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Project Summary

Modeling the Benthos-Water Column Exchange of Hydrophobic Chemicals

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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 bedload 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 columnμ 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

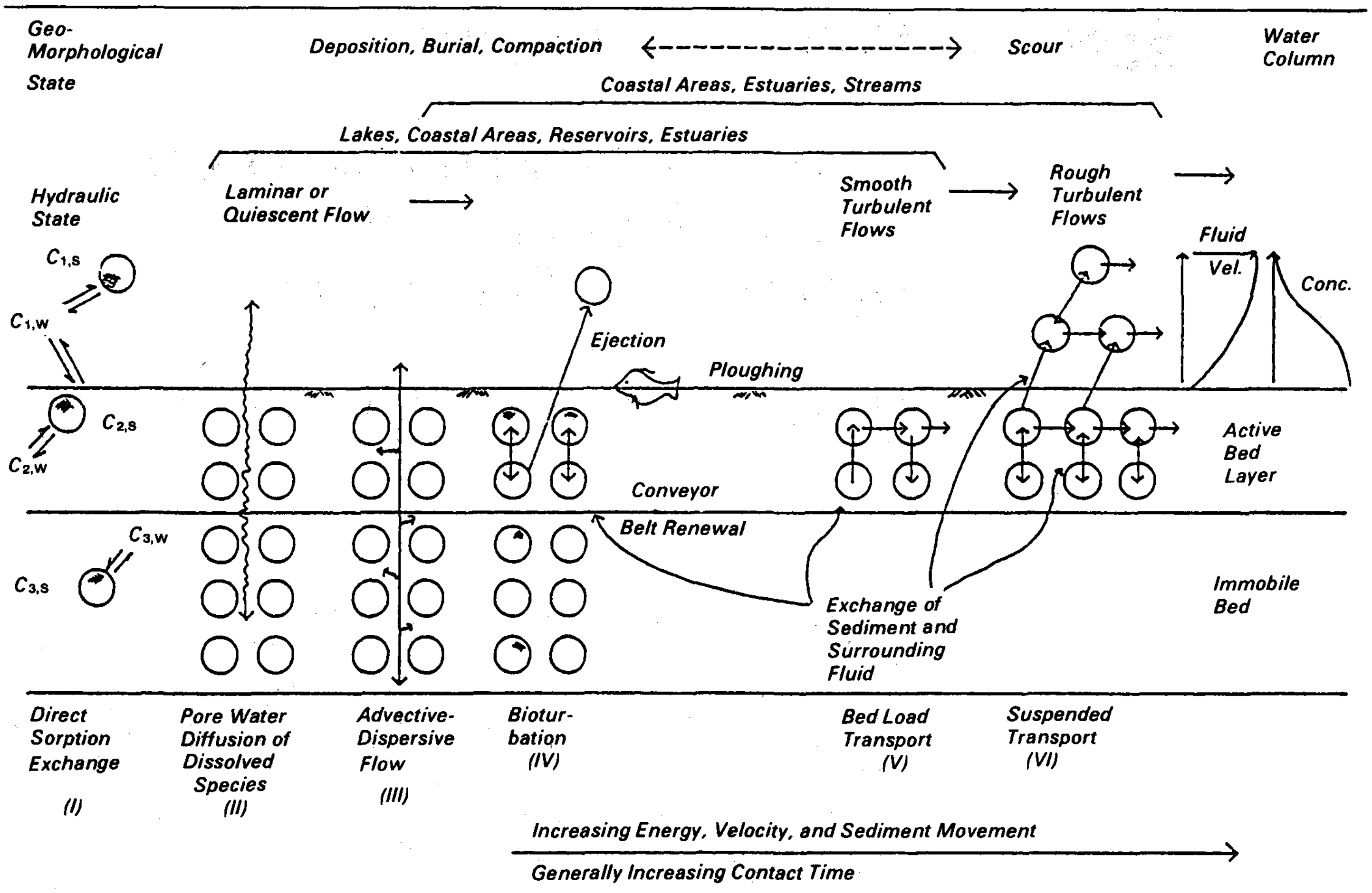

Figure 1. *Processes involved in bed-water column exchange.*

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 cohesive 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

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

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

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

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

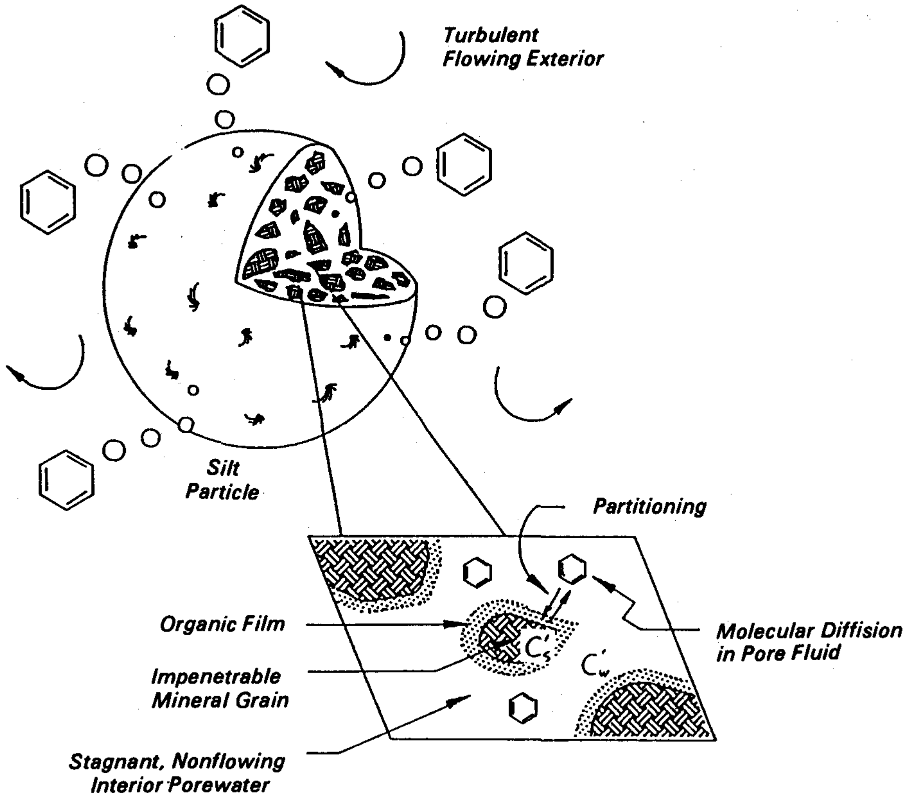

Figure 2. *Physical picture of processes controlling sorption kinetics.*

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

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

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, tr, 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

$$\text{Flux} = -(n)_2^{i+1} D_m \frac{\partial C_w}{\partial z} - (n)_2^{i+1} D_c \frac{\partial S_c C_c}{\partial z} = w_2 C_w = w_2 S_c C_c \quad (4)$$

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 cohensionless 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(cm^2/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	Yoldia, Nucula	4	$1.2\text{-}3.5 \times 10^{-6}$	^{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	Leptosynapta, Scoloplos	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	Euzonous mucronata (=Thoracophelia)	30	1.5×10^{-5}	Dimensional analysis[b]
Barnstable Harbor,	Pectinaria gouldii	6	7.6×10^{-8}	Dimensional analysis[b]
Long Island Sound	Yoldia limatula	2	3.2×10^{-7}	Dimensional analysis[b]
Long Island Sound	Yoldia limatula	3	2×10^{-6}	Dimensional analysis[c]
Laboratory	Yoldia limatula	3	1×10^{-5}	Pore water profiles
Laboratory	Clymenella torquata	11	$2\text{-}3 \times 10^{-4}$	Pore water profiles[d]
Laboratory	Clymenella torquata	11	4.5×10^{-5}	Pore water profiles[e]
Laboratory	Molpadia oolitica	7-9	$5.7\text{-}9.4 \times 10^{-5}$	Depth of oxidized layer[a]

[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 Swarts)*

Species	Guild	Individual Reworking Rate (mg/ind/day)	Total Reworking Rate (g/m^2/yr)	Depth of Reworking	Comments	Source
Annelids						
Abarenicola claparedi	FUN	3,600	—	—	Average high and low tide, 1-3.5 g/ind.	O[a]
Abarenicola pacifica	FUN	10,900	—	—	Average high and low tide, 1-3.5 g/ind.	O
Abarenicola pacifica	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]
Amphitrite ornata	SISDF	5,100	—	Surface	∞ 17°C	O
Amphitrite ornata	SISDF	2,600-5,200	—	Surface	22°C	O
Arenicola marina	FUN	4,700	—	—	Average of field measurements	O
Clymenella torquata	CB	900	54,000	20 cm	11°C	O
Clymenella torquata	CB	1,650	73,000	20 cm	Beaufort, North Carolina Annual rate adjusted for T'	O
Euzonous (=Thoracophelia) mucronata	MISSDF-V	230	—	—		O
Melinna palmata	SISDF	290	—	Surface	Cephalic plate width 2-8 mm, all sediment	P[c]
Pectinaria californiensis	CB	0.5-330	8,600	5 cm	Cephalic plate width 2-8 mm, all sediment	O
Pectinaria gouldii	CB	6,000	6,000	6 cm	All sediment, annual rate adjusted for T'	O
Pectinaria gouldii	CB	2,000	—		Just feces	O
Polycirrus eximius	SISDF	7	0-173	Surface	Just feces, April-October	C
Tharyx acutus	MISDF-V	7	0-1,300	Surface	Just feces, April-October	C
Scoloplos robustus	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						
Macoma balthica	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
Macoma balthica	MISDF-V	520	—	Surface	Feces and pseudofeces, 15°C	O
Macoma nasuta	MISDF-V	15-550	—	1 mm	Just feces, 10-50 mm/ind.	O
		7,300			Feces and pseudofeces, 48 mm/ind.	
Scrobicularia plana	MISDF-V	14,400	—	Surface	Feces and pseudofeces	P
Scrobicularia plana	MISDF-V	3.9-90	—	Surface	Just feces	H[d]
Yoldia limulata	MISSDF-V	280	2,300	2 cm	Feces and pseudofeces	O
Gastropods						
Hydrobia minuta	MESDF	1	26-8,900	2 mm	Annual rate not adjusted for T'	O
Hydrobia ventrosa	MESDF	1	0-12,000	2 mm	Annual rate not adjusted for T'C	O
Littorina irrotata	MESDF	0.4	100	Surface	Just feces, recalculated from data	C
Crustaceans						
Callianassa californiensis	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/m² /yr)	Depth of Reworking	Comments	Source
Callianassa major	*MISSDF-E*	*3,500*	*12.6-630 kg*	—	*Amount deposited per entrance, just feces*	*O*
6 species				*to <10 cm*		
Paraphoxus spinosus	*MISDF-V*	*8,910*	*54-2,200 kg*	*0-1 cm*	*Burrowing*	*C*
Uca pugillator	*MISDF-E*	*96*	*230*	—	*Just feces, recalculated from data*	*C*
Uca pugnax	*MISDF-E*	*75*	*820*	—	*Just feces, recalculated from data*	*C*
Echinoderms						
Caudina chilenses	*CB*	*160,000*	—	—		*P*
Echinocadrium cordatum	*MSSDF-V*	*3,000*	—	—		*P*
Holothuria spp.	*MESDF*	*25,000-220,000*	—	—		*P*
7 species						
Leptosynapta tenuis	*FUN*	*10,400-18,400*	—	*0.5-10 cm*	*Feces and below surface reworking*	*O*
Leptosynapta tenuis	*FUN*	*34,000*	*590-3,000 kg*	*1.15 cm*	*Feces and below surface reworking*	*C*
Scotoplanes sp.	*MESDF*	*100,000*	—	*1 mm*	*Feces*	*O*
Stichopus moebil	*MESDF*	*38,000*	—	—		*P*
Stichopus variegatus	*MESDF*	*49,000*	—	—		*P*
Enteropneust						
Balanoglossus gigas	*FUN*	*200,000-250,000*	—	—		*P*

[a] *O = original data* [b] *C = calculated from data* [c] *P = calculated by Power (1977)* [d] *H = 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

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

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 = 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

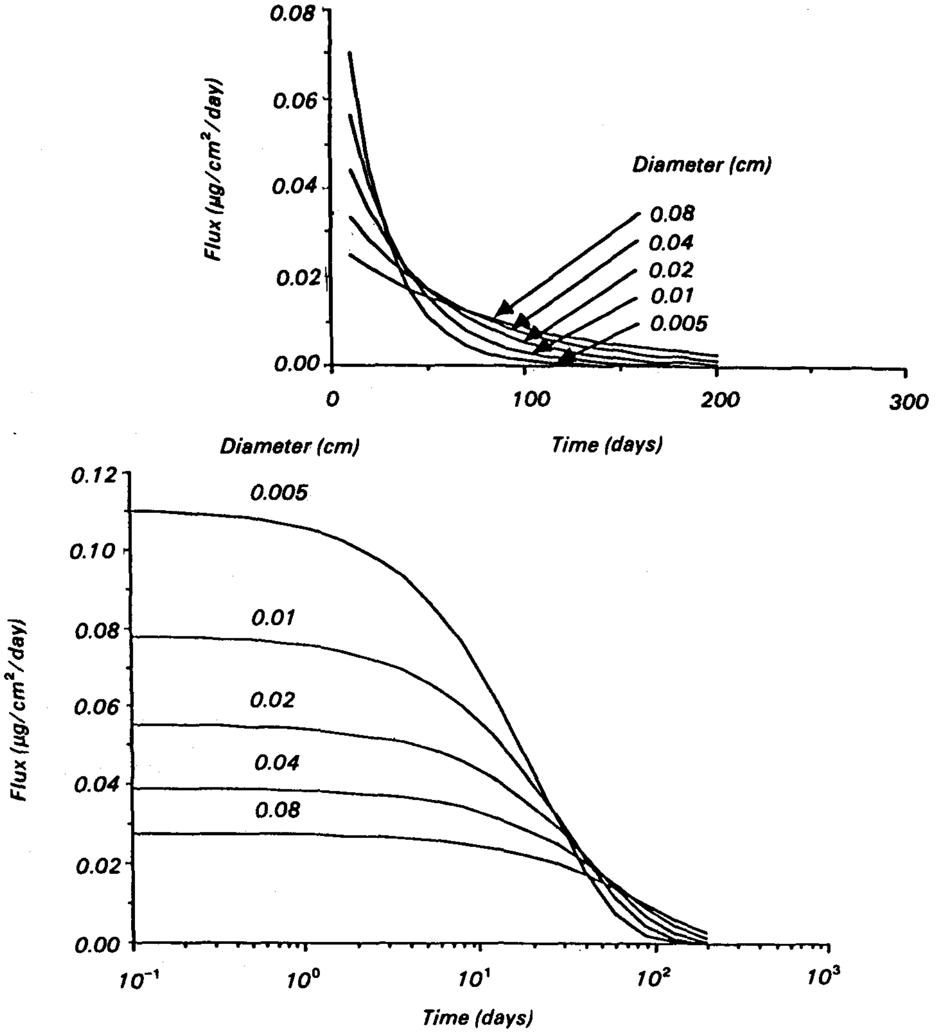

Figure 3. *Sensitivity of the plow-like bioturbation mediated pollutant flux to 5 different sediment particle sizes. The values of other parameters are same as those in the example problem in Section 3.3.2.3 of final report.*

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.

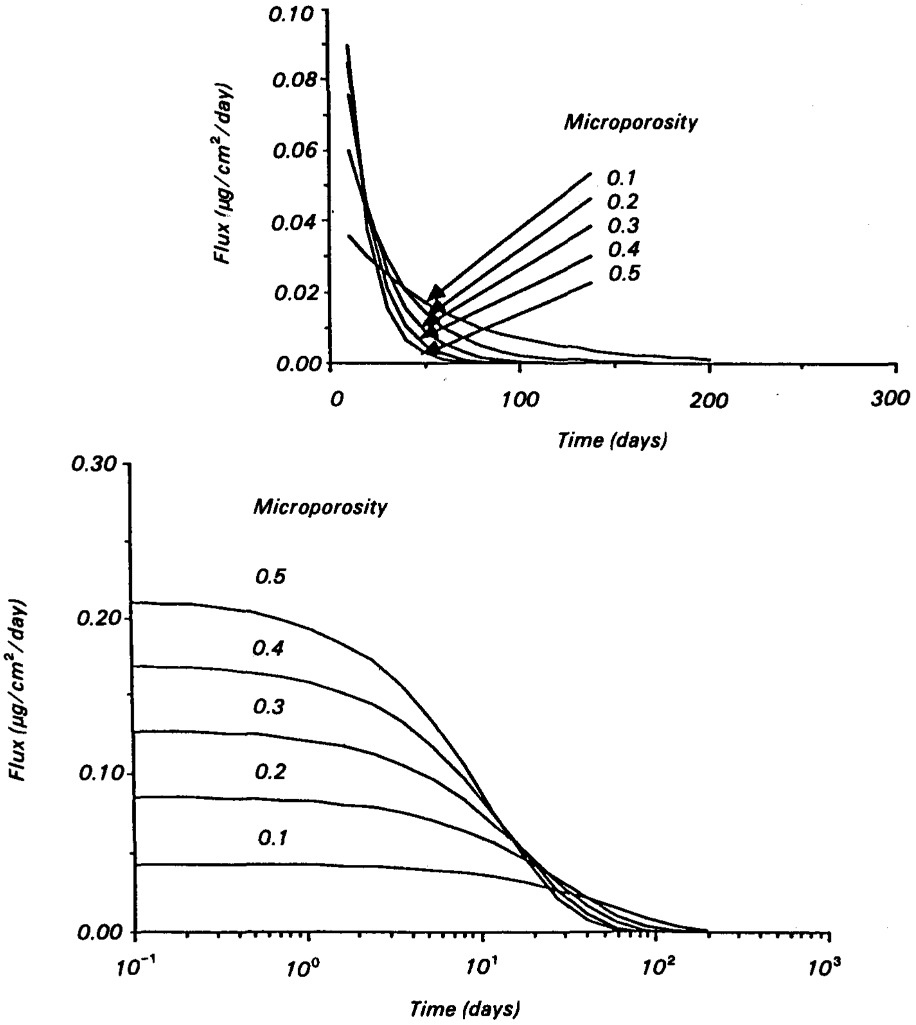

Figure 4. *Sensitivity of the plow-like bioturbation mediated pollutant to 5 different sediment intraparticle porosities. The values of other parameters are same as those in the example problem in Section 3.3.2.3 of final report.*

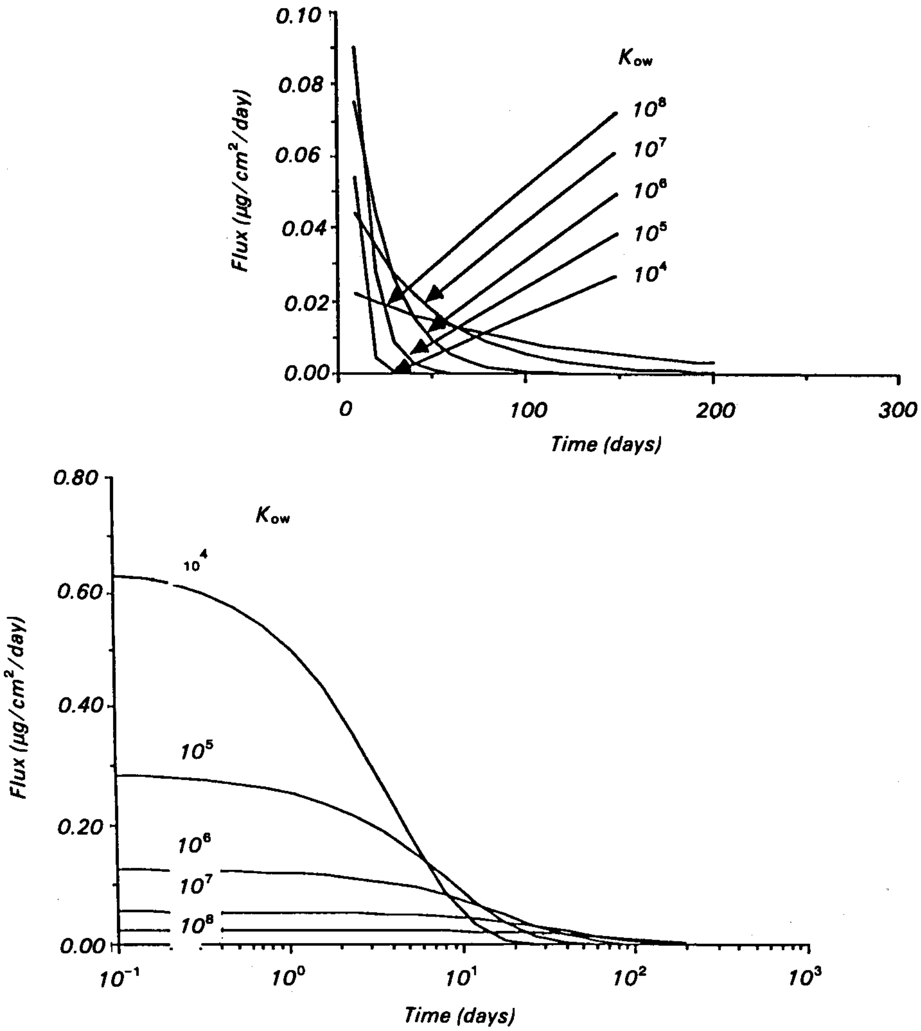

Figure 5. *Sensitivity of the plow-like bioturbation mediated pollutant to chemical partitioning. The values of other parameters are same as those in the example problem in Section 3.3.2.3 of final report.*

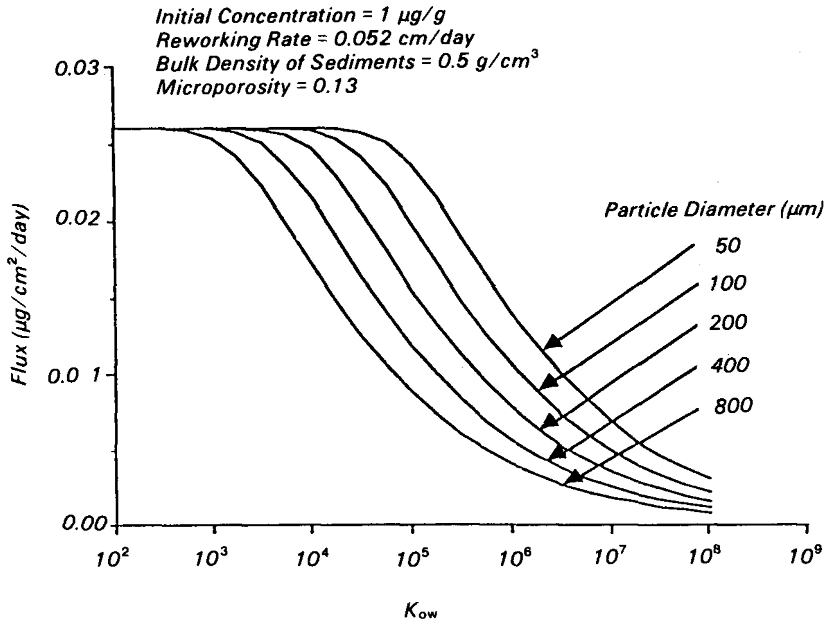

Figure 6. *Sensitivity of conveyor-belt type bioturbation mediated flux to K_{ow} and pellet size. The values of other parameters are same as those in the example given in Section 3.3.2.4 of final report.*

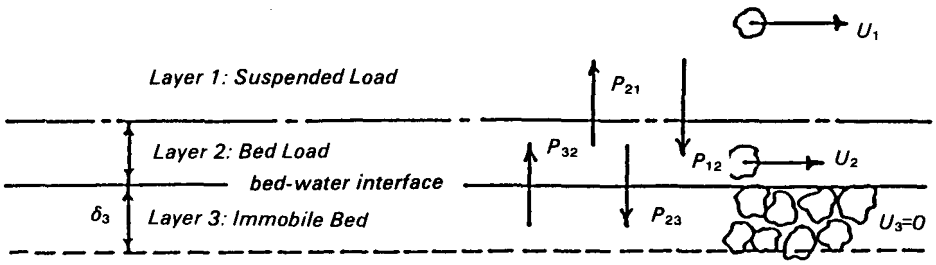

Figure 7. *Definition sketch: three-layer transport model.*

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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
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