

USING NATURAL PROCESSES TO DEFINE EXPOSURE FROM SEDIMENTS

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EXECUTIVE SUMMARY

Natural fate and transport processes normally control the recovery of unremediated contaminated sediments, the effectiveness of in situ remedial processes, and the amount and fate of any residual contamination after disturbance of the sediment. For example, deposition and biological degradation processes control the natural recovery of sediment, COC desorption and migration generally controls the effectiveness of in situ containment or treatment processes, and COC desorption and deposition significantly impact the effectiveness of any removal action. Natural processes determine the exposure and risks resulting from any activity involving contaminated sediments. Ultimately, it is the portion of the COC that moves via natural processes into the water or food chain that is the source of exposure and potential risk even if human actions increase the amount of COC available for these processes.

The fate, transport, and biouptake of contaminants in sediments is controlled by a number of physical, chemical, and biological processes. When viewed as a whole, these processes can be quite complex and overwhelming. However, significant progress in understanding each of these processes has been achieved allowing many to be described by basic principles and equations. Integration of these processes together into computer models, coupled with the use of site specific data for calibration permits the development of a tool that allows one to provide reasonably accurate representations of these systems so that well informed management decisions can be made. This paper summarizes the key processes affecting contaminants in aquatic systems.

Among the more important processes are the natural release processes due to exposure, removal, or resuspension of sediment. These dynamic processes serve to relate COC concentration levels found in the overlying water body with that found in the sediment (Valsaraj, Thibodeaux, and Reible 1997). Thus, natural fate and transport processes define the availability of COCs and the potential for exposure and risk to human and ecological receptors. The purpose of this paper is to summarize these natural processes and compare their importance in attenuating COC migration and exposure.

Any attempt to summarize and compare natural attenuation processes in sediments must recognize the different environments in which contaminated sediments are found. The relative importance of these processes differ significantly between lacustrine, riverine, estuarine, and coastal environments. The range and significance of natural processes are influenced heavily by site-specific characteristics. The paper that follows attempts to identify all of the potentially important natural attenuation processes and builds a matrix relating sediment and water body characteristics to these processes. The individual processes are discussed, including a means of assessing the importance of each process in particular field situations.

The most important natural fate and transport processes at contaminated sediment sites include the following:

- In-bed fate processes, including irreversible adsorption and chemical or biological reactions
- In-bed transport processes, including diffusion and advection as influenced by reversible sorption/desorption and colloidal transport
- Interfacial transport processes, including sediment deposition and resuspension, bioturbation, and water-side mass transfer

Table C-1 in the paper summarizes the relative importance of these processes in various sediment environments. These processes and the reasons for their importance in the individual environments are discussed in more detail in subsequent sections. The most important factor in defining the fate and transport processes influencing COCs in sediment is the energy of the overlying flow. In high energy environments, the sediment tends to be coarse grained and noncohesive with little sorptive capacity and low depositional rates. These sediments pose little barrier to advective transport and allow oxygen transport deep within the sediment. In low energy environments, a significant deposition of fine-grained sediments exists, providing high sorptive capacity and significant slowing of advection and oxygen transport. Somewhat offsetting these differences is the fact that many organisms, especially head-down deposit feeders, prefer fine-grained sediments. Therefore, bioturbation (i.e., the mixing associated with the normal life-cycle activities of sediment-dwelling organisms) is often enhanced in areas of finer-grained sediments, which may be repositories of hydrophobic COCs such as polychlorinated biphenyls (PCBs) and some heavy metals.

The exposure and risks to fish and higher level organisms depend on the availability of the COCs in the sediment. Generally, it is assumed that the only portion of the COC that is directly available is the fraction that partitions into the dissolved phase of the water. In this molecular form, the COC can move across biological membranes and accumulate in fish and other animal tissues. The risks of sediment contaminants to higher organisms can arise via one of the following three pathways, which are discussed below:

- Direct exposure to fish and higher animals by COC release from resuspended contaminated sediment or by incidental ingestion of contaminated bed sediments
- Indirect exposure to higher animals by predation and harvesting of plants and animals living directly exposed at the contaminated sediment-water interface
- Direct exposure to fish and higher animals from COC release from bed sediment to the overlying water or through consumption of filter-feeding or benthic infaunal organisms that obtain their food via the water column

The first pathway, direct exposure to resuspended sediment, can be described generally by assuming chemical equilibrium between the suspended sediment load and water. The second pathway, indirect exposure to contaminated sediment through the food chain, can be described generally by chemical equilibrium between the bed sediment and the benthic organisms that inhabit the sediment-water interface. The third pathway, direct exposure to fate and transport processes from stable sediments, requires analysis of the fate and transport processes in the sediment.

While many of the fate and transport processes vary significantly in importance from site to site, it is possible to rank the potential importance of each mechanism using characteristic times. Characteristic times are order of magnitude estimates of time required to remove COCs from an initially uniformly contaminated layer of height (H) by each of the various transport mechanisms. In most cases, the characteristic times represent $1/e$ times (i.e., times required to achieve 37% of the initial sediment bed concentration or 63% percent recovery). In the case of advective processes, the characteristic times represent complete removal times. Table C-2 in the paper summarizes the relationships comparing the characteristic recovery times of contaminated sediment by each of the processes. Processes that exhibit a shorter characteristic time are likely to be the most important transport processes.

In general, active sediment processes in which COCs are transported by bulk movement of pore water or particles exhibit the shortest characteristic transport times and, therefore, the fastest sediment recovery times. These processes also exhibit the highest sediment to water fluxes and the potential for relatively high exposure and attendant risk to fish and higher animals. For example, in

Table C-2 in the paper, sediment erosion and bioturbation are the only sediment bed processes occurring at significant rates. For hydrophobic or other strongly sorbed COCs, the processes that result in particle movement are much more significant than transport via pore water processes. In high energy environments, sediment resuspension and movement are likely to be dominant factors in particle transport; in low energy environments, bioturbation is likely to dominate COC movement in the upper layer of sediments. It is important to note that short characteristic times imply short sediment recovery times, but may also result in higher exposure and risk to fish and higher animals in the overlying water during the period of recovery.

Although Table C-2 in the paper provides general guidance as to the relative importance of various fate and transport mechanisms, it is important to note that each site is different and that only through detailed studies can the dominant process at a particular site be identified and quantified, allowing the evaluation of the effect of these processes on natural recovery and more active remedial options.

INTRODUCTION

Natural fate and transport processes normally control the recovery of unremediated contaminated sediments, the effectiveness of in situ remedial processes, and the amount and fate of any residual contamination after disturbance of the sediment. For example, deposition and biological degradation processes control the natural recovery of sediment, contaminant desorption and migration generally control the effectiveness of in situ containment or treatment processes, and contaminant desorption and deposition significantly impact the effectiveness of any removal action. Natural processes determine the exposure and risks resulting from any activity involving contaminated sediments. Ultimately, it is the portion of the chemical of concern (COC) that moves via natural processes into the water or food chain that is the source of exposure and potential risk even if human actions increase the amount of COC available for these processes.

The fate, transport, and biouptake of contaminants in sediments is controlled by a number of physical, chemical, and biological processes. When viewed as a whole, these processes can be quite complex and overwhelming. However, significant progress in understanding each of these processes has been achieved allowing many to be described by basic principles and equations. Integration of these processes together into computer models, coupled with the use of site specific data for calibration allows for the development of a tool that allows one to provide reasonably accurate representations of these systems so that well informed management decisions can be made. This paper summarizes the key processes affecting contaminants in aquatic systems.

Natural processes include the physical, chemical, and biological processes that occur without human intervention or control. Among the more important processes are the natural release processes due to exposure, removal, or resuspension of sediment. These dynamic processes serve to relate COC concentration levels found in the overlying water body with that found in the sediment (Valsaraj, Thibodeaux, and Reible 1997). Thus, natural fate and transport processes define the availability of COCs and the potential for exposure and risk to human and ecological receptors. The purpose of this paper is to summarize these natural processes and compare their importance in attenuating contaminant migration and exposure.

Any attempt to summarize and compare natural attenuation processes in sediments must recognize the different environments in which contaminated sediments are found. The relative importance of these processes differ significantly between lacustrine, riverine, estuarine, and coastal environments. The range and significance of natural processes are influenced heavily by site-specific characteristics. This paper attempts to identify all of the potentially important natural attenuation processes and builds a matrix relating sediment and water body characteristics to these processes. The individual processes are discussed, including a means of assessing the importance of each process in particular field situations.

The most important natural fate and transport processes at contaminated sediment sites are illustrated in Figure C-1 and include the following:

- In-bed fate processes, including irreversible adsorption and chemical or biological reactions
- In-bed transport processes, including diffusion and advection as influenced by reversible sorption/desorption and colloidal transport
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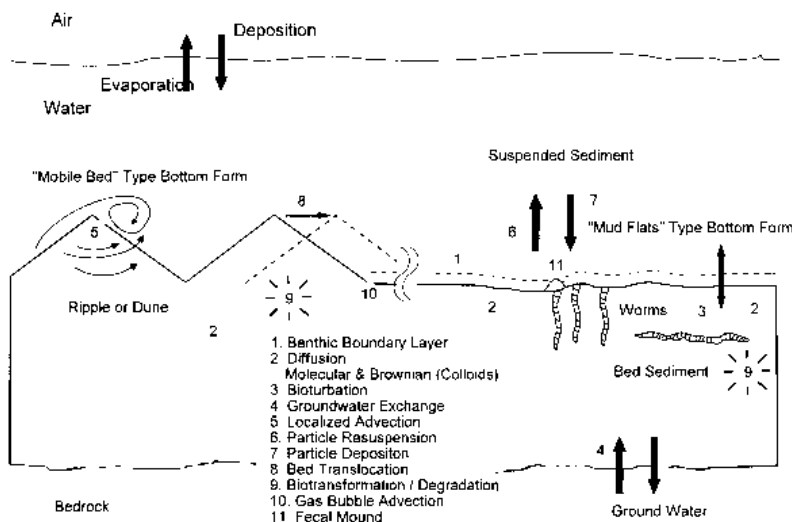


Figure C-1. Contaminant transport mechanisms between sediment/water.

Table C-1 summarizes the relative importance of these processes in various sediment environments. These processes and the reasons for their importance in the individual environments are discussed in more detail in subsequent sections. The most important factor in defining the fate and transport processes influencing COCs in sediment is the energy of the overlying flow. In high energy environments, the sediment tends to be coarse grained and noncohesive with little sorptive capacity and low depositional rates. These sediments pose little barrier to advective transport and allow oxygen transport deep within the sediment. In low energy environments, a significant deposition of fine-grained sediments exists, providing high sorptive capacity and significant slowing of advection and oxygen transport. Somewhat offsetting these differences is the fact that many organisms, especially head-down deposit feeders, prefer fine-grained sediments. Therefore, bioturbation (i.e., the mixing associated with the normal life-cycle activities of sediment-dwelling organisms) is often enhanced in areas of finer-grained sediments, which may be repositories of hydrophobic COCs such as polychlorinated biphenyls (PCBs) and some heavy metals.

Table C-1
Sediment Processes and their Relationship to Various Sediment Environments

Environment	Environmental Characteristics	Key Fate and Transport Processes
Lacustrine	Low energy environment Generally depositional environment Groundwater interaction decreasing away from shore Organic matter decreasing with distance from shore Often fine-grained sediment	Sediment deposition Water-side mass transfer limitations Groundwater advection in near-shore area Bioturbation (especially in near-shore area) Diffusion in quiescent settings Metal sequestration Aerobic and anaerobic biotransformation of COCs Biotransformation of organic matter (e.g., gas formation)
Riverine	Low to high energy environment Depositional or erosional environment Potential for significant groundwater interaction Variable sediment characteristics (fine to coarse grained)	Local and generalized groundwater advection Sediment deposition and resuspension Aerobic biotransformation processes in surficial sediments (potentially anaerobic at depth) Bioturbation

Environment	Environmental Characteristics	Key Fate and Transport Processes
Estuarine	Generally low energy environment Generally depositional environment Generally fine-grained sediment	Bioturbation Sediment deposition Water-side mass transfer limitations Aerobic and anaerobic biotransformation of COCs Biotransformation of organic matter (e.g., gas formation)
Coastal Marine	Relatively high energy environment, decreasing with depth and distance from shore Often coarse sediments	Bioturbation Sediment erosion and deposition Localized advection processes

EXPOSURE PATHWAYS

The exposure and risks to fish and higher level organisms depend on the availability of the COCs in the sediment. Generally, only the portion of the COC that is directly available is the fraction that partitions into the dissolved phase of the water. In this molecular form, the COC can move across biological membranes and accumulate in fish and other animal tissues. The available portion of the COC is generally limited by transport and/or equilibrium partitioning considerations. The risks of sediment contaminants to higher organisms can arise via one of the following three pathways, which are discussed below:

- Direct exposure to fish and higher animals by COC release from resuspended contaminated sediment or by incidental ingestion of contaminated bed sediments.
- Indirect exposure to higher animals by predation and harvesting of plants and animals living directly exposed at the contaminated sediment-water interface.
- Direct exposure to fish and higher animals from COC release from bed sediment to the overlying water or through consumption of filter-feeding or benthic infaunal organisms that obtain their food via the water column

Sediment Resuspension and Erosion

The dominant characteristic that controls COC mobility is resuspension and erosion of particles from the sediment bed. Since most persistent sediment COCs are associated with the solid phase, any mobilization of this phase dramatically increases COC mobility. As a result, COCs are distributed over large areas, and significantly increased water column concentrations are observed relative to less active sediment-water transport. Erosion and resuspension conditions also eliminate natural recovery that might occur in less active environments due to deposition and burial of the contaminated sediment.

Under high energy conditions in a stream, significant erosion of the sediment bed occurs and individual sediment particles can be carried downstream either by sliding along the surface of the sediment or by being suspended in the stream. The process normally results in the formation of dune-like structures that progress downstream by the process of erosion on the upstream face and deposition on the downstream face. This process is depicted in Figure C-2.

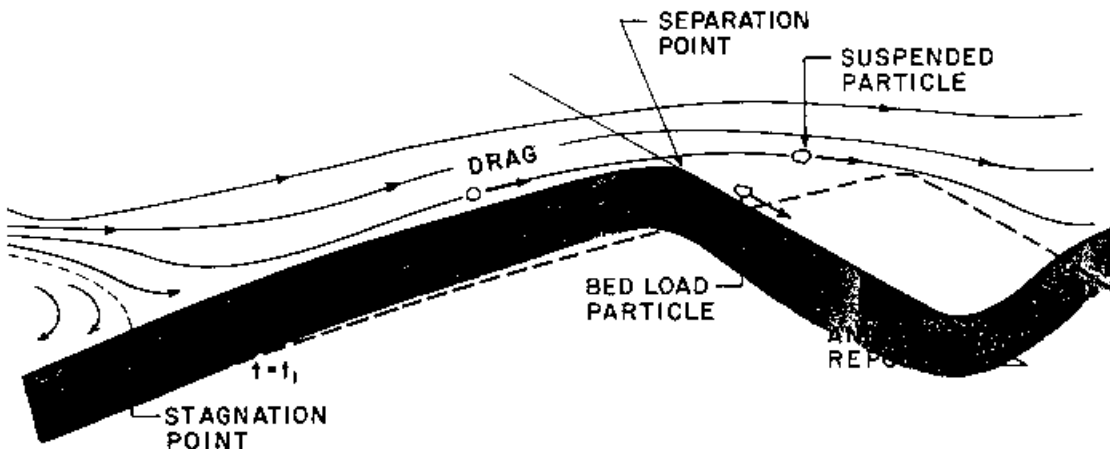


Figure C-2. Sediment movement due to erosion process.

During this overturning and migration process, sediment particles are exposed and either scoured and suspended in the stream or reburied by other sediment particles. During exposure to the stream water, COCs sorbed onto the sediment particles can be desorbed, and COCs in the adjacent pore water can be mixed into the overlying water. Once particles are set in motion, the following three types of movement can be recognized:

- Rolling and sliding along the bed surface (i.e., bed load transport)
- Suspension in the free stream (i.e., suspended load)
- A transitional motion characterized by saltation and particle jumps

The ability to predict the onset of resuspension in a sediment remains largely limited to cohesionless, coarse-grained particles. Site-specific measurements of bed and/or suspended load sediment transport are needed to characterize cohesive, fine-grained sediment. The onset of particle motion in a cohesionless sediment is determined by the balance between the submerged weight of a particle and the lift associated with the water flow over the particle. Raudkivi (1967) discusses the physics of the onset of the particle motion and shows that the onset of particle

$$u_{*c} = B \sqrt{\left(\frac{\rho_p - \rho_w}{\rho_w} \right) g d_p} \quad (1)$$

motion occurs when a critical threshold friction velocity is exceeded.

Here u_{*c} is the critical threshold velocity; ρ_p and d_p are the particle density and diameter, respectively; ρ_w is the density of water; and B is a coefficient incorporating the angle of repose of the article (i.e., the slope of the upstream face of the sediment dune) and the partial coverage by other sediment particles. This relationship simply emphasizes that resuspension of the sediment occurs when the lift caused by the overlying flow overcomes the weight of the particle. The friction velocity is a parameter related to the surface friction that can be determined by velocity profile measurements. Raudkivi (1967) suggests that B equals 0.2. For cohesive sediments, the friction velocity required to produce particle motion is significantly larger for a particular particle size than would be suggested by this relationship.

This paper addresses COCs that are released if the sediment is resuspended. Should significant resuspension occur, the water column concentration tends to approach equilibrium conditions with the resuspended sediment. It is possible to measure the resuspended sediment load in the overlying water, C_s . This sediment carries with it an initial contaminant loading, W_s , in milligrams per kilogram (mg/kg). This original sediment loading distributes according to equilibrium partitioning with the water giving

$$C_w = \frac{C_s W_s}{1 + C_s K_{sw}} \quad (2)$$

Here K_{sw} is a distribution coefficient between the sediment and the water and C_w is the water phase concentration. For a hydrophobic organic compound, the distribution coefficient is often assumed to be given by the product of the organic carbon based partition coefficient K_{oc} , a compound specific parameter, and the fraction of organic carbon in the sediment, f_{oc} , a sediment-specific parameter. Predictions normally assume linearity as indicated in Equation 2 and complete reversibility, deviations from which are often observed in practice.

Thus, for compounds that do not partition strongly to the sediment or if the resuspended sediment levels are low (K_{sw} and/or C_s are small), the water concentration is simply the suspended sediment concentration times the initial contaminant load of the sediment. For strongly sorbing compounds,

however, the full equilibrium relationship governs; that is, the overlying water approaches equilibrium with the contaminated sediment bed as given by Equation 3.

$$C_w = \frac{W_s}{K_{sw}} \quad (3)$$

For metals and other elemental species, the equilibrium state is much more complicated and depends on the chemical state of the water and sediment, particularly the pH and oxidation-reduction conditions. The ratio of sediment loading to equilibrium water concentration is often very large for metals but only a very small fraction of the metals are typically available. Myers, et al. (1996) indicate that the leachable fraction of metals is typically less than 10%, sometimes much less, and that the partition coefficient between the leachable fraction and the water is typically between 3 and 10. For both organic and metal species, a site-specific measurement of the sediment-water partition coefficient is preferred.

When sediment is dredged, an artificial situation is created equivalent to high flow rates and sediment resuspension in the water body. Under such conditions, the water again tends to equilibrate with the sediment resuspended by the dredge head (DiGiano, et al. 1993). Therefore, the approach outlined above also can be used to assess exposure and risks due to dredging, at least for organic compounds, if an estimate or measurements of sediment resuspension is available. DiGiano, et al. (1995) also developed an experimental protocol for estimating metals release and equilibration with a body of water during dredging.

Sediment-Dwelling Organisms and Food Chain

Plants and animals living at the sediment-water interface are often assumed to be equilibrated with the surficial sediments. The partitioning of the COC between the surficial sediments defines the pore water concentration, and the dissolved pore water concentration is often assumed to define the portion that is available for uptake by the plants and animals [U.S. Environmental Protection Agency (USEPA) 1993]. It is important to note that the COC concentration in the surficial sediments may not be represented well by the depth averaged composite concentration that is typically measured. Freshwater benthos, for example, may only populate the upper 5 to 10 centimeters (cm) of sediments in significant quantities. In marine sediments, animals living at the sediment-water interface tend to be larger and influence a larger sediment depth. The ratio of the concentration in the surficial sediments to the deep sediments depends on the COC transport rate to the surface layer and the transport rate and fate processes that remove COCs from that layer.

If the upper sediment layers are assumed in equilibrium with the adjacent pore water, the water concentration available to plants and animals living at the sediment-water interface is as given by Equation 3. The uptake of the COC into sediment-dwelling animals depends on the ability of the organisms to accumulate the COC. The ratio of the loading in the organism to that in the sediment is termed the biota-sediment accumulation factor (BSAF). For hydrophobic organic compounds, the partitioning of the COC is assumed to be controlled by the organic "solvent" fraction that exists within a particular phase. Thus, a more useful biota-sediment accumulation factor for such compounds is one that normalizes the concentration in each phase with the organic fraction in that phase. For the biota, this is the lipid fraction, f_{lipid} , and for the sediment, it is the organic carbon fraction, f_{oc} .

$$BSAF = \frac{W_b / f_{lipid}}{W_s / f_{oc}} \quad (4)$$

The BSAFs vary as a function of sediment, organism, and time of exposure, but its value for benthic organisms tends to approach unity (Ingersoll, et al. 1997). This approach to unity implies that the organic normalized concentration in the organism and the sediment are identical and that the organism is in equilibrium with the dissolved concentration of the COC in pore water. It is important to note that due to the bioaccumulation of COCs in higher organisms, effective BSAF values may be considerably higher than unity for higher trophic levels.

The normalization with organic carbon content assumes that essentially all of the COC in the sediment and organism is available for partitioning to organic matter. A significant fraction of the COC, however, seems largely unavailable and is held in a desorption-resistant fraction. This phenomena has been noted most often in aged sediments where significant quantities of COCs appear not to follow the assumed linear, reversible partitioning. At this stage, no predictive guidance is available on the amount or extent of this desorption-resistant and potentially nonbioavailable fraction and either 1) all of it is assumed available or 2) site-specific measurements of availability are required for a more precise characterization.

The concentration of metals and ionic species are significantly more complicated; however, the dissolved pore water concentration in the sediment has been seen increasingly as the best indicator of metals and ionic species in both plants and animals. As indicated previously, the fraction that is ultimately leachable into the pore water is typically less than 10% of the total metal loading on the sediment, and the effective partition coefficient for this leachable fraction is typically 3 to 10 (Myers, et al. 1996). Another indicator for specific metal contaminants is the ratio of the acid volatile sulfides (AVS) to the simultaneously extractable metals (SEM). A number of metals, including cadmium, copper, lead, nickel, and zinc, tend to form insoluble metal sulfides in sediments. As long as the AVS exceeds the SEM, these metals are essentially unavailable in dissolved form to living organisms.

As a result of the complex and varied behavior primarily of metal species and some other chemicals, toxicity tests often are used to assess the potential for adverse sediment effects rather than specific physico-chemical tests. The USEPA Assessment and Remediation of Contaminated Sediments (ARCS) Program performed a comparative evaluation of a number of toxicity tests for sensitivity and discriminatory power (USEPA 1994). The discussion of the individual tests and their ability to identify severely contaminated sediments is beyond the scope of the present discussion. Please see Ingersoll, et al. (1997) for additional information.

Thus, the assessment of the COC levels entering the food chain via uptake into plants and animals at the sediment-water interface is largely a question of COC availability. In the absence of site-specific toxicity information, equilibrium partitioning for organic carbons and the AVS/SEM for some metals are useful predictors of availability.

Contaminant Migration from Stable Bed Sediments

COC movement from the bed to the overlying water is inherently a dynamic process controlled by the transport processes within the bed and at the sediment-water interface. Rarely are these processes sufficiently fast that the overlying water is equilibrated with the surficial sediments (although, as described in the previous two pathways, equilibration of the overlying water with any suspended sediment and between benthic organisms and surficial sediments is often assumed). The direct exposure of fish and higher animals to COCs in stable, noneroding beds is a rate-limited process controlled by the natural fate and transport processes that are the subject of this discussion.

It is perhaps easiest to characterize quantitatively the various natural processes depicted in Figure C-1 by their intrinsic rates, as established by their effective time constants. A time constant

is simply a measure of the time required for a certain process or combination of processes to achieve recovery of the sediment. Typically half-lives, $1/e$ times (i.e., times required to achieve 37% of the initial sediment bed concentration or 63% percent recovery), or essentially complete recovery times (e.g., 95 or 99% recovery) are used as characteristic times for a process. Unless otherwise stated, the $1/e$ time is used to characterize the time required for a particular process. The rate of recovery of a sediment, as measured by the time rate of decrease of sediment loading, W_s , is written as follows:

$$\text{Rate of sediment recovery} = \frac{W_s}{\tau_{fate}} + \frac{W_s}{\tau_{transport}} \quad (5)$$

Here τ_{fate} and $\tau_{transport}$ are the effective time constants (time⁻¹) characterizing fate and transport processes, respectively. The remaining COC at any time from an initial contaminant loading, W_0 , is then associated with an overall time constant, τ_c , given by

$$W_s(t) = W_0 e^{-t/\tau_c} \quad \text{where} \quad \frac{1}{\tau_c} = \frac{1}{\tau_{fate}} + \frac{1}{\tau_{transport}} \quad (6)$$

This simple conceptual model makes no attempt to recognize the spatial variability in the sediments but serves simply to organize the effect of the various processes on the average COC concentration. Estimates of the characteristic times of the various natural processes are provided in "Analysis of Sediment Bed Fate and Transport Mechanisms" and allow a ranking and comparison to be drawn.

WATER-SIDE MASS TRANSFER PROCESSES

The first application of the conceptual model is to define the relative importance of water-side mass transfer resistances. This is critically important in evaluating the influence of natural attenuation processes in that *if* the overlying water transport processes control the rate of release from the sediment, measurements of in-bed processes are largely superfluous. Because of its importance, this process is evaluated in more detail in Box C-1.

Box C-1 Water-Side Mass Transfer Processes

The first application of this conceptual model is to define the relative importance of water-side mass transfer resistances. The transport time constant, $\tau_{transport}$, is a function of both transport processes internal to the sediment and transport processes in the overlying water, and one phase or the other may limit the overall mass transfer. It is related to the mass transport coefficient, $k_{transport}$, through the surface area available for transport, A , and the volume of the contaminated sediment, V by

$$t_{transport} = \left(\frac{V}{A} \right) \left(\frac{1}{k_{transport}} \right)$$

This is critically important to the evaluation of the influence of natural attenuation processes in that the overlying water transport processes control the rate of release from the sediment, measurements of in-bed processes are largely superfluous. The potential mass transfer resistance afforded by the water-side mass transfer processes should be evaluated at the outset of any assessment of natural attenuation processes in the sediment. It is often assumed incorrectly that the intrinsically slower sediment-side processes always control mass transfer to the overlying water. A comparison of in-bed to overlying water processes can be developed by using the two resistance theory for mass transfer processes in series.

$$\frac{1}{k_{transport}} = \frac{1}{k_s} + \frac{K_{sw}}{k_w}$$

where

$$Flux = k_s \Delta W_s = k_w \Delta C_w$$

Here k_s and k_w are the sediment and water side mass transfer coefficients, respectively, as defined by the appropriate driving force (total sediment COC loading difference, ΔW_s , in the sediment and water concentration difference, ΔC_w , in the overlying water). Note that as the partition coefficient between the sediment and the water increases (i.e., for more strongly sorbed COCs), the contribution of the water-side mass transfer increases. Thus, the rate of recovery of the sediment is controlled by water-side processes as long as

$$\frac{K_{sw}}{k_w} \gg \frac{1}{k_s}$$

and not simply by the condition $k_w \gg k_s$, which is normally true. Illustrative models of the water-side mass transfer coefficient under flowing and quiescent (generally wind-driven circulation) conditions are given by

$$k_w = \frac{\sqrt{\rho_w} v_*^{1/2}}{Sc^{2/3} y_0^{1/2}} \quad \text{flowing, typically } O(10\text{cm/hr})$$

$$k_w = \left(0.031 \frac{\text{sec}}{m^2} \right) \frac{v_a^2 h^2}{M_w^{1/2} L} \quad \text{wind - driven, typically } O(1\text{cm/hr})$$

where

k_w water-side mass transfer coefficient

ν_w	kinematic viscosity of water [0.01 cm ² /second (sec) at 20°C]
Sc	Schmidt number (ν_w/D_w , typically O(1000) for hydrophobic organic compounds)
D_w	molecular diffusivity of contaminant [typically O(10 ⁻⁵ cm ² /sec)]
y_0, ν^*	surface roughness and friction velocity (estimated from water velocity profile)
v_a	wind velocity [meters (m)/sec]
h	depth of wind-driven lake (m)
L	width of wind-driven lake along wind-direction (m)
M_w	molecular weight of compound being transported

As indicated below, the sediment-side mass transfer coefficient is often of the order of 1 cm/year (yr) in a stable, noneroding sediment. This suggests that the water-side mass transfer is of equal importance as the sediment side processes for a sediment-water partition coefficient of

$$K_{sw} \approx \frac{k_w}{k_s} \approx \frac{1 \text{ cm/hr}}{1 \text{ cm/yr}} \approx \frac{8770 \text{ cm/yr}}{1 \text{ cm/yr}} \approx 8770$$

The mobile fraction of most metals in sediments exhibit a partition coefficient much less than this suggesting their release from stable sediments is controlled by sediment-side processes. Many hydrophobic organic compounds, however, exhibit partition coefficients of this order and larger, suggesting that, at least under some conditions, their release is influenced or controlled by water-side mass transfer processes. Under such conditions, measurements of sediment properties and processes are not important.

The potential resistance afforded by the water-side mass transfer processes must be evaluated at the outset of any assessment of natural attenuation processes. Often, it is assumed incorrectly that the intrinsically slower sediment-side processes always control mass transfer to the overlying water. As shown in Box C-1, water-side control of the overall rate of COC migration from the sediment is indicated when the compound is strongly sorbed by the sediment or when the in-bed transport processes (e.g., via bioturbation) is extremely fast. For typical transport rates in sediment and in quiescent overlying bodies of water, water-side mass transfer resistances can be important for sediment-water partition coefficients much greater than 1,000 and in higher energy water bodies when the sediment-water partition coefficient is much greater than 10,000. Therefore, water-side mass transfer resistances can be important for compounds more sorbing than moderate molecular weight polycyclic aromatic hydrocarbons (PAHs). As an illustration, consider the four-ring PAH, pyrene. Pyrene exhibits an organic carbon based partition coefficient of about 10⁵ liters (L)/kg. Assuming that all of the pyrene sorbs reversibly to only the organic carbon fraction of the sediment, a typical value of 1%, the sediment-water partition coefficient is

$$K_{sw} = f_{oc} K_{oc} = (0.01)(10^5 \text{ L/kg}) = 1000 \text{ L/kg} \quad (7)$$

This suggests that the water-side mass transfer resistance may be important for pyrene under some environmental conditions (e.g., in quiescent lakes) or when the organic carbon fraction and the sorption of pyrene onto the sediment are greater than that suggested by 1,000 L/kg.

ANALYSIS OF SEDIMENT BED FATE AND TRANSPORT MECHANISMS

Fate and transport processes are examined separately below to determine the most important mechanisms influencing contamination mobility in sediment. Fate and transport mechanisms are separated into two categories: those operable in stable, immobile beds and those operable in an active bed. For this purpose, an active bed is one in which either the pore water or the sediment grains are in motion.

Passive Sediment Fate and Transport Processes

Sediment fate and transport involve the following passive processes:

- *Molecular Diffusion*

Molecular diffusion is the most basic and ubiquitous chemical transport process within a sediment bed. Due to their thermal state, molecules are in a constant state of motion, characterized by random molecular velocities (directions and magnitudes) and frequent collisions involving both the solvent (i.e., water) and COCs. The net result is the movement of COC molecules from pore water regions of high concentration to those of low concentration.

The existence of a concentration gradient within the pore water of a porous sediment bed is sufficient to initiate transport by this molecular process. The magnitude of the COC flux is quantified by Fick's first law and couples the concentration gradient to the diffusion coefficient. The diffusion coefficient in porous sediments is reduced by the finite porosity of the sediments. Typically, a model such as that of Millington and Quirk (1961) is employed

$$D_{eff} = D_w \epsilon^{4/3} \quad (8)$$

Here ϵ represents the sediment porosity and D_w is the molecular diffusion coefficient of the COC in water, typically of the order of 10^{-5} square centimeters per second (cm^2/s).

Field investigations of COC levels in sediment beds typically involve analytical chemistry measurements performed on the sediment solids to measure total sediment loading. The concentration profiles can be averaged over sediment depth and reflect a mixed sample from a few cm to 30 cm of core length. Profiles of concentration based on thin slices less than 1 cm in depth spanning the entire depth of contamination are rare. Concentration profile data usually are limited in that they generally represent a snapshot in time and seldom reflect trends over time. Typically, single profiles for a particular year are available for hydrophobic organics and metals. These measurements are not very useful in assessing the influence of diffusivity that is manifested over longer time periods and results in depletion of COC levels over short distances. In addition, diffusion normally occurs at significant rates only within the pore water phase, suggesting pore water concentrations can be much more useful.

A better approach for both conceptual and quantitative fate and transport model development is the use of high resolution coring with both total and speciated measurements via phase and constituent. In this manner, the fraction of the available COC dissolved in the pore water is identified. For metals in particular, total sediment loading measurements are not very useful. By discriminating between soluble and insoluble fractions of metals, a much better assessment of potential adverse effects is made. High resolution coring enables comparison to detailed mathematical models and can be very useful in identifying the most important processes. For example, diffusional processes give rise to concentration profiles that are quite different from advectively dominated transport processes.

It is recognized that it can be difficult to justify the cost and time commitment of high resolution coring in some marginally contaminated sediment sites. It must also be recognized,

however, that fewer high resolution core samples can be more useful in understanding a site and selecting a remedial alternative than a larger number of composite or depth-averaged samples. This may be especially appropriate if noninvasive acoustic sounding techniques are employed prior to sampling to define the basic character of the bed and determine spatial heterogeneity. In this manner, a sampling program can be designed to avoid atypical bed locations.

- *Adsorption and Desorption Equilibrium between the Solid Surface and Pore Water*

The hypothetical transport of COCs out of the sediment bed via molecular diffusion in the sediment pore water was discussed previously. Organic compounds that are hydrophobic by nature are capable of being adsorbed on the organo-clay fractions of the sediment. Thus, an adsorption-desorption equilibrium exists at the sediment and pore-water interface. In the case of transport into a clean sediment, adsorption on the particles retards the movement of a concentration front (e.g., the depth leached to an arbitrary concentration level) due to transient accumulation of material in the sorbed phase. DiToro, et al. (1985); Formica, et al. (1988); and Wang, et al. (1991) have reported experiments that isolate the partitioning and diffusion processes. Both experiment and theory demonstrate that adsorption slows transient pore water processes (including diffusion) according to a retardation factor that is essentially the ratio of the total concentration in the sediment to the concentration in the mobile phase.

$$R_f = \frac{\text{total concentration}}{\text{mobile phase concentration}} \approx e + r_b K_{sw} \quad (9)$$

A simple estimate of the time required to recover the sediments as a result of retardation is the product of R_f and the time required to recover by diffusion assuming no retardation. It is important to note that retardation applies to any pore water process where the bulk of the COC is held in a nonmobile phase (relative to the pore water process). As in previous discussions, the sediment-water partition coefficient in Equation 9 is the apparent partition coefficient and represents only that portion of the COC held in a reversibly sorbed phase. As described earlier, a significant fraction of the COCs may not readily desorb and, therefore, does not participate in this process. Laboratory measurement of partition coefficients used in Equation 9 under such conditions must be measured via desorption experiments. It is also important to recognize that retardation affects only transient processes. Under steady conditions, there is no transient accumulation of COCs in the sorbed phase and, therefore, no retardation.

Diffusion is an extremely slow process if retarded by sorption. If diffusion is the primary transport process or can be made to be the primary process through containment of more active processes, COC release and exposure is generally negligible. To illustrate, the characteristic time for depletion of a finite layer of depth (H) as defined by the 1/e time or time until only 37% of the material remains is given by

$$t_{diff} = \frac{4}{p^2} \frac{H^2 R_f}{D_{eff}} \quad (10)$$

Considering a 10 cm thick layer of 1% organic carbon sediment initially uniformly contaminated with pyrene, the characteristic time for diffusion to occur is on the order of 870 years. That is,

if diffusion were the only natural transport process, 870 years would be required before the 10 cm thick layer sediment would recover to a concentration 37% of its initial value.

Although sorption onto an immobile phase can retard COC migration in the sediment, sorption onto a mobile particulate phase (e.g., fine particulate, colloidal matter) can enhance or facilitate transport. Natural organic colloids are fine particulate suspensions that are primarily the decomposition products of plant and animal life. Colloids form in a marine sediment through fermentation reactions of degraded cellular material to form low molecular weight dissolved organic matter such as amino acids. Condensation reactions then give rise to higher molecular weight dissolved organic matter such as fulvic and humic acids. These higher molecular weight compounds generally constitute what is referred to as dissolved organic matter. Dissolved phase material is generally operationally defined as anything that passes a 0.45 micrometer (μm) filter. They become colloids when groups of these compounds form large diameter suspensions in water. These groups have a negative electrical surface charge and their stability is dependent on the structure of the electrical double layer formed, van der Waals forces, hydration phenomena, and the effects of adsorbed substances. These groups represent a sink for hydrophobic organic COCs in the water in that they effectively increase the solubility of organic COCs by increasing the mass of COC that can partition into the pore water or mobile phase. In this manner, the mobility of organic COCs can be enhanced. Various metals and metal complexes also form colloidal species. Just as organic colloids can enhance the mobility of hydrophobic organics, metal colloids can enhance the effective solubility of metal and ionic COCs. The net effect of the increased effective solubility of a COC is a change in the retardation factor (Reible, et al. 1991)

$$R_f = \frac{\text{Total}}{\text{Mobile}} = \frac{e + r_b K_{sw} + e C_c K_{cw}}{1 + C_c K_{cw}} \quad (11)$$

Here C_c is the concentration of colloidal particles in the water while K_{cw} is the partition coefficient between the colloids and the water. The effective retardation factor represented by Equation 11 assumes that the colloidal particles are transported through the sediment pore water at the same rate as the water molecules themselves. A commonly used but approximate estimate of the partitioning of an organic COC to colloidal or dissolved organic carbon is that K_{cw} equals K_{oc} . The concentration of dissolved organic carbon in sediments is typically in the range of 10 to 100 mg/L. These values suggest that the effect of colloidal organic carbon for the previous example of pyrene is to decrease the retardation factor by a factor of 2 to 10. Thus, the presence of colloidal matter can decrease the time for diffusion to result in recovery of a contaminated sediment layer by a factor of 2 to 10.

- *Chemical Reaction and Biodegradation*

Sediment contaminants are routinely assumed to be refractory and to degrade at low or negligible rates. The sediment environment does not lend itself to rapid degradation dynamics, and many of the COCs are persistent hydrophobic organic compounds. The long-time scales required for diffusive recovery of contaminated sediments suggests that even extremely slow chemical or biological reactions can be significant if there are no faster transport processes active in the sediment. Unfortunately, very little information exists about the long-term persistence of COCs in the sediment environment. This information is necessarily site and COC specific. Most chemical speciation studies have a lifetime of a few years or less and, over this period of time, it generally is possible only to identify the parent compound and a few potential degradation products. Generally, it is not possible to gather enough information to determine reaction rates or close the material balance. In addition, all sediments exhibit

significant variability, with vast changes in the sediment environment over vertical distances of a few millimeters and over horizontal distances of meters or less. The assessment of chemical fate over long time periods is especially difficult in the face of the composited samples that are normally collected. Further complicating the situation are the dynamic changes that sediments undergo in high energy environments (e.g., in riverine systems that undergo flooding and sediment resuspension events).

Although sediment chemical and biological transformation processes are often slower than similar processes in near-surface soils, the general trends are repeated. That is, aerobic biodegradation processes are generally faster than anaerobic processes, and degradation rates depend on the presence of sufficient nutrients and substrate components. It is largely for these reasons that sediment fate processes are relatively slow. Much of the COC, especially in depositional environments, is in fairly deep layers of sediment where oxygen and other nutrients are largely unavailable. Anaerobic processes also occur in sediments but rely on conditions and nutrients that may not be available. Anaerobic processes are especially important for chlorinated COCs in that dechlorination is favored by anaerobic conditions. The assessment of the natural attenuation of chlorinated compounds is relatively well developed in groundwater literature, but no assessment of its applicability to sediment conditions has been completed. The assessment of natural attenuation of chlorinated compounds in groundwater, however, is focused on the relatively rapidly degrading lighter organic solvents that are rarely sufficiently hydrophobic to be of interest as sediment contaminants.

To form a complete picture of chemical and biological transformation processes at a particular site, high resolution sampling of both parent compounds and potential daughter products with measurements over time is required. There have been efforts to accomplish this with PCBs, which have gained notoriety as being refractory or nonbiodegradable, although these labels have been challenged by reports that have shown the capability of certain microbes to dechlorinate PCBs. In most cases, dechlorination of PCBs renders them less toxic; hence, much work has been achieved in this area. The question still remains as to whether natural microbes in sediments can mediate the dechlorination of PCBs at a sufficient rate to compete with other remedial options. If this can be proven, *in situ* containment of the PCBs during this process represents a very attractive remedial alternative that reduces contaminant mass without the concerns for adverse environmental impacts that occurs during removal options.

Several investigations have revealed that reductive dehalogenation is a main pathway that converts dichlorodiphenyltrichloroethane (DDT) to dichlorodiphenyldichloroethene (DDE) (Glass 1972 and Zoro, et al. 1974) and lindane to benzene (Beland, et al. 1976) under reducing environments. Pesticides such as toxaphene have been known to be anaerobically degraded in soils and salt marsh sediments (Parr and Smith 1976 and Williams and Biddleman 1978). However, the role of these biological processes has been disputed by some who argue that the reduction purely is chemical in nature (Zoro, et al. 1974). Reduced iron porphyrins may be important in catalyzing these reductive chemical dehalogenation reactions. It was suggested by Beland, et al. (1976) that those organochlorine compounds with first reduction potentials more positive than -1.521 V (versus standard calomel electrode) will undergo reductive dehalogenation while those with potentials less than -1.757 V will not. Most PCBs have reductive potentials between -1.771 V and -2.126 V and can be regarded as nonreactive under purely chemical reducing conditions.

The depletion of PCBs in sediment cores of the Upper Hudson River has been reported by Brown, et al. (1984) and has been suggested to be biologically mediated by anaerobic bacteria. Tiedge and Quenson (1988) also reported the anaerobic dechlorination of PCBs by microbes from Hudson Bay sediments. Sulfito, et al. (1983) provide ample evidence of the reductive dehalogenation of haloaromatics by microbial methanogenic bacteria in culture. These

reductive dehalogenation processes mediated by bacteria have been observed to be specific to certain PCBs. For example, monochlorobiphenyls have been degraded by certain microorganisms, leaving the higher chlorinated congeners untouched (Shiaris and Saylor 1982). Furukawa, et al. (1978) reported the rates of biodegradation of 31 chlorobiphenyl congeners by two species of microbes. Tetra- and penta-PCBs were shown to have very low rates of biodegradation. 2,4,4'- and 2,4,5-tri PCBs degraded between 6 and 25 times faster than the 2,2',5-tri PCBs.

Active Sediment Transport Processes

Each fate and transport mechanism discussed above was considered in the absence of sediment or bulk pore water movement. If sediment or pore water is moving, there is the possibility of advective flux which complements and generally dominates any diffusive flux. Mechanisms resulting in advective transport in sediments and their implications for COC transport is discussed below. The focus of this discussion remains on stable sediments (i.e., the active processes assumed to avoid complete scouring of the sediment bed). The situation of high suspended sediment loads was discussed previously while examining the influence of resuspended sediment on water column concentrations and exposures. Sediment transport processes to be discussed herein are such that the basic character of the sediment remains largely intact and the resulting changes in COC concentration are slow. Slow in this case implies that the dynamics of the overlying water concentration remains controlled by the sediment bed processes and not simply the steady state suspended sediment load, as discussed previously.

- *Uniform Deposition or Erosion*

Uniform deposition or erosion occurs when any deposition or erosion is occurring at a uniform and constant rate. For contaminated sediments, deposition tends to cap the COCs and reduce the net flux to the overlying water while the opposite is true with sediment scouring or erosion. Erosion enhances the COC removal rate by exposing the contaminated pore water and removing sediment particles that can carry sorbed COCs. If erosion is considered at a rate, U , as the only operative process over a layer of contaminant of depth, H , the characteristic time to remove the COCs (in this case, the time to remove all of the contamination) is simply

$$t_{ero} = \frac{H}{U} \quad (12)$$

If deposition rather than erosion is occurring, the COCs are increasingly buried. Although no contamination mass is unchanged in the sediment under this scenario (barring degradation processes), the exposure and risks associated with the sediment are decreased. A depositional environment leads to isolation of the COCs and elimination of exposure and risks to fish and higher animals. Sediment traps placed at the sediment-water interface are a common means of measuring deposition rates. Long-term deposition rates also can be inferred from radiotracers. Several radionuclides were introduced into the environment only at the onset of nuclear weapons testing, and there are radionuclides that differentiate between fission weapons and fusion weapons. Thus, the presence of a particular radionuclide can be used to date a particular layer in an undisturbed sediment core, and the location of the layer to the sediment surface defines the amount of deposition that has occurred.

- *Dune Formation and Transport by Bed Load*

In the previous two sections, deposition and erosion were considered well behaved processes that did not influence any portion of the sediment except its surface. While this may be valid

under low water velocity conditions or in a low energy environment in an estuary, this view of erosion and deposition is inappropriate under high energy or high velocity conditions. Under high energy conditions in a stream, dune-like structures are formed that progress downstream by the process of erosion on the upstream face and deposition on the downstream face (see Figure C-2). During this overturning and migration process, sediment particles are exposed and either scoured and suspended in the stream or reburied by other sediment particles. During exposure to the stream water, COCs sorbed to the sediment particles can be desorbed and COCs in the adjacent pore water diluted by mixing.

To quantify the transport rate of sorbed and dissolved COCs from the sediment bed, it is necessary to determine the spatial dynamics of the particle relocation process. The locations of particles as a function of time allow definition of the location of contamination as a function of time, the exposure time at the surface of the dune, and the total time required to overturn the dune. The onset of particle motion in a cohesionless sediment is determined by the balance between the submerged weight of a particle and the lift associated with the water flow over the particle as discussed previously. Once particles are set in motion, the following three types of movement can be recognized:

- Rolling and sliding along the sediment surface
- Suspension in the free stream
- A transitional motion characterized by saltation and particle jumps

The focus here is on low sediment transport rates associated with rolling and sliding of particles along the sediment surface. The bed load layer is approximately two particle diameters thick, and particles moving in this layer are transported up the upstream face of a dune and fall on the lee side. The steady growth on the lee side results in a slow downstream migration of the dune. When the transport is such that the migrating sediment waves do not lose their shape, a state of limiting equilibrium is said to exist (Haque and Mahmood 1986). Savant-Malhiet and Reible (1993) developed a model of contaminant dynamics under these conditions that provides a means to estimate sediment recovery rates by bed load transport of surface particles. The model is beyond the scope of the present paper but results emphasize that bed turnover and COC release can be rapid (compared to processes such as diffusion) even under relatively low sediment migration rates. The model assumes that the sediment bed is composed of cohesionless uniform diameter particles. Bed movement in broad particle size distribution sediments generally would be less due to the preferential movement of fines and the resulting armoring of the sediment dune by the heavier particles.

- *Advection due to Groundwater Flow*

Streams, lakes, and estuaries are hydraulically connected to groundwater aquifer systems. These surface water bodies can gain or lose water depending on their level relative to the aquifer. The bulk flow through the sediment can result in an advective flux of COC that complements the diffusive flux described above. The relative magnitudes of advective and diffusive transport can be quantified with a Peclet number

$$N_{Pe} = \frac{vH}{D_{eff}} \quad (13)$$

Here v is the velocity perpendicular to the contaminated layer of height (H). For low values of the Peclet number, the process is dominated by diffusion and the previous discussion applies. For large values of the Peclet number, advection dominates and the characteristic time for recovery of a layer of sediment of height (H) is

$$t_{adv} = \frac{H}{v} R_f \quad (14)$$

Here, as with the erosion case, the characteristic time presented is the time to completely remove the COCs. The characteristic time for diffusion was the $1/e$ time or the time to reach 37% of the initial concentration in the sediment. Although these times are indications and not exact and the different definitions are not generally significant, their different bases must be recognized.

It is important to note that the retardation factor arises in Equation 14. Since advection is a pore water process, it is subject to retardation due to accumulation on the immobile solid particles and enhancement by sorption onto mobile fine and dissolved particulate matter. Advection differs from the erosion processes discussed previously that involve both particle and associated pore water movement. Therefore, advection is not retarded by sorption onto an immobile phase.

The measurement of groundwater flow velocities and, in particular, stream bed seepage velocities is difficult. Seepage meters (i.e., containers covering a portion of the sediment bed that collects any water that seeps through the sediment) are common. It is particularly important that such measurements reflect the seasonal nature of groundwater flow. Unfortunately, the wide variability in sediment characteristics (e.g., permeability) make interpretation of such data difficult. A better measure is the groundwater flow in the surrounding aquifer because it represents an average inflow or outflow from the water body. The general direction of the groundwater flow can be measured by piezometers placed at different elevations below the bed of the water body. If the underlying water head is greater than the head in the stream, inflow occurs; outflow occurs in the reverse situation. In addition to defining direction, this information is used to estimate flow rate if the permeability of the medium can be measured. An alternative means of detecting slow vertical transport by groundwater flow is through tracers, such as described by Cornett (1989).

- *Advection due to Local Pressure Variations on the Sediment Surface*
Even in the absence of a mean hydraulic gradient, an advective flux may still be observed. Local pressure variations of the order of 100 to 1,000 Newtons per square meter (N/m^2) can be observed between the upstream and downstream faces of the typically triangular shaped dune-like sediment structures that form at the sediment-water interface. Figure C-2 includes a depiction of the basic character of the flow over these dunes. The flow is characterized by a simple turbulent shearing flow on most of the upstream face and a recirculating wake on the downstream face that also influences a portion of the subsequent sediment dune. It is the weak and poorly organized flow in the wake that results in the immobility of these sediment grains under bed load conditions. In addition to modifying the sediment dynamics, the formation of a separated recirculating wake on the downstream face results in an observed pressure difference. Thibodeaux and Boyle (1987) approximated the dunes as simple geometric shapes such as cylinders and showed that measured pressure data on those simple shapes are sufficient to generate a potentially significant in-bed flow.

Savant, et al. (1987) used the pressure profile data generated by Vittal, et al. (1977) to predict head distributions and, through Darcy's law, velocity profiles in triangular sediment dunes in a laboratory flume. The relatively high pressure on the upstream face resulted in a flow down and into the dune turning upward and out of the lower pressure downstream face. Savant, et al. (1987) showed excellent agreement between the predicted and observed flow patterns. The

experiments and modeling indicated that the induced in-bed flow could extend as much as four to five dune heights into the sediment. By using measured permeabilities and estimated dune geometries in several river systems, Savant, et al. (1987) showed that this mechanism could lead to advectively dominated transport in these rivers. In-bed N_{pe} ranged from the order of 100 in the Nile (Egypt) and Red (Louisiana, U.S.) Rivers to 300 to 1,700 in the Mississippi River (Louisiana, U.S.). This mechanism likely is important mostly in sediment beds subject to significant organism burrowing activity and in permeable, sandy sediments as might be observed on the continental shelf of the coastal US.

In summary, the following factors are required before localized in-bed transport processes are important:

- Uneven bed surface
- Significant water flow over these surfaces
- Sandy or other permeable sediment bed

These conditions are most likely to occur in riverine or near-shore marine environments in which the flows are sufficiently high so that the sediment bed is largely composed of permeable sands. Note that much of the continental shelf is composed of sands and advection is receiving considerable attention for this region (Proceedings of Workshop on Animal-Sediment Relations 1998).

- *Bioturbation-Induced Transport*

The previous discussion largely considered sediment as a collection of sediment particles separated by water-filled pore spaces. In reality, a variety of plants and animals reside in sediments. Root systems and animal burrows can provide channels for preferential water flow and COC transport. Even more importantly, the near surface sediment is often continuously mixed by the activities of benthic organisms such as clams and worms. Sediment processing by animals residing in the upper layers includes burrowing, ingestion/defecation, tube building, and biodeposition. Taken together, these processes are termed bioturbation; a depiction of the type of animals that can be present and their interaction with sediments is provided on Figure C-3. The net result of bioturbation is the vertical and horizontal movement of sediment particles and pore water. COCs on the particles or in the pore spaces likewise are transported in the bioturbation process, which is especially important in the transport of hydrophobic COCs that are heavily retarded by pore-water processes.

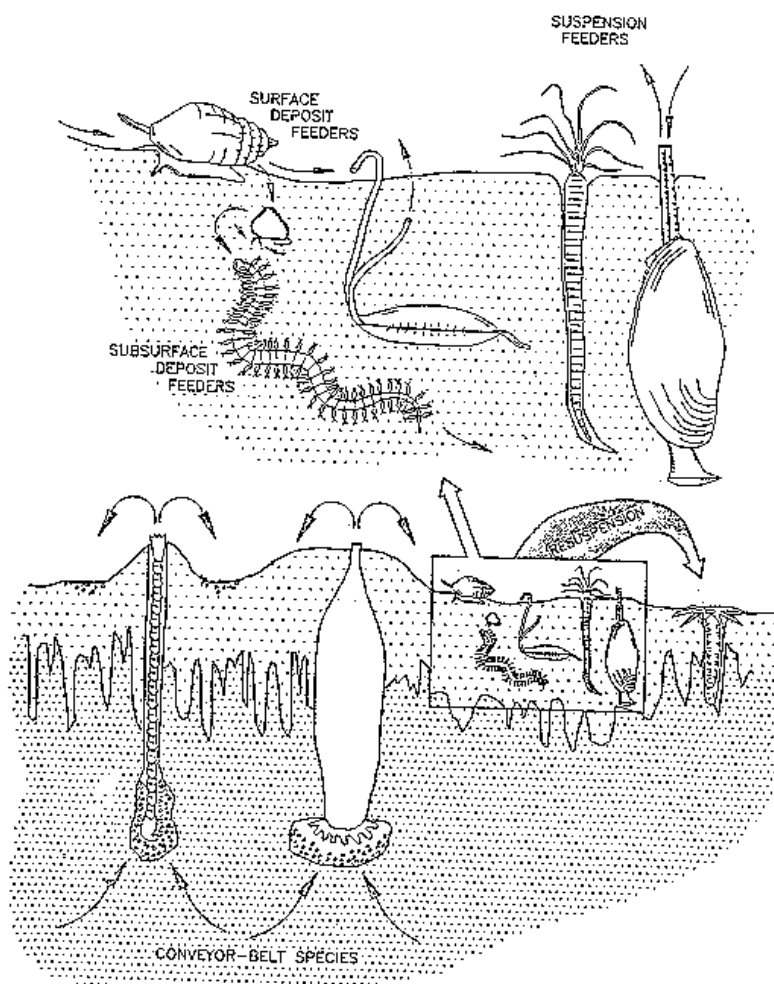


Figure C-3. Feeding types of benthic organisms after Rhoads (1974).

The possibility of bioturbation as a transport mechanism has long been recognized. Boudreaux (1986a) refers to references on the effect of biological activity on sediment composition and properties as old as Davison (1891). A wide variety of animal organisms that live on and in the upper sediment layer exist, and they interact with sediments in a variety of ways. If the scale of the individual mixing events is very small compared to the depth and area of the sediment of interest (e.g., the depth and area of a box core sample of a sediment), then bioturbation gives the appearance of a diffusive process. Boudreaux (1986a) examined the conditions under which a diffusive model of bioturbation is appropriate. Because of the decrease in organism density and activity with depth in sediment, some investigators have speculated that a depth-dependent biodiffusion coefficient is appropriate. However, as Boudreaux (1986b) noted it is often difficult to differentiate between a constant and depth-dependent biodiffusion coefficient on the basis of available data.

If the scale of the individual organism-related mixing events is not sufficiently small so that the appearance of a random, diffusive process is achieved, other models must be postulated. Worm tubes and other macroscopic animal burrows can significantly enhance the COC transport rate across the sediment-water interface. In addition, some marine worms feed by passing sediment through their bodies from depth to the surface, a process that has been called conveyor-belt feeding Rhoads (1974). Neither of these processes can be described on a fundamental basis as diffusive processes. However, as indicated by Boudreaux and Imboden (1987), even nonlocal (i.e., macroscale) mixing events of this sort often give rise to COC profiles that give the appearance of a diffusive transport process.

Therefore, although diffusion characterized by a constant biodiffusion coefficient is not an adequate description of the actual physical processes that constitute bioturbation, it can be used to correlate the overall characteristics of the observed COC transport. The primary difficulty with such an approach is that due to the inadequacy of the assumption of a diffusive process, biodiffusion coefficients that adequately describe a particular sediment may not be applicable to another site, even a nearby site, if the density, distribution, and type of organisms are different.

Despite this, biodiffusion coefficients can show surprising similarity between different sites. For example, Aller (1982) estimated an effective biodiffusion coefficient of 5 to 32 cm²/year (yr) in Narragansett Bay, Brownawell (1986) estimated a biodiffusion coefficient of 9.4 cm²/yr in Buzzards Bay, and, finally, Thibodeaux (1989) using the data of Spaulding (1987) observed an essentially identical biodiffusion coefficient of 9 to 13 cm²/yr in the Upper Estuary of New Bedford Harbor. An analysis of the data of Matisoff (1982) suggests that more than 2/3 of the available measurements in both freshwater and saltwater conditions suggest an effective particle diffusion coefficient of 0.3 to 30 cm²/yr. The vast majority of these measurements of effective bioturbation diffusivities were made by estimating particle reworking rates using strongly sorbed radionuclides associated with nuclear testing. The time and amounts of the release of particular radionuclides and their current distribution within sediment provide allow the measurement of the reworking rates in stable sediments.

The measurement range of 0.3 to 30 cm²/yr is consistent with the measurements of Reible, et al. (1996) of effective bioturbation mass transfer coefficients equivalent to 1 to 10 cm²/yr for tubificid worms at field densities in freshwater sediments. The tubificid worms studied were found at very high densities and represented the bulk of the biomass in all sediment bioassays conducted during the ARCS program in the Great Lakes (USEPA 1993b). These worms are head-down deposit feeders capable of processing ten or more times their own weight in sediment every day. In addition to transporting significant quantities of sediment to the sediment-water interface, these organisms also apparently contribute to the degradation of at least PAH compounds (Millward, et al. 1998). There is very little information on the effect of benthic organisms on the COCs, but they may represent significant fate processes in the surficial sediments.

Focusing specifically on the transport effect of bioturbation, the diffusive models discussed previously can be applied to bioturbation. The characteristic time for recovery of a layer of contaminated sediment of depth, H , assuming uniform bioturbation over the entire layer is given by

$$t_{bio} = \frac{4}{p^2} \frac{H^2}{D_{bio}} \quad (15)$$

A key difference between biodiffusion and molecular diffusion is that biodiffusion includes particle movement so there is no retardation factor in the characteristic time. Therefore, for a hydrophobic COC that is strongly sorbed to the sediment, bioturbation is a much more effective mixing process than molecular diffusion in the pore water. As stated previously, effective molecular diffusion coefficients in sediments (as given by Equation 8) are on the order of 10⁻⁶ cm²/s, which corresponds to approximately 30 cm²/yr or about the same as the largest of the typical effective bioturbation diffusion coefficients. For many elemental species, whose leachable fraction may partition only weakly into the solid phase, the enhancement by bioturbation is minimal. For a hydrophobic COC such as pyrene, however, bioturbation is expected to control COC migration in the upper layers of a stable sediment bed. In general,

bioturbation is the primary migration mechanism of sorbing COCs in stable surficial sediments unless the physical character of the sediment or its level of contamination precludes significant colonization by benthic organisms.

SUMMARY AND CONCLUSIONS

Exposure and risk to the higher trophic organisms (e.g., piscivorous birds, and mammalian predators) are controlled by the relative rates of the various natural fate and transport processes. COCs that are buried, sequestered, or degraded pose essentially no risk, while COCs that can be mobilized by natural physical, chemical, and biological processes can pose significant risks. This paper quantitatively summarizes the most important fate and transport processes that attenuate COC levels and exposure in river, estuarine, lacustrine, and marine sediments.

Exposures and risks to fish and higher animals were attributed to one of three contaminant pathways. The first pathway, direct exposure to resuspended sediment, can be described generally by assuming chemical equilibrium between the suspended sediment load and water. The second pathway, indirect exposure to contaminated sediment through the food chain, can be described generally by chemical equilibrium between the bed sediment and the benthic organisms that inhabit the sediment-water interface. The third pathway, direct exposure to fate and transport processes from stable sediments, requires analysis of the fate and transport processes in the sediment.

While many of the fate and transport processes vary significantly in importance from site to site, it is possible to rank the potential importance of each mechanism using characteristic times. Characteristic times are order of magnitude estimates of time required to remove COCs from an initially uniformly contaminated layer of height (H) by each of the various transport mechanisms. In most cases, the characteristic times represent 1/e times. In the case of advective processes, the characteristic times represent complete removal times. Table C-2 summarizes the relationships comparing the characteristic recovery times of contaminated sediment by each of the processes. Processes that exhibit a shorter characteristic time are likely to be the most important transport processes.

Table C-2
Summary of Characteristic Times of Sediment Fate and Transport Processes

Process	Characteristic Time Relationship	Typical Range of Key Parameter Values	Illustrative Value of Characteristic Time [†]
Diffusion	$t_{diff} = \frac{4}{p^2} \frac{H^2 R_f}{D_{eff}}$	$R_f > 1,000$ (Hydrophobic organics) $D_{eff} \sim 10^{-6} \text{ cm}^2/\text{s}$	1,280 years
Advection	$t_{adv} = \frac{H R_f}{v}$	Groundwater velocity, v , widely variable	100 years
Sediment Erosion	$t_{ero} = \frac{H}{U}$	Bed erosion rate, U , widely variable	10 years
Bioturbation	$t_{bio} = \frac{4}{p^2} \frac{H^2}{D_{bio}}$	$0.3 \text{ cm}^2/\text{yr} < D_{bio} < 30 \text{ cm}^2/\text{yr}$	13 years
Reaction	$t_{fate} = \frac{1}{k_{rxn}}$	Reaction rate, k_{rxn} , widely variable	100 years

* Assumes a 10 cm thick surficial layer contaminated with a hydrophobic organic with an effective retardation factor of 1,000. A groundwater velocity of 1 meter/yr, a bed erosion rate of 1 cm/yr, an effective bioturbation diffusion coefficient of $3 \text{ cm}^2/\text{yr}$ and a reaction rate of 0.01 yr^{-1} are assumed for purposes of illustration.

In general, active sediment processes in which COCs are transported by bulk movement of pore water or particles exhibit the shortest characteristic transport times and, therefore, the fastest sediment recovery times. These processes also exhibit the highest sediment to water fluxes and the potential for relatively high exposure and attendant risk to fish and higher animals. For example, in Table C-2, sediment erosion and bioturbation are the only sediment bed processes occurring at significant rates. For hydrophobic or other strongly sorbed COCs, the processes that result in particle movement are much more significant than transport via pore water processes. In high energy environments, sediment resuspension and movement are likely to be dominant factors in particle transport; in low energy environments, bioturbation is likely to dominate COC movement in the upper layer of sediments. It is important to note that short characteristic times imply short sediment recovery times, but may also result in higher exposure and risk to fish and higher animals in the overlying water during the period of recovery.

Although Table C-2 provides general guidance as to the relative importance of various fate and transport mechanisms, it is important to note that each site is different and that only through detailed studies can the dominant process at a particular site be identified and quantified, allowing the evaluation of the effect of these processes on natural recovery and more active remedial options. In all cases, the nature of the physical environment (e.g., sediment texture, water depth and flow velocities, temperature effects, climatographic effects), the nature of the COCs (e.g., hydrophilic versus hydrophobic, persistent versus ephemeral), and the biotic elements of the environmental setting all contribute to the fate of the COCs in sediments.

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