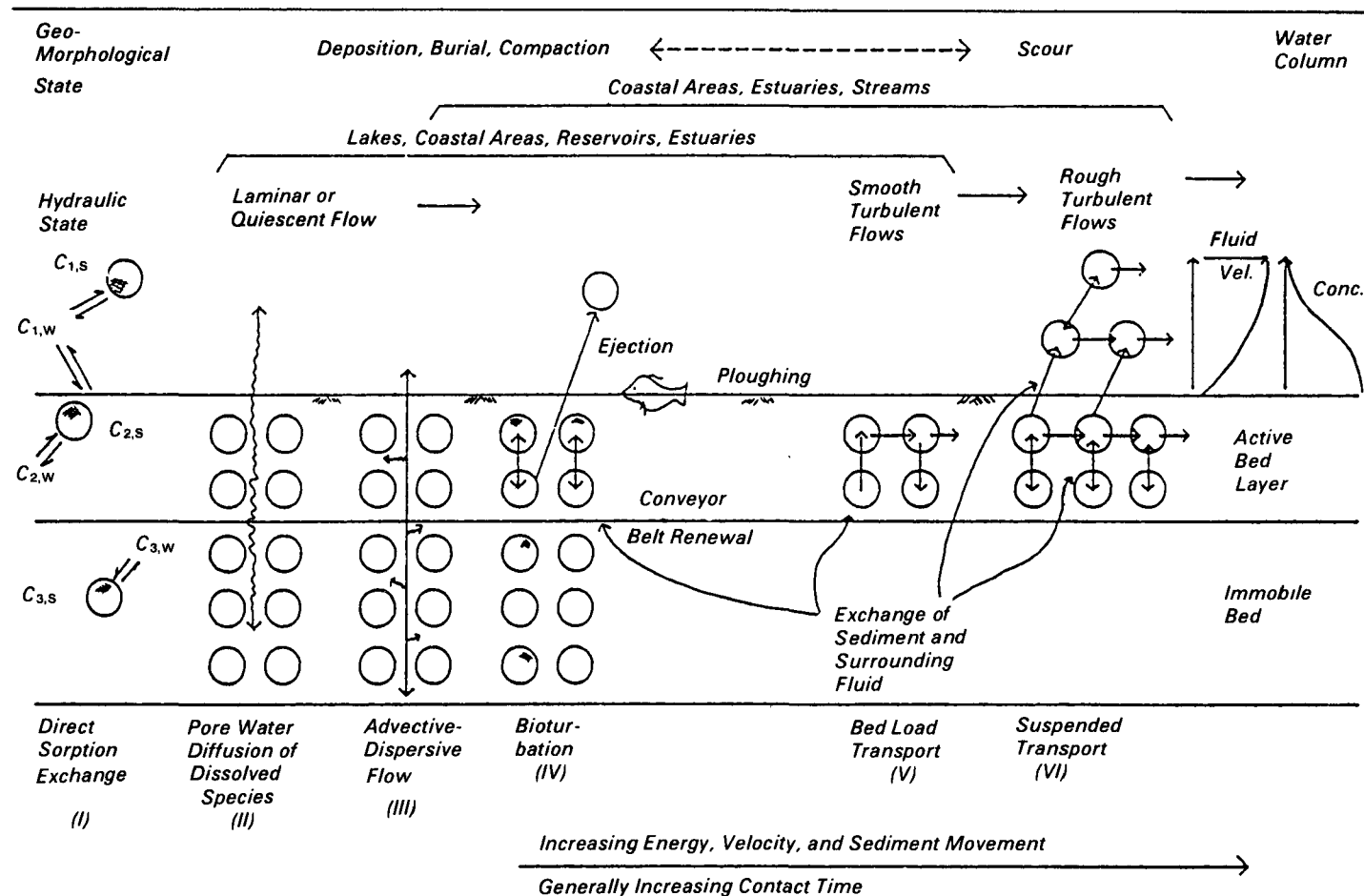


Figure 1. Processes involved in bed-water column exchange

chemical in the water column. Direct sorption is expected to be the least energetic and slowest exchange process, whereas sediment transport is expected to be the most energetic and, to involve some of the largest fluxes of material. However, the limiting process may involve the slowest, least energetic process.

Although this work significantly improves our understanding and modeling capability for bed-water pollutant exchange, several other important issues remain incompletely developed. For example, the inclusion of colloids and their impact on transport. We do not understand the sources and sinks of these nonsettling sorbents, particularly in sediment beds, and our knowledge of their mobility in porous media and ability to bind pollutants is limited. Additionally, the importance of bioturbation and other sediment modifying activities of benthic organisms to bed load transport and resuspension is uncertain. Finally, suspension of sediment particles from cohe-

sive beds remains poorly understood, and therefore modeling of bed-water column exchange for pollutants where cohesive sediment is involved is limited to diffusion and bioturbation-controlled situations.

Sorption Kinetics

The formulation for sorption kinetics is a physically based description of the microscale processes encompassing diffusion of nonpolar hydrophobic chemicals into the pore space of natural aggregate particles coupled with local partition equilibrium as illustrated in Figure 2. The research conducted during this study indicates that many natural particles of importance to the sorption process can be described as porous spheres having an intraparticle porosity of about 0.13. Based on this conceptual model the sorption kinetics can be described as

$$\frac{\partial C_{sw}(r)}{\partial t} = D_{eff} \left[\frac{\partial^2 C_{sw}(r)}{\partial r^2} + \frac{2}{r} \frac{\partial C_{sw}(r)}{\partial r} \right] \quad (1)$$

where $C_{sw}(r)$ = total concentration of sorbate (chemical) at a radial distance r from the center of a particle and

$$D_{eff} = \frac{D_m n^{n+1}}{(1-n) \rho_s K_p + n} \quad (2)$$

in which D_m = molecular diffusivity that can be determined by the method of Hayduk and Laudie, n = intraparticle porosity of about 0.13, ρ_s = specific gravity of the particles, and K_p = partition coefficient that can be predicted from the normalized octanol-water partition coefficient, K_{ow} , and the fraction of organic carbon contained in the natural particles. Thus equation 2 provides a physically based method for predicting sorption and desorption.

The flux of material from a layer of particles on the surface of the bed can be determined from the description of the fraction that is sorbed or desorbed at the end of the residence time, t_r . The fraction

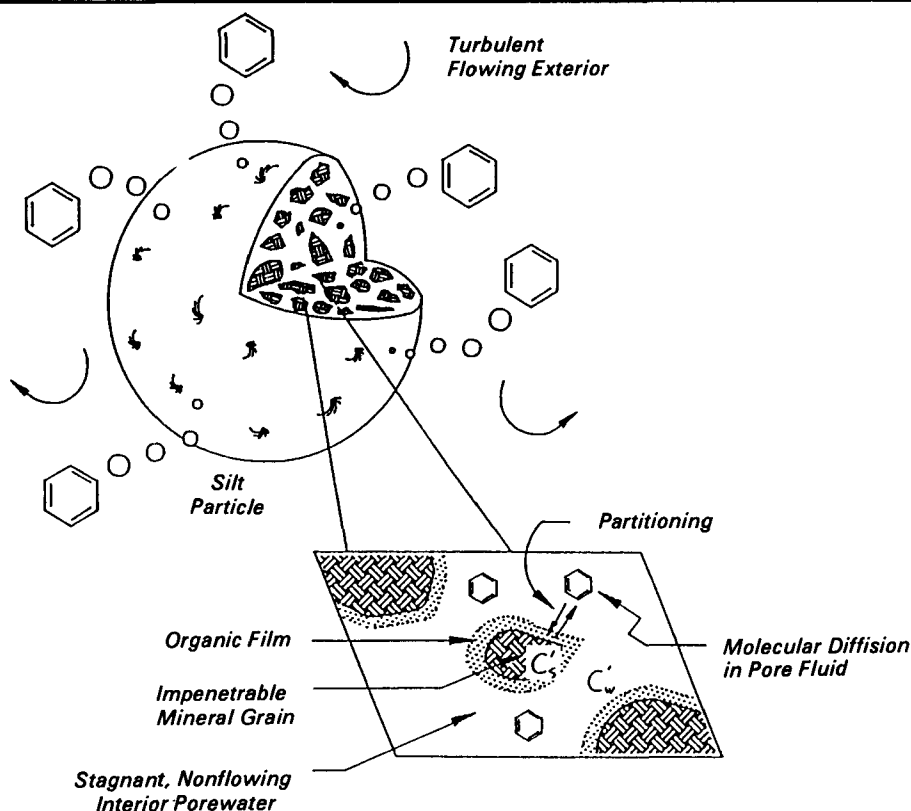


Figure 2. Physical picture of processes controlling sorption kinetics.

sorbed or desorbed from or to an infinite volume of water is given by:

$$\frac{M_t}{M_\infty} = 1 - \frac{(6/\pi) \sum_{m=1}^{\infty} \{(1/m^2) \exp(-D_{\text{eff}} m^2 (\pi)^2 t_r / R^2)\}}{(3)} \quad (3)$$

where M_t = mass sorbed to the layer of surficial bed particles over time t_r , M_∞ = mass attached to surficial bed particles after infinite time, m = the number of particle sizes the sediment is arbitrarily divided into, D_{eff} = effective intraparticle diffusivity that is essentially molecular diffusivity retarded by sorption, and R = particle radius. The residence time, t_r , for sediment particles can be determined from descriptions of bioturbation and sediment transport. Equation 3 for infinite water bodies is expected to be accurate for many streams, lakes, and estuaries where water volumes are large compared to the volume of surficial sediments. In cases where this may not be true, a numerical solution is derived to compute

M_t/M_∞ and this solution is incorporated in a basic program included in the final report.

Diffusion and Advection

The diffusive and advective flux of dissolved and colloidal material is described by

$$\begin{aligned} \text{Flux} = & - (n_2)^{i+1} D_m \frac{\partial C_w}{\partial z} - (n_2)^{i+1} \\ & D_c \frac{\partial S_c C_c}{\partial z} = w_2 C_w = w_2 S_c C_c \end{aligned} \quad (4)$$

where n_2 = porosity of the bed, i = an empirical factor dependent upon n_2 and determined by the formation factor that describes the effect of tortuosity on molecular diffusion, D_m = molecular diffusivity, D_c = diffusivity of colloidal material, S_c = concentration of colloidal and nonsettling material, and w_2 = pore water velocity in the bed. Here it is assumed that the size of the pores is large compared to the colloidal material.

Bioturbation

In the case of bioturbation, mixing by benthic organisms is described using an eddy viscosity scheme. This results in a flux expression of the form

$$\text{Flux} = - E_b \frac{\partial C}{\partial z} = w_b C = \int_0^z f(z) C dz \quad (5)$$

where E_b = mixing coefficient, C = total concentration of chemical in the dissolved, colloidal-bound, and sediment-sorbed phases, w_b = vertical sediment velocity induced by biological mixing, and $f(z)$ = feeding activity due to ingestion of particles.

For plow-like bioturbation involving mixing at the surface, Equation 5 can be applied by noting that w_b and $f(z)$ are zero. Table 1 gives the known values of E_b and the depth of the mixed layer for several species of benthic animals. The widespread application of the method will require determination of E_b and mixing depth for all species of interest. Alternatively, the rate of benthic mixing is related to individual reworking rates, r' , depth of mixed layer, L , population density, and bulk density of the sediments, ρ_b via

$$E_b = L r' (\text{population}) / \rho_b \quad (6)$$

Table 2 gives estimates of individual reworking rates and mixing depths for benthic ploughers and conveyor-type species. Figures 3, 4, and 5 show the sensitivity of the computed flux to particle diameter, particle porosity, and phase partitioning. The values on which these calculations are based are given in Section 3.3.2.3 of the final report.

Conveyor-belt bioturbation involves worms that ingest sediment at some depth z into the bed and egest the reworked sediment at the bed surface. The worms ingest the sediment for the organic carbon contained in the sediments and in the process rework the sediment into pellets or trails of inorganic sediment bound by mucous. The reworking rate is

$$w'_b = (r' / \rho_b) \text{ population} \quad (7)$$

Figure 6 shows the sensitivity of the flux to pellet diameter and the partitioning coefficient. See Section 3.3.2.4 for more details.

Sediment Transport

The description of sediment transport is based on a physical framework for cohesionless particles where the resistance to movement derives from the

Table 1. Biogenic Mixing Coefficients. (Source: review by Lee and Swartz)

Location	Species	L(cm)	$E_b(\text{cm}^2/\text{sec})$	Method
Deep Sea, various sites	?	10-48	3.6×10^{-11} - 3.16×10^{-8}	Dimensional analysis
Mid-Atlantic Ridge	?	8	6×10^{-9}	^{210}Pb pattern
Long Island Sound	<i>Yoldia</i> , <i>Nucula</i>	4	1.2 - 3.5×10^{-6}	^{234}Th pattern
Chesapeake Bay	?	10-15	1×10^{-6}	Dimensional analysis?
New York Bight	?	?	5×10^{-7}	^{234}Th pattern
Rhode Island				
0-1 cm	<i>Leptosynapta</i> , <i>Scoloplos</i>	1	2.9×10^{-6} - 1.6×10^{-5}	Dimensional analysis ^a
2-10 cm		8	8.3×10^{-7} - 4.3×10^{-6}	Dimensional analysis ^a
La Jolla, California	<i>Euzonous mucronata</i> (=Thoracophelia)	30	1.5×10^{-5}	Dimensional analysis ^b
Barnstable Harbor,	<i>Pectinaria gouldii</i>	6	7.6×10^{-8}	Dimensional analysis ^b
Long Island Sound	<i>Yoldia limatula</i>	2	3.2×10^{-7}	Dimensional analysis ^b
Long Island Sound	<i>Yoldia limatula</i>	3	2×10^{-6}	Dimensional analysis ^c
Laboratory	<i>Yoldia limatula</i>	3	1×10^{-5}	Pore water profiles
Laboratory	<i>Clymenella torquata</i>	11	2 - 3×10^{-4}	Pore water profiles ^d
Laboratory	<i>Clymenella torquata</i>	11	4.5×10^{-5}	Pore water profiles ^e
Laboratory	<i>Molpadia oolitica</i>	7-9	5.7 - 9.4×10^{-5}	Depth of oxidized layer ^f

^a Calculated from data.^b Calculated by Guinasso and Schink (1975).^c Calculated by Aller (1978).^d Vertical diffusion coefficient.^e Horizontal diffusion coefficient.**Table 2.** Individual Particle Reworking Rates, Annual Reworking Rates, and Depth of Reworking. (Source: review by Lee and Swartz)

Species	Guild	Individual Reworking Rate (mg/ind./day)	Total Reworking Rate (g/m ² /yr)	Depth of Reworking	Comments	Source
Annelids						
<i>Abarenicola claparedi</i>	FUN	3,600	—	—	Average high and low tide, 1-3.5 g/ind.	O ^a
<i>Abarenicola pacifica</i>	FUN	10,900	—	—	Average high and low tide, 1-3.5 g/ind.	O
<i>Abarenicola pacifica</i>	FUN	0-4,500	—	—	0.7 g/ind., 9°C	O
		0-15,000	—	—	2 g/ind., 9°C	O
		—	310 kg	≤15 cm	Site 3, mean 3 samplings	O ^b
<i>Amphitrite ornata</i>	SISDF	5,100	—	Surface	∞ 17°C	O
<i>Amphitrite ornata</i>	SISDF	2,600-5,200	—	Surface	22°C	O
<i>Arenicola marina</i>	FUN	4,700	—	—	Average of field measurements	O
<i>Clymenella torquata</i>	CB	900	54,000	20 cm	11°C	O
<i>Clymenella torquata</i>	CB	1,650	73,000	20 cm	Beaufort, North Carolina	O
					Annual rate adjusted for T'	
<i>Euzonous</i> (=Thoracophelia) <i>mucronata</i>	MISSDF-V	230	—	—		O
<i>Melinna palmata</i>	SISDF	290	—	Surface	Cephalic plate width 2-8 mm, all sediment	P ^c
<i>Pectinaria californiensis</i>	CB	0.5-330	8,600	5 cm	Cephalic plate width 2-8 mm, all sediment	O
<i>Pectinaria gouldii</i>	CB	6,000	6,000	6 cm	All sediment, annual rate adjusted for T'	O
<i>Pectinaria gouldii</i>	CB	2,000	—	—	Just feces	O
<i>Polycirrus eximius</i>	SISDF	7	0-173	Surface	Just feces, April-October	C
<i>Tharyx acutus</i>	MISDF-V	7	0-1,300	Surface	Just feces, April-October	C
<i>Scoloplos robustus</i>	MISSDF-V	99	1,200-11,000	2-13 cm	Ingestion, April-October	C
		510	6,200-56,000		Burrowing, April-October	
Freshwater oligochaetes, CB, 3 species	MISSDF-V	1-250	18-230 kg	4-6 cm	Just feces, annual rate adjusted for T'	O
Bivalves						
<i>Macoma balthica</i>	MISDF-V	1.7	420	Surface	Just feces, 10°C, annual rate not adjusted for T'	O
		370	90,500		Feces and pseudofeces, 10°C	O
<i>Macoma balthica</i>	MISDF-V	520	—	Surface	Feces and pseudofeces, 15°C	O
<i>Macoma nasuta</i>	MISDF-V	15-550	—	1 mm	Just feces, 10-50 mm/ind.	O
		7,300			Feces and pseudofeces, 48 mm/ind.	
<i>Scrobicularia plana</i>	MISDF-V	14,400	—	Surface	Feces and pseudofeces	P
<i>Scrobicularia plana</i>	MISDF-V	3.9-90	—	Surface	Just feces	H ^d
<i>Yoldia limulata</i>	MISSDF-V	280	2,300	2 cm	Feces and pseudofeces	O
Gastropods						
<i>Hydrobia minuta</i>	MESDF	1	26-8,900	2 mm	Annual rate not adjusted for T'	O
<i>Hydrobia ventrosa</i>	MESDF	1	0-12,000	2 mm	Annual rate not adjusted for T'C	O
<i>Littorina irrorata</i>	MESDF	0.4	100	Surface	Just feces, recalculated from data	C
Crustaceans						
<i>Callinassa californiensis</i>	MISSDF-E	33,000-82,500	—	<76 cm	Amount deposited per entrance, Excavation and feeding?	C

Table 2. (continued)

Species	Guild	Individual Reworking Rate (mg/ind/day)	Total Reworking Rate (g/m ² /yr)	Depth of Reworking	Comments	Source
<i>Callinassa major</i>	MISSDF-E	3,500	12.6-630 kg	—	Amount deposited per entrance, just feces	O
6 species				to <10 cm		
<i>Paraphoxus spinosus</i>	MISDF-V	8,910	54-2,200 kg	0-1 cm	Burrowing	C
<i>Uca pugillator</i>	MISDF-E	96	230	—	Just feces, recalculated from data	C
<i>Uca pugnax</i>	MISDF-E	75	820	—	Just feces, recalculated from data	C
Echinoderms						
<i>Caudina chilenses</i>	CB	160,000	—	—		P
<i>Echinocadrium cordatum</i>	MSSDF-V	3,000	—	—		P
<i>Holothuria</i> spp.	MESDF	25,000-220,000	—	—		P
7 species						
<i>Leptosynapta tenuis</i>	FUN	10,400-18,400	—	0.5-10 cm	Feces and below surface reworking	O
<i>Leptosynapta tenuis</i>	FUN	34,000	590-3,000 kg	1.15 cm	Feces and below surface reworking	C
<i>Scotoplanes</i> sp.	MESDF	100,000	—	1 mm	Feces	O
<i>Stichopus moebii</i>	MESDF	38,000	—	—		P
<i>Stichopus variegatus</i>	MESDF	49,000	—	—		P
Enteropneust						
<i>Balanoglossus gigas</i>	FUN	200,000-250,000	—	—		P

^aO = original data ^bC = calculated from data ^cP = calculated by Power (1977) ^dH = calculated by Hargrave (1972)

NOTE: Guilds CB, FUN, SISDF, MISDF-V, MISSDF-E are primarily tube, funnel, or deep burrow forming species whereas MISSDF-V, MESDF and MIFF are primarily surface ploughing or mixing species.

weight of the individual particles rather than through interparticle bonds. Thus this component of the description is limited to silty sediment and coarser sizes. Furthermore the formulation is limited to particles of a uniform size, and following the work of Einstein, assumes that several discrete size classes can be separately described. This ignores the effect of large sizes on the critical shear stress of the small particles and vice versa. Finally, the conceptualization assumes that the transport system is instantaneously in equilibrium between the suspended, bed, and immobile-bed loads illustrated in Figure 7.

Based on this conceptual model, the distribution of sediment mass at equilibrium between the suspended, bed, and immobile compartments is given by

$$m_{3\infty} = \frac{p_{23}}{p_{23} + p_{32} + p_{21} p_{32}/p_{12}} M \quad (8)$$

$$m_{2\infty} = \frac{p_{32}}{p_{23} + p_{32} + p_{21} p_{32}/p_{12}} M \quad (9)$$

$$m_{1\infty} = \frac{p_{21} p_{32}/p_{12}}{p_{23} + p_{32} + p_{21} p_{32}/p_{12}} M \quad (10)$$

where M is the total mass in the three compartments and p_{nm} are exchange coefficients for sediment between layers n and m.

The mean downstream velocity for the sediment mass is given as

$$M\bar{U} = m_{1\infty} U_1 + m_{2\infty} U_2 \quad (11)$$

where U_1 is the velocity of the suspended sediment mass and U_2 is the velocity of the sediment mass in the bed-load layer. From the average velocity of the sediment mass, it is possible to compute the exposure time of the sediment particles to the water column over reaches of given length as $t_r = \text{length}/U$.

The time of exposure or residence time is coupled with the sorption kinetics model given in Equation 3 to describe the transfer of a contaminant to or from the sediment moving in the stream. The solution of Equations 8 through 10 in the downstream direction describes distribution of contaminated sediment. The final report illustrates the solution of these equations in examples for a river and deep river or reservoir.

Summary and Recommendations for Future Research

To estimate bed-water exchange of hydrophobic organic pollutants, a two-step modeling approach or description is recommended. First, particle-water exchange on the microscopic scale must be quantified; this can be done using the retarded radial diffusion model, which treats each case as a function of compound solution diffusivity and hydrophobicity and sediment particle size and organic content. Section 2 of the final report describes a numerical simulation routine to handle such solid-water exchange of chemicals even in cases where there is a spectrum of particle sizes involved and the solution concentrations

vary in time. Second, this particle-water exchange kinetics description must be coupled with descriptions of the relative translations of sediment particles and the adjacent fluids (i.e., due to porewater advection, bioturbation, bed-load transport, or particle resuspension). This produces a prediction of the overall exchange of chemicals between the bed and the water column. Section 3 of the final report demonstrates the coupling of particle-water pollutant exchange in biologically mixed beds. Section 4 develops a quantitative description of the exposure of a moving bed particle to the overlying water column and then couples this transport to sorption kinetics. In any case of interest, decisions concerning the intensity of various processes facilitating bed particle-water column contact are necessary before good predictions of pollutant transfer can be expected.

Several areas of future research are suggested to improve and extend these analytical methods:

(1) The sources and fates of colloidal materials in sediments needs to be examined. Additionally, the sorbent properties of these macromolecules or microparticles should be assessed. These sorbents may be particularly important in transporting very hydrophobic pollutants from beds that are not biologically mixed.

(2) The nature of bed particle and pore water movements under the influence of benthic infauna should be explored further. Pore water pumping (or irrigation) was neglected here for want of a general

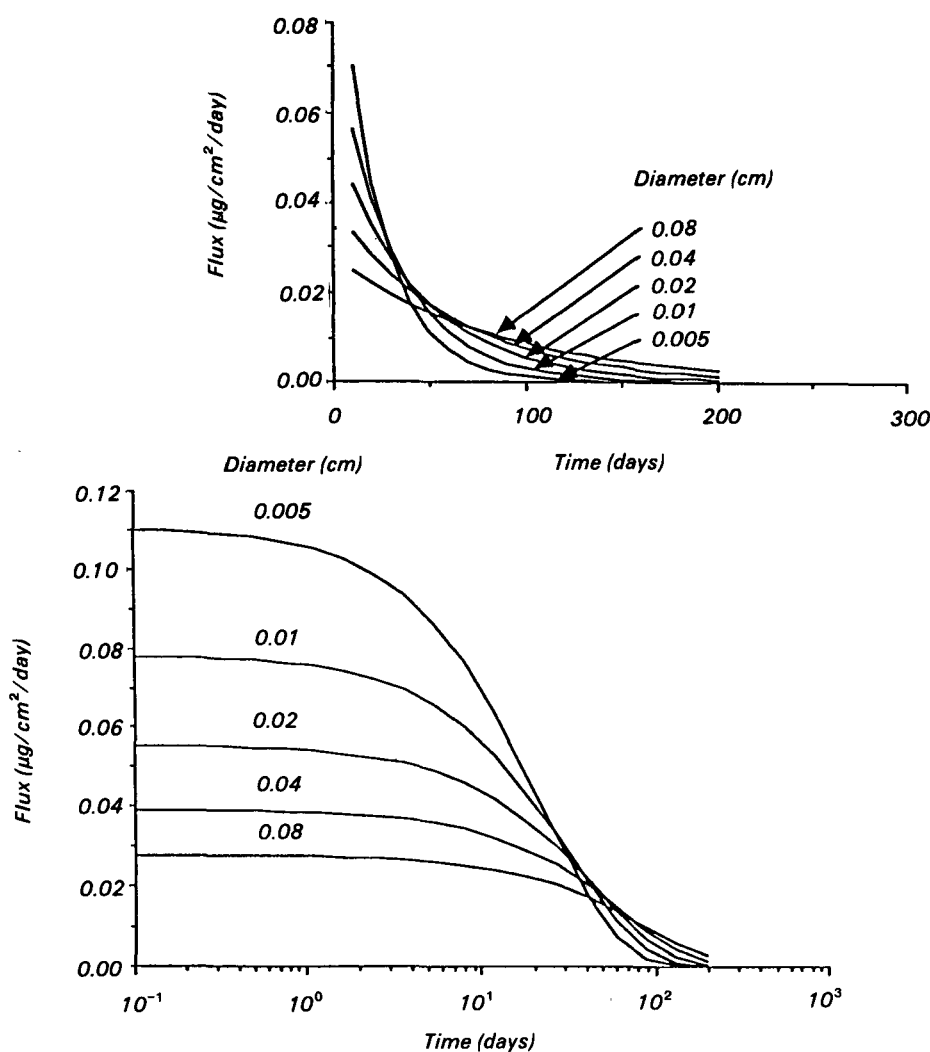


Figure 3. Sensitivity of the plow-like bioturbation mediated pollutant flux to 5 different sediment particle sizes. The values of other parameters are same as those in the example problem in Section 3.3.2.3 of final report.

quantitative description of this process as a function of organisms involved. Also, approaches for estimating parameters and better quantifying the mixing activities of benthic infauna from field measurements are needed.

(3) The development of a basic understanding for the factors and processes governing cohesive sediment resuspension and transport is also necessary. These cohesive organic-rich muds are the predominant sites for collection of many pollutants discharged to natural waters, yet our ability to quantitatively describe the movements of particles in these beds remains poor.

(4) In the sediment transport models formulated here, steady flow conditions were assumed. The impact of unsteady (e.g., tides in estuaries), and even catastrophic (e.g., storms) phenomena to the modeling of sediment transport still remains an important area to be examined.

(5) Further assessment of the conceptualization of the microscopic scale particle-water exchange of chemicals from particles in beds to the surrounding pore waters should be done. The retarded radial diffusion model has been tested primarily for aggregate particles in suspension. Issues such as the appropriate

diffusion length scales and intra-aggregate porosity for solids as they exist in a bed should be researched further. Also, to extend this approach to other contaminants such as trace metals and polar organic compounds, the mechanisms controlling their sorption kinetics interactions with sediment particles should be examined.

(6) Finally, efforts should be made to test the accuracy of model predictions against real world situations. Currently, there is a dearth of field data for comparison with model predictions. Thus, bed-water fluxes must be measured at times and places where the prevailing bed mixing processes are known and ancillary data are obtained to estimate their intensity.

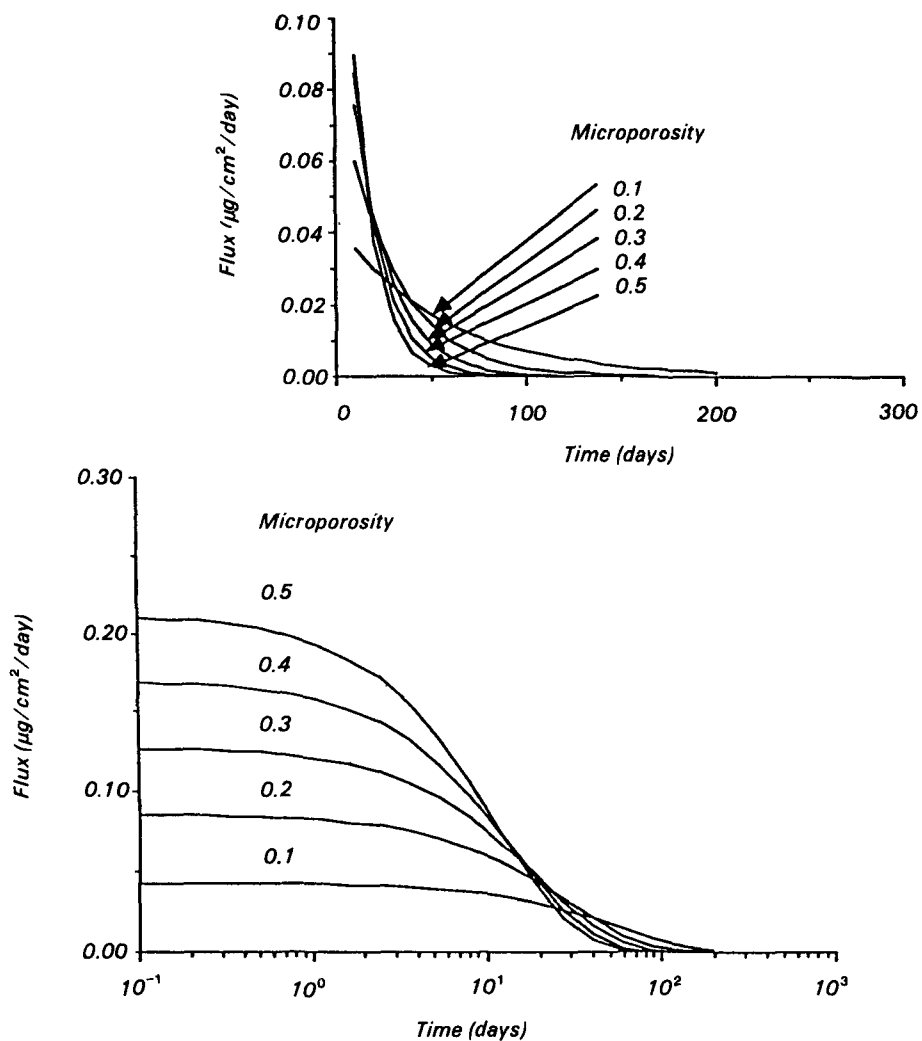


Figure 4. Sensitivity of the plow-like bioturbation mediated pollutant to 5 different sediment intraparticle porosities. The values of other parameters are same as those in the example problem in Section 3.3.2.3 of final report.

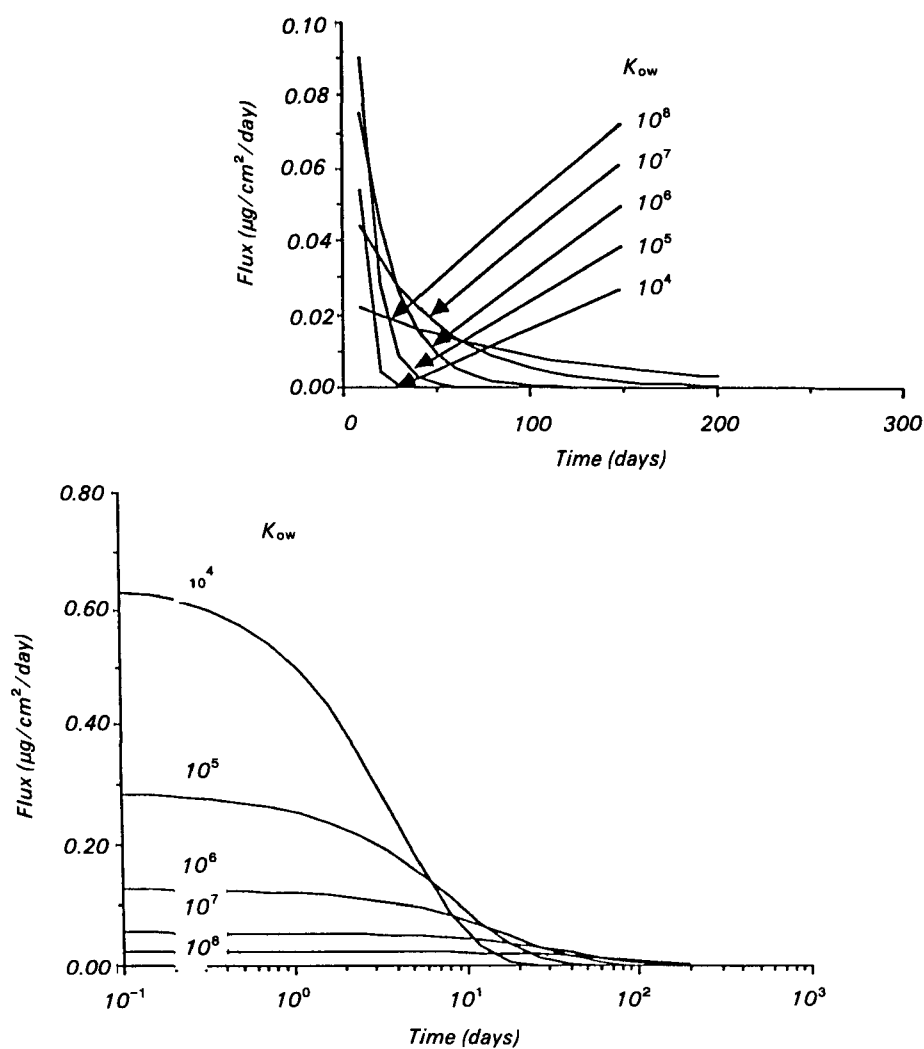


Figure 5. Sensitivity of the plow-like bioturbation mediated pollutant to chemical partitioning. The values of other parameters are same as those in the example problem in Section 3.3.2.3 of final report.

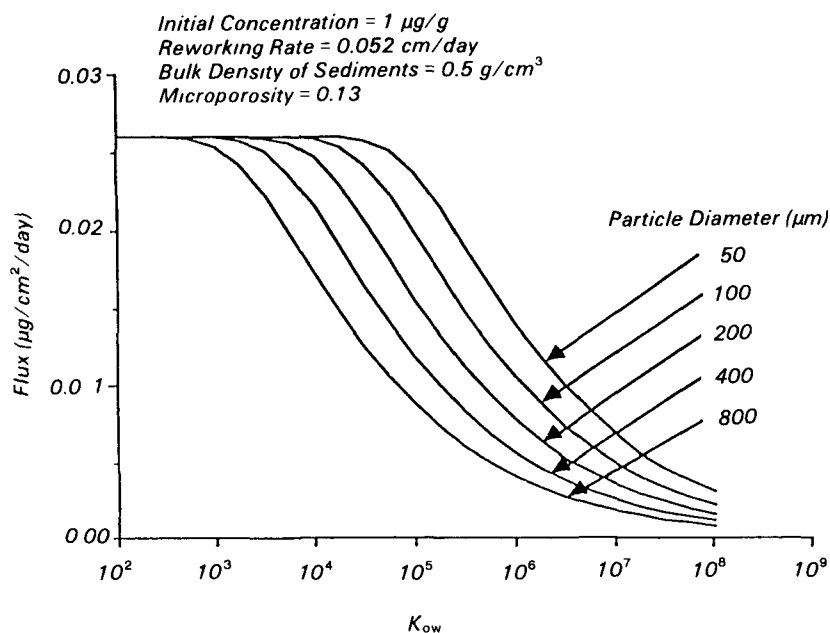


Figure 6. Sensitivity of conveyor-belt type bioturbation mediated flux to K_{ow} and pellet size. The values of other parameters are same as those in the example given in Section 3.3.2.4 of final report.

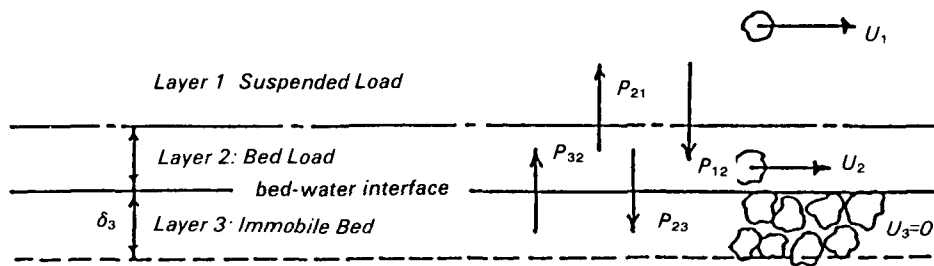


Figure 7. Definition sketch: three-layer transport model.

P. M. Gschwend, S-C. Wu, O. S. Madsen, and J. L. Wilken are with the Massachusetts Institute of Technology, Cambridge, MA 02139; the EPA authors R. B. Ambrose, Jr., and S. C. McCutcheon (also the EPA Project Officer, see below) are with the Environmental Research Laboratory, Athens, GA 30613.

The complete report, entitled "Modeling the Benthos-Water Column Exchange of Hydrophobic Chemicals," (Order No. PB 87-145 389/AS; Cost: \$24.95, subject to change) will be available only from:

National Technical Information Service
 5285 Port Royal Road
 Springfield, VA 22161
 Telephone: 703-487-4650

The EPA Project Officer can be contacted at:
 Environmental Research Laboratory
 U.S. Environmental Protection Agency
 Athens, GA 30613

Agency

Cincinnati OH 45268

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