

CHAPTER 21

Contaminant Processes in Sediments

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21.1 INTRODUCTION

Many of the most toxic and most persistent environmental contaminants in bodies of water are strongly associated with sediments, either suspended or settled to the bed. As a result, the transport and fate of sediments also often define the dynamics of associated contaminants. Contaminants are also influenced, however, by a variety of physical, chemical, and biological processes that involve no net movement of sediments. These processes include pore-water transport processes such as diffusion and advection and sediment mixing processes such as reworking by benthic organisms that involve no net downstream particle movement. Understanding these processes is critical to development of appropriate strategies for managing the risks these contaminants may pose to human health and the environment. Assessment of the processes that control contaminant migration and fate in a water body allows development of a conceptual model of the system and identification of intervention approaches that are most likely to succeed. Evaluation of these processes provides an assessment of the potential for natural attenuation of contaminants in a system. These processes are also critical to the evaluation of more active remedial approaches, such as dredging or capping, because the success of these approaches typically depends upon the fate of the residual contaminants in the water body. This paper will examine processes that influence the fate and transport characteristics of contaminants in sediments and interaction of these processes with common management or remedial approaches.

Any attempt to summarize and compare natural processes in sediments must recognize the different environments in which contaminated sediments are found. The relative importance of these processes differs 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 processes influencing

contaminants and build 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 Fig. 21-1 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;
- Interfacial transport processes (bed to water column or vice versa), including sediment deposition and resuspension, bioturbation, and water-side mass transfer.

Table 21-1 summarizes the relative importance of these processes in various sedimentary environments. These processes and 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 that influence contaminants in sediment beds is the energy of the overlying flow. In high-energy environments, bed 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 often allow oxygen transport deep within the sediment. In low-energy environments, significant deposits of fine-grained sediments exist, 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.

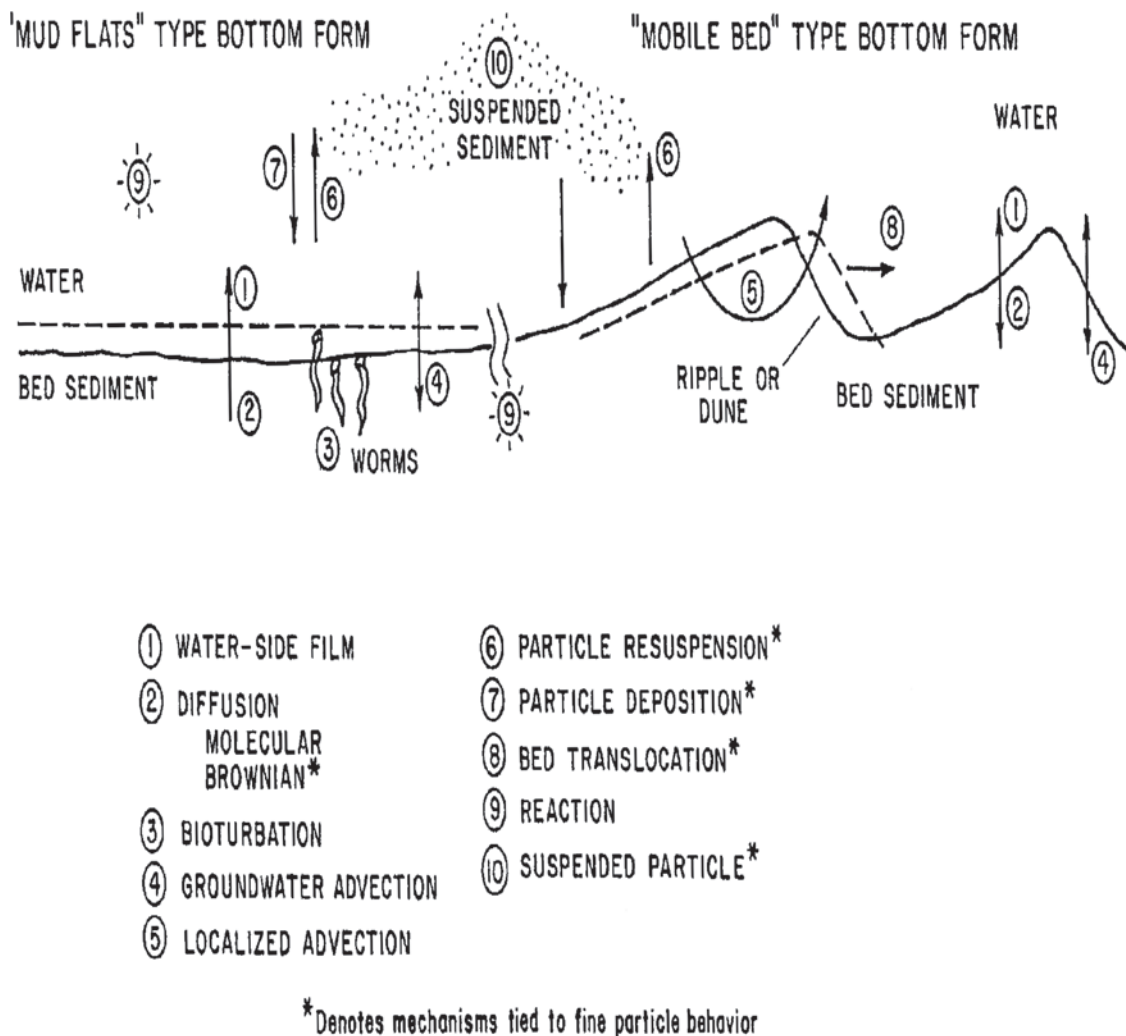


Fig. 21-1. Depiction of selected processes at the sediment-water interface.

21.2 CONTAMINANTS OF CONCERN

Relatively uncontrolled historical wastewater effluents often introduced priority pollutants and other contaminants of concern to the environment. Many of these compounds tended to accumulate in sediments because of persistence and hydrophobicity. Because wastewater effluents are now more controlled, the accumulation of contaminants in the sediments is reduced and other sources, such as atmospheric deposition and rural and urban runoff, may be equally or more important in contributing individual pollutants to the sediment. In addition, the sediments now often constitute a significant source controlling surficial water quality. Contaminants that do not strongly associate with solids, such as polar organic compounds or soluble metals, rarely accumulate in sediments, because these compounds are efficiently released to the overlying water. In this section we will examine some of the most important sediment contaminants and the physical

and chemical characteristics that relate to fate and mobility in the environment. These contaminants include conventional pollutants such as nutrients and oxygen-demanding contaminants, heavy metals, pesticides, polycyclic aromatic hydrocarbons (PAHs), and chlorinated organic compounds such as polychlorinated biphenyls (PCBs) and multiply chlorinated benzenes.

21.2.1 Conventional Pollutants

Conventional pollutants include nutrients, oxygen demanding contaminants, and undifferentiated oil and grease. Sediments may harbor a significant inventory of nitrogen and phosphorus, release of which may dramatically change the biological characteristics of the overlying water. A variety of organic and inorganic compounds in sediments consume oxygen. The cumulative effect of these reactions is measured by sediment oxygen demand, a parameter similar

Table 21-1 Sediment Processes and 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 sorption Aerobic and anaerobic biotransformation Biotransformation of organic matter (e.g., gas formation)
Riverine	Low- to high-energy environment Depositional or erosional environment Potential for significant groundwater interaction Significant variability in flow and sediment characteristics within and between rivers	Local and generalized groundwater advection Sediment deposition and resuspension Aerobic biotransformation processes in surficial sediments (anaerobic at depth) Bioturbation
Estuarine	Generally low-energy environment Generally depositional environment Generally fine-grained sediment Grading to coarse sediment at ocean boundary	Bioturbation Sediment deposition Water-side mass transfer limitations Aerobic and anaerobic biotransformation of contaminants 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

in significance to oxygen-demanding measures in the overlying water. Sediment oxygen demand serves to reduce available oxygen and encourage anaerobic conditions within the sediment. This may affect the rate of fate processes, such as biological degradation of contaminants in the sediments, and the chemical state of metals, influencing mobility. The sediment oxygen demand can also impact oxygen levels in the overlying water. There are no specific levels of oxygen demanding constituents that are considered problematic. The impact of these contaminants depends upon the dynamics of the sediment, associated groundwaters, and overlying water column.

Long-chain nonpolar organic compounds, such as oil and grease, associate strongly with solids and sediments. Measures of these compounds include both oil and grease concentration and total petroleum hydrocarbon concentration. The source of these compounds is generally petroleum hydrocarbon production or processing facilities, or facilities that use or process significant amounts of these compounds. In addition, municipal and industrial wastewater-treatment effluents can lead to significant accumulation of hydrocarbons in sediments over time. Because many of these sources are much more carefully controlled than in times past, oil and grease or total petroleum hydrocarbons levels in sediments often represent excellent indicators of historical pollution.

21.2.2 Heavy Metals

The toxic metals and metalloids include antimony, arsenic, beryllium, cadmium, copper, lead, mercury, nickel, silver, thallium, and zinc. Importantly, these pollutants are nonbio-degradable, toxic in solution, and subject to biomagnification. The chemistry of many of these compounds is complex in sediments. A portion is generally chemically fixed and largely unavailable to fish and other organisms without significant chemical changes in the sediment. Often a portion is ion-exchangeable and may become available simply with the substitution of a more surface-active contaminant. Finally, a portion is soluble, mobile, and directly available for uptake by organisms.

Historically, the metals extraction and processing industries, as well as urban and rural runoff, provided the most significant sources of these elements. Lead was widely distributed in the environment as a result of the use of tetraethyl-lead in gasoline to control premature ignition (knocking). These sources have largely been controlled. Some sources of metals, however, are only poorly controlled and represent a continuing source of metals to sediments. These sources include leaching from abandoned mining sites and urban runoff. Unlike oxygen-demanding wastes, these pollutants are not easily neutralized or assimilated by natural processes.

21.2.3 Polycyclic Aromatics

The polycyclic aromatic hydrocarbon compounds are used as chemical intermediates and are present in fossil fuels. Polycyclic aromatics tend to be present in coal liquids and the heavier oil stocks as a result of lesser volatility. Many of the compounds have been found to be carcinogenic in animals and are assumed to be carcinogenic in humans. These tend to be intermediate in persistence and bioaccumulation potential compared with monocyclic aromatics/halogenated aliphatics and the PCBs. Production during combustion of industrial fuels and oils (diesel, coal liquids, heavy fuel oils) has resulted in the presence of PAHs at old industrial sites where contamination levels might be especially high. Sediment contaminant with PAHs is often associated with historical release of oils in wastewater but atmospheric deposition contributes to widespread contamination and specific locations may be influenced by oil seeps. Examples of PAHs include naphthalene, fluoranthene, pyrene, and chrysene. The compounds composed of two aromatic rings (naphthalene) tend to be the most volatile, soluble, and mobile, while solubility and volatility tend to decrease as the number of rings increases.

21.2.4 Pesticides

Priority pesticides are generally chlorinated hydrocarbons. These include such compounds as aldrin, dieldrin, DDT (dichlorodiphenyltrichloroethane), DDD (dichlorodiphenyl-dichloroethane), endosulfan, endrin, heptachlor, lindane, and chlordane. These organic compounds are readily assimilated by aquatic animals, and are subject to *bioaccumulation* and *biomagnification*. Bioaccumulation is the uptake and partitioning of contaminants by organisms, whereas biomagnification is the concentration of pollutants by natural processes such as the food chain. Greater amounts of pollutants may be accumulated higher in the food chain. These particular pesticides are also persistent contaminants. DDT, for example, remains an environmental contaminant many years after being banned in the United States.

DDT is an excellent example of the potential problems associated with these compounds. Although not considered extremely toxic and despite decreased usage during the 1960s, DDT use was banned in the United States in 1972 (although production and export continued after 1972) as a result of persistence and potential for biomagnification. Hickey et al. (1966), for example, reported biomagnification of DDT by more than 170,000 times between Lake Michigan sediments and fish-eating birds. Bottom-feeding crustacea exhibited about 30 times sediment concentrations, where as the fish that fed off the crustacea exhibited concentrations about 10 times still higher than found in the crustacean. Finally, fish-eating birds exhibited concentrations of DDT 500 times higher than observed in the fish. The magnification at each level is dependent on the feeding habits

and animal metabolism and, because the organochlorines tend to build up in the lipid or fat fraction of the body, the proportion of body fat.

21.2.5 Chlorinated Organic Compounds

Multiply chlorinated, high-molecular-weight organic compounds such as hexachlorbenzene and PCBs tend to be strongly hydrophobic and therefore partition into sediments. Due to low degradation rates, tendency to sorb, and high molecular weight, these compounds tend to exhibit low mobility in the environment and are persistent in sediments. PCBs are complex mixtures of organochlorines that are extremely stable. In addition, as with the organochlorine pesticides, PCBs are readily assimilated by aquatic animals and soluble in body fats and will biomagnify in the food chain. Although the toxicity of many of the individual PCBs is relatively low, specific isomers plus trace contamination with other chlorinated compounds give rise to significant health concerns. As a result, PCB production was banned in the United States in 1979. It should be emphasized that PCBs are a complex mixture of compounds and, in fact, are generally named only by the total percentage of chlorine in the mixture. Specific PCB mixtures are referred to as Aroclors, and Aroclor 1254 is 54% chlorine and Aroclor 1260 is 60% chlorine.

Again, as a result of persistence, significant quantities remain in the environment. Industrialized harbor areas in the Great Lakes and northeastern United States are often contaminated with PCBs. Fish advisories exist in many of the Great Lakes as a result of health concerns from eating PCB-contaminated fish. Because of the potential for PCBs to sorb onto organic materials in sediments and in fish lipids, such advisories are aimed primarily at fatty, bottom-feeding fish where PCB concentration is the highest, and will biomagnify in the food chain.

21.3 CONTAMINANT RELEASE AND EXPOSURE PATHWAYS

The risks of sediment contaminants to higher organisms such as fish and animals that feed off fish can arise via one of the following three pathways:

- Exposure by contaminant release due to erosion and resuspension of the sediment bed;
- Exposure by predation and harvesting of plants and animals living directly exposed at the contaminated sediment-water interface or by incidental ingestion of contaminated bed sediments;
- Exposure by contaminant release in dissolved or other form from a stable sediment bed by any of a variety of stable bed processes including advection, diffusion, and bioturbation.

Each of these pathways involves interaction of the higher organisms with the contaminants of and near the sediment-water interface. The absolute and relative importance of these pathways largely depends upon the rate of the various fate and transport processes that influence the pathway. Each of these will be examined in more detail.

These pathways are largely limited to the upper few cm of sediment, and thus exposure and risk due to sediment contaminants is largely related to surficial sediment concentrations. Due to significant erosion, it may be that the dynamics of the surface layer may result in exposure of previously buried contaminants, but at any given time, the surficial sediment concentrations largely define exposure and risk to organisms in the overlying water. In recognition of this fact, the surface-area-weighted average concentration ($\langle W_s \rangle$) has come to be used as a good indicator of exposure and risk:

$$\langle W_s \rangle = \frac{\int_A W_s(0) dA}{\int_A dA} \quad (21-1)$$

where

$W_s(0)$ = Surficial sediment-contaminant concentration (e.g., in $\mu\text{g/g}$), which may vary in space over the area A .

Similarly, the time-integrated $\langle W_s \rangle$ is related to the time-integrated exposure, or dose,

$$\text{Integrated exposure} \sim \int_t \langle W_s \rangle dt \quad (21-2)$$

The assessment of exposure is thus largely reduced to defining quantitatively the relationship between exposure and $\langle W_s \rangle$ (or time-integrated $\langle W_s \rangle$) for the different processes relevant to a particular environmental system. Especially challenging is the definition of future exposure associated with contaminants currently buried below the surface layer. The use of a relationship such as Eq. (21-1) does not imply that currently buried contaminants will not become a source of exposure and risk at some point in the future.

21.3.1 Exposure by Contaminant Release from Resuspended Sediment

The dominant characteristic that controls direct exposure of fish and other animals to contaminated sediment is resuspension and erosion of particles from the sediment bed. Since most persistent sediment contaminants are associated with the solid phase, any mobilization of this phase dramatically increases contaminant mobility. As a result, contaminants can be distributed over large areas, and significantly increased water-column concentrations can be observed relative to less active sediment-water transport. Erosion and resuspension

conditions also hinder natural recovery that might occur in less active environments through deposition and burial of the contaminated sediment.

Under high-energy conditions in a stream, significant sediment transport occurs and individual sediment particles can be carried downstream either by bed-load or by suspended-load transport. This process normally results in the formation of dunes, ripples, and antidunes that progress downstream by erosion on the upstream face and deposition on the downstream face. 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, contaminants sorbed to the sediment particles can desorb, and contaminants in the adjacent pore water can be released into the overlying water.

Should significant erosion and resuspension occur, the water-column concentration tends to approach the equilibrium defined by desorbable contaminants in the resuspended sediment. If K_{sw} is a distribution coefficient of the sorbed contaminant between the sediment and the water (units of volume per mass, e.g., cm^3/g), the aqueous phase concentration, C_w (mass/volume, e.g., $\mu\text{g}/\text{cm}^3$), is a function of the resuspended sediment concentration in the overlying water, C_s (mass/volume, e.g., g/cm^3). If the sediment carries an initial contaminant concentration, W_s (mass/mass, e.g., $\mu\text{g}/\text{g}$), the contaminant concentration in the overlying water is given by

$$C_w = \frac{C_s W_s}{1 + C_s K_{sw}} \quad (21-3)$$

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. Theoretical predictions normally assume linearity, as indicated in Eq. (21-3), and complete reversibility, but deviations are often observed in practice. Equation (21-3) may still prove useful, however, if measured, rather than predicted, values of the effective partition coefficient are employed.

Equation (21-3) shows that for complete desorption (low suspended-sediment concentrations), the water concentration is simply the suspended-sediment concentration times the initial contaminant concentration in the sediment. At high suspended concentrations, however, the overlying water approaches equilibrium with the contaminated sediment bed as given by the equation

$$C_w = \frac{W_s}{K_{sw}} \quad (21-4)$$

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 because only a small fraction of the metals is typically available for partitioning. 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 L/kg. For both organic and metal species, a site-specific measurement of the sediment-water partition coefficient is preferred.

As shown by Eq. (21-3), the concentration and exposure in the overlying water is a function of the concentration of sediment resuspended. The concentration of resuspended sediment is a function of the rate and depth of erosion. The ability to predict the rate of erosion based solely upon physical characteristics of the sediment such as grain size and density remains largely limited to cohesionless, coarse-grained particles. Site-specific measurements of sediment response to shear flows are needed to characterize erosion of cohesive, fine-grained sediment. Erosion of both cohesive and non-cohesive sediments is discussed in detail in Chapters 2 and 4.

Because contaminants tend to be strongly associated with fine-grained sediments, the discussion of Chapter 4 is especially relevant. As discussed there, erosion of a sediment bed can occur via one of four processes: surface erosion, mass erosion, fluid mud generation, and fluid mud entrainment. Of these, surface erosion is likely to be the most important except in specific locations where mass erosion (erosion of clumps of bottom material) or fluid mud entrainment (mobilization of very soft sediments) may be important.

For cohesive sediments, the friction velocity required to produce particle motion is significantly larger for a given particular particle size than for noncohesive sediments. Offsetting this is the fact that cohesive sediments tend to be very fine-grained and thus may be subject to significantly more erosion than coarse-grained noncohesive sediments. The property of cohesiveness is a complicated function of particle size, bulk density, mineralogy, organic content, and salinity. These properties vary significantly with position and time. Often, due to the lack of sufficient data on the deposit properties with position and time, these variations are not fully incorporated in sediment transport models. Instead, the rate of erosion, E (i.e., the sediment erosion flux in $\text{g}\cdot\text{cm}^{-2}\cdot\text{hr}^{-1}$), is related to the local bed density, ρ_s , and the probability of a particle becoming resuspended, P_{ero} , which for a cohesive sediment is related to the bottom shear stress, τ_b , and the bed density,

$$E = P_{\text{ero}} \tau_b^N \rho_s = A \tau_b^n \rho_s^m \quad (21-5)$$

The exponent on the bottom shear stress depends on the bed properties but is typically between 2 and 3 for cohesive sediments. This implies that the erosion rate depends on the fourth to sixth power of stream velocity, because bottom shear stress typically depends on the square of velocity. The strong dependence on stream velocity emphasizes that a

critical component of any effort to model sediment dynamics is knowledge of the stream hydrodynamics. Although it is not yet possible to predict the relationship between erosion rate and shear stress for cohesive sediments, it is possible to make measurements from which the values of A , n , and m can be determined (McNeill et al. 1996). The flux of contaminants returned to the sediment column, F_{ero} (e.g., in $\mu\text{g}\cdot\text{cm}^{-2}\cdot\text{hr}^{-1}$), as a result of erosion is then given by

$$F_{\text{ero}} = E W_s \quad (21-6)$$

where

W_s = sediment contaminant concentration (e.g., in $\mu\text{g/g}$).

When sediment is dredged, an artificial situation is created that is equivalent to high flow-related erosion of the sediment bed. 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 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 are available. DiGiano et al. (1995) also developed an experimental protocol for estimating metals release and equilibration with a body of water during dredging.

Deposition may serve to isolate contaminants from the overlying water column and reduce the influence of erosion. The net sediment transport is the difference between the erosion rate, defined above, and the deposition rate. In general, the rate of deposition, D , can be modeled with relationships of the form

$$D = P_{\text{dep}} w_s C_s \quad (21-7)$$

where P_{dep} is the probability of capture of the depositing particle, w_s is the vertical settling velocity of the particles, and C_s is the suspended-sediment concentration. The probability of deposition tends to decrease as the bed shear stress increases. The local particle concentration can be modeled as a decreasing exponential function of height above the bed (Jones and Lick 2000). There are also significant differences between cohesive (flocculating) sediment and noncohesive (i.e., sandy) sediment. Sandy sediment deposition can be modeled employing the formulation of Cheng (1997). In cohesive sediments, deposition is affected by aggregation and/or disaggregation processes that are complex functions of sediment and stream conditions (Lick and Lick 1988). The flux of contaminants, F_{dep} , carried by deposition to the sediment bed is given by

$$F_{\text{dep}} = D K_{\text{sw}} C_w \quad (21-8)$$

Here the contaminant concentration on any depositing particles is assumed to be given by equilibrium with the overlying water concentration. The quantity $K_{\text{sw}} C_w$ is the sediment concentration that would be in equilibrium with the overlying water, W_s^* . The net contaminant flux from the

sediment bed due to erosion and deposition processes can thus be written by combining Eqs. (21-4) and (21-6) to give

$$F_{\text{net}} = E W_s - D W_s^* \quad (21-9)$$

For a sediment bed in a state of quasi-equilibrium where the average erosion and deposition rates are equal, the net contaminant flux can be written as proportional to the difference between the actual surficial sediment concentration and the surficial sediment concentration that would be in equilibrium with the overlying water.

21.3.2 Exposure by Ingestion of Sediments or Organisms at the Bed Surface

The evaluation of the ingestion exposure pathway involves two steps: (1) the assessment of the contaminant concentrations in plants and animals living at the sediment-water interface as a result of exposure to the sediments, and (2) the assessment of uptake of these organisms by fish and other higher animals. In this paper we are focused on the processes within sediments and so will largely limit our discussion to the first step, that is, defining the relationship between the sediments and the accumulation of contaminants in the sediment-dwelling organisms. Plants and animals living at the sediment-water interface are often assumed to be in equilibrium with the surficial sediments. Similarly, incidental ingestion of sediments by fish or higher animals involves direct exposure to the surficial contamination. Thus uptake into fish and higher animals by these mechanisms depends upon the rate of ingestion of sediments or benthic organisms and the sediment concentration that is bioavailable. The contaminant capable of partitioning into the adjacent pore water from the sediment solids is often assumed to define the portion that is available for uptake by the plants and animals (USEPA 1993b). In principle, therefore, partitioning measurements or predictions can largely define the quantity of contaminant available to sediment-dwelling organisms or to higher organisms coming into direct contact with or ingesting sediments. It is important to note, however, that the contaminant concentration in the surficial sediments may not be represented well by a depth-averaged composite concentration, even though that is what is typically measured. Freshwater benthos, for example, may only populate the upper 5 to 10 cm of sediments in significant quantities. In marine sediments, animals living at the sediment-water interface tend to be larger and influence a somewhat greater depth of sediment, although the bulk of the activity remains within 15 cm of the surface. More than 90% of the 240 observations of the layer depth effectively mixed by organisms reported by Thoms et al. (1995) were 15 cm or less and more than 80% were 10 cm or less. It is the sediment concentrations within this layer that are expected to control the body burden of sediment-dwelling organisms.

If the upper sediment layers are assumed in equilibrium with the adjacent pore water and if uptake is assumed to be defined by porewater concentrations, the contaminant concentration available to plants and animals living at the sediment-water interface is as given by Eq. (21-4). The rate of uptake to a benthic or higher organism depends upon the rate of uptake or ingestion but will ultimately approach a steady state defined by a balance between uptake and elimination mechanisms. The ratio of the concentration in the organism, W_b , to that in the sediment, W_s , is termed the biota-sediment accumulation factor (BSAF). For hydrophobic organic compounds, the partitioning of the contaminant 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} . Benthic organisms are in intimate contact with the sediment and pore water and often exhibit only slow metabolism or elimination of the contaminants of interest. Thus benthic organisms rapidly approach equilibrium with these phases. The BSAF then approaches the ratio of the organic-carbon-normalized partition coefficients,

$$\text{BSAF} = \frac{W_b / f_{\text{lipid}}}{W_s / f_{\text{oc}}} = \frac{K_{\text{lipid}} C_w}{K_{\text{sw}} / f_{\text{oc}} C_w} \approx \frac{K_{\text{lipid}}}{K_{\text{oc}}} \quad (21-10)$$

In the final relationship, $K_{\text{sw}} / f_{\text{oc}}$ is equal to the commonly tabulated organic-carbon-based partition coefficient, K_{oc} , only if the desorption is governed by linear, reversible sorption to the sediment organic fraction. As indicated below, the effective partition coefficient, K_{sw} , may not be equal to $K_{\text{oc}} f_{\text{oc}}$ due to desorption resistance or nonlinear sorption-desorption equilibrium. The BSAFs for organic contaminants vary as a function of sediment, organism, and time of exposure, but the value for benthic organisms, especially those that ingest sediment as food, tends to approach unity (e.g., Ingersoll et al. 1997), suggesting that the organic-normalized partition coefficients in lipids and sediment are approximately equal ($K_{\text{lipid}} = K_{\text{sw}}$). It is important to note that BSAFs in organisms not intimately associated with the sediment may vary considerably from unity. In addition, no equivalent basis for the estimation or normalization of the accumulation of metals in organisms exists.

The normalization by organic carbon content assumes that essentially all of the hydrophobic organic contaminant in the sediment and organism is available for partitioning. A significant fraction of the contaminant, though, is often unavailable and is held in a desorption-resistant fraction. The results of many laboratory and field observations indicate, though, that a significant fraction of soil- and sediment-bound contaminants desorb slowly, if at all, are not biodegraded, and are difficult to remove by extraction with surfactants or cosolvents. For example, Pereira et al. (1988) found that the concentration of halogenated organic compounds in native

water, suspended sediments, and biota was far below the values predicted from concentrations in the contaminated bottom sediments collected from Bayou d'Inde, Louisiana. Similarly, McGroddy and Farrington (1995) and Readman and Montoura (1987) observed a fraction of PAHs in river sediments not available for desorption. For most of these sediments, the contamination source had ceased for many years, yet the sediment-bound contaminants persisted over tens of years without significant reduction in concentration or changes in the compound distribution.

The sorption of organic chemicals to soils and sediments is a complex process, given the diversity, magnitude, and activity of chemical species, phases, and interfaces commonly present in contaminated subsurface environments, which may also be quite variable in particle size and organic carbon content. The quantity sorbed is often found to be well represented by the combination of a compartment exhibiting linear, reversible sorption and a compartment that exhibits nonlinear and thermodynamic irreversible sorption. Note that thermodynamically irreversibility simply means that the desorption process does not occur at the same rate or extent as sorption and does not imply that desorption does not occur. In addition to biphasic equilibrium behavior, the approach to equilibrium is controlled by different kinetics in the reversible and irreversible compartments. The kinetics of sorption and desorption in the reversible compartment are typically on the order of a day or less whereas desorption of the sequestered fraction may take weeks or months to approach completion (White et al. 1999).

Pignatello and Xing (1996) have presented a slow-sorption model in which sorption and desorption can be divided into a slow and a fast fraction. The quantity sorbed in each fraction can be described using a Freundlich isotherm or, if the fast release fraction is assumed linear and reversible and given by the organic-carbon-based partition coefficient, by

$$W_s = (W_s)_f + (W_s)_s = K_{oc} f_{oc} C_w + K_w C_w^{n_s} \quad (21-11)$$

Here

W_s = sorbed quantity of solute;
 C_w = adjacent porewater concentrations;
 and the subscripts f and s represent fast and slow, respectively.

K_s and n_s are fitting parameters. Slow sorption may be strongly nonlinear and, combined with entrapment of contaminants in desorption-resistant compartments, is expected to be responsible for the effect of contaminant age on desorption and reduced bioavailability. Pignatello and Xing (1996) have related the different rates of sorption and desorption to the quality of the organic matter (i.e., soft and rubbery versus diagenetically aged hard and glassy).

Huang and Weber (1997) have presented the dual-reactive-domain model (DRDM), which is focused on this difference in sorbent character, to describe hysteresis in sorption-desorption. The soft, rubbery carbon that represents diagenetically young

soils exhibits linear, reversible sorption, whereas aged, hard glassy carbon represents a nonlinear contribution to sorption-desorption. The degree of nonlinear desorption phenomena and contaminant sequestration is presumably related to the fraction of aged carbon. For many sediments, the fraction of diagenetically aged carbon is relatively small, although the capacity of that material for contaminant sorption may be large. Assuming Langmuir-type sorption in the nonlinear domain and that the linear reversible sorption is defined by the organic-carbon-based partition coefficient, the sorbed quantity for the dual-reactive domain-model can be written

$$W_s = (W_s)_\ell + (W_s)_s K_{oc} f_{oc} C_w + \frac{QbC_w}{1+bC} \quad (21-12)$$

where ℓ represents linear or labile fraction and s represents slow or sequestered fraction. Q and b represent the Langmuir fitting parameters of capacity factor and site energy, respectively. The model of Tomson and coworkers (Hunter et al. 1996; Kan et al. 1997; Kan et al. 1998) also assumes a biphasic sorption-desorption model that combines the linear and Langmuir sorption isotherms for the quantity sorbed.

Note that the net effect of a biphasic sorption model such as described by Eq. (21-11) or Eq. (12-12) is that the effective partition coefficient W_s/C_w increases:

$$K_{sw} \frac{W_s}{C_w} = K_{oc} f_{oc} + \frac{Qb}{1+bC_w} \quad (21-13)$$

This can be used to estimate the steady-state accumulation in benthic organisms in which $K_{lipid}^{-1} K_{oc}$. The effect of the desorption-resistant fraction is an effective increase in the sediment-water partition coefficient and reduction in the pore-water concentration. Thus the effect of the desorption-resistant-related reduction on pore-water concentration is a decrease in the BSAF according to

$$BSAF = \frac{K_{lipid}}{K_{sw} f_{oc}} \approx \frac{K_{oc}}{K_{oc} + \frac{Qb}{f_{oc}(1+bC_w)}} \quad (21-14)$$

As noted by Pignatello and Xing (1996), the rate of release from the desorption-resistant contaminant fraction is significantly lower than that from the more labile fraction. Thus the normalized accumulation may be significantly lower than shown in Eq. (21-14) due to kinetic limitations in some plants or animals or under some environmental conditions.

The bioaccumulation behavior of metals and ionic species is 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 reduced sediments. As long as the AVS exceeds the SEM, these metals are in reduced form and essentially unavailable in dissolved form to living organisms (SAB 1995). For some metals, however, such as arsenic, the reduced form may be of more environmental consequence than other forms. Considerably more complicated is mercury, which undergoes biologically mediated reduction reactions that may encourage the formation of methylmercury.

As a result of the complex and varied behavior of metal species and other chemicals, toxicity tests, rather than specific physicochemical tests, are often used to assess the potential for adverse sediment effects. 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). Discussion of the individual tests and their ability to identify severely contaminated sediments is beyond the scope of the present discussion.

Thus, the assessment of the contaminant levels entering the food chain via uptake into plants and animals at the sediment-water interface is largely a question of contaminant availability. In the absence of site-specific toxicity information, measurements or predictions of pore-water concentrations or the AVS/SEM for some metals are useful indicators of availability under steady-state conditions, such as might apply for benthic animals that process large amounts of sediments. For organisms in the water column or for benthic plants and animals with only passive contact with sediments, the kinetics of release from the sediments and uptake and elimination from the organism significantly complicate assessment of exposure and risk.

21.3.3 Exposure by Release from Stable Bed Sediments

The rate of contaminant movement into the water column through either of the two previous pathways was controlled by processes that are largely unrelated to the presence of the contaminant (i.e., erosion of the sediment bed and the rate of ingestion of sediment or benthic organisms). The dominance of these external factors led to the usefulness of approximations based on local equilibrium between any resuspended sediment and the overlying water and between benthic organisms and surficial sediments. The direct exposure of fish and higher animals to contaminants in stable, noneroding beds, however, is a rate-limited process controlled by a variety of natural fate and transport processes, as depicted in Fig. 21-1. Among the most important of these in-bed fate and transport processes are biotransformation, sorption, diffusion, advection, and bioturbation. Under specific circumstances, a variety of other processes identified in Fig. 21-1 may be important.

The local flux from the sediment to the overlying water is related to the sediment concentration and an overall mass-transfer coefficient that lumps the effects of the individual processes. The relationship between sediment contamination and exposure in the overlying water by these processes is controlled by the surficial sediment concentrations. Deep in-bed processes may be responsible for transport of contaminants to the sediment-water interface, but release into the overlying water column is still controlled by the interfacial concentration. Thus, the surficial average sediment concentration remains a useful indicator of the potential release to the overlying water. The average flux from the sediment by stable bed-sediment processes, F_{bed} (e.g., in $\mu\text{g}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$) can then be estimated by

$$F_{\text{bed}} = K_s \rho_s (<W_s> - K_{sw} C_w) \quad (21-15)$$

where

ρ_s = bulk (or dry) density of the sediments (g/cm^3) and
 K_s = average sediment bed-mass transfer coefficient
 (e.g., in cm/h).

The concentration driving force in this equation is the deviation between the actual surficial sediment concentration ($<W_s>$) and that which would be in equilibrium with the overlying water ($K_{sw} C_w$). Alternatively, a water-based overall coefficient, K_w , can also be defined by $F_{\text{bed}}/(<W_s>/K_{sw} - C_w)$, where $K_w = K_s \rho_s / K_{sw}$. In general, K_s is a combination of sediment- and water-side mass transfer resistances, as characterized by sediment- and water-side mass transfer coefficients k_s and k_w , defined by

$$k_s = \frac{F_{\text{bed}}}{\rho_s (<W_s> - W_i)} \quad k_w = \frac{F_{\text{bed}}}{C_i - C_w} \quad (21-16)$$

where the subscript i defines the hypothetical interfacial concentrations at the sediment-water interface. Assuming that the resistances act in series and that the interfacial concentrations are in equilibrium, $W_i = K_{sw} C_i$, the overall mass transfer coefficient, K_s , can be written

$$K_s \rho_s = \frac{1}{1/k_s \rho_s + K_{sw}/k_w} \quad (21-17)$$

Thibodeaux et al. (2001) showed that a range of both laboratory and field data were consistent with $12.5 \text{ cm}/\text{day} < k_w < 33.3 \text{ cm}/\text{day}$ and $2 \text{ cm}/\text{yr} < k_s < 3.6 \text{ cm}/\text{yr}$.

It is perhaps easiest to characterize the effect of the various natural processes depicted in Fig. 21-1 that make up K_s by the time required to achieve specified reductions in contaminant concentration. Because the surficial sediments are typically mixed by the action of benthic organisms or other processes, the response of the surficial-area-averaged sediment concentration can be modeled as

$$\frac{d}{dt}(\langle W_s \rangle \rho_s A h) = -K_s \rho_s \langle W_s \rangle A \quad (21-18)$$

assuming that there are no fate processes other than release by transport processes to the overlying water and the overlying water is always at zero concentration. Thus,

$$\frac{\langle W_s \rangle}{\langle W_s \rangle(0)} = e^{-\frac{K_s}{h}t} \quad (21-19)$$

From the above equation, the concentration half-life (time to 50% reduction) and the time to 95% reduction (5% remaining) in the surficial area averaged sediment concentration is given by

$$\tau_{0.5} = 0.693 \frac{h}{K_s} \quad \tau_{0.05} = 3 \frac{h}{K_s} \quad (21-20)$$

As indicated previously, the depth of the surficial sediment layer that is relatively well-mixed by the action of benthic organisms is typically 5 to 10 cm. The average value of K_s reported by Thibodeaux et al. (2001) in several laboratory experiments and in the Hudson River is approximately 1.3 cm/yr. Similarly, a surface area of 3,300 acres of the Lower Fox River, Wisconsin, containing an average surficial sediment concentration of 3.1 mg/kg PCBs accounts for the bulk of the approximately 125–280 kg/yr estimated to be transported into Green Bay (WDNR 2001). This is equivalent to a K_s of between 0.47 and 1.0 cm/yr. Employing $K_s \approx 1$ cm/yr and a 10-cm surface layer, the contaminant half-life, assuming no exposure of freshly contaminated material and no resupply from upstream sources, is $\tau_{0.5} = 6.9$ yr and the time to 95% reduction in contaminant concentrations $\tau_{0.05} = 30$ yr. These estimates make no attempt to differentiate between the individual mechanisms that contribute to the average mass transfer coefficient. Estimates of the times required to achieve 50% and 95% recovery of the surficial sediment concentrations based upon individual mechanisms are provided in Section 21-5, and allow the mechanisms to be compared and ranked in their importance. The estimates of overall mass-transfer coefficients presented by Thibodeaux et al. (2001) and in the Fox River, however, incorporate mass-transfer resistances in both the sediment bed and in the benthic boundary layer of the water. Before the in-bed transport processes are assessed, the water-side mass-transfer resistances should be examined in more detail.

21.4 WATER-SIDE MASS TRANSFER PROCESSES

The relative importance of water-side mass transfer resistances increases as the hydrophobicity and K_{sw} of the contaminants increase, as shown by Eq. (21-17). If the overlying

water-transport processes control the rate of release from the sediment, measurements of in-bed processes are less important. It is often incorrectly assumed that the intrinsically slower sediment-side processes always control mass transfer to the overlying water. As shown by Thibodeaux et al. (2001), however, the effective coefficient mass transfer from the sediments approaches a limiting value defined by the water-side mass transfer resistances.

From Eq. (21-17), the water-side mass transfer resistances control overall mass transfer as long as

$$k_w < k_s \rho_s K_{sw} \quad (21-21)$$

thus $k_w \gg k_s$, which is normally true, does not necessarily mean that water-side resistances are negligible. Illustrative models of the water-side mass transfer coefficient under flowing and quiescent (generally wind-driven circulation) conditions are given by Thibodeaux (1996) as

$$k_w = \frac{\sqrt{v_w v_*^{1/2}}}{Sc^{2/3} y_o^{1/2}} \quad \text{flowing, typically } \leq 10 \text{ cm/h}$$

$$k_w = \left(0.031 \frac{\text{sec}}{m^2}\right) \frac{\rho_a v_a^2 d^2}{\rho_w M_w^{1/2} L} \quad \text{wind-driven,} \quad (21-22)$$

typically ≤ 1 cm/h

where

v_w is the kinematic viscosity of water (0.01 cm²/s at 20 C);
 Sc is the Schmidt number (typically $O(1000)$ for hydrophobic contaminants);
 y_o, v_* are the flow parameters surface roughness and friction velocity, respectively (m, m/s);
 ρ_a, ρ_w are the density of air and water, respectively;
 v_a is the wind velocity (m/s);
 d is the water depth (m);
 L is the fetch of the lake or water body in the direction of the wind (m);
 M_w is the molecular weight of the contaminant of interest (g/mol).

As indicated previously, Thibodeaux et al. (2001) showed that a range of both laboratory and field data from streams were consistent with 12.5 cm/day $< k_w < 33.3$ cm/day and 2 cm/yr $< k_s < 3.6$ cm/yr. Using these estimates of magnitude for k_w , this suggests that the water-side mass transfer is of equal importance to the sediment side processes for a sediment-water partition coefficient of

$$K_{sw} = \frac{k_w}{k_s \rho_s} = \frac{12.5 - 33.3 \text{ cm/h}}{(2 - 3.6 \text{ cm/yr})(\sim 1 \text{ kg/L})} \quad (21-23)$$

$\approx 30,000 - 150,000 \text{ L/kg}$

Strongly sorbing compounds such as PCBs and heavy PAHs may exhibit partition coefficients in this range for moderate organic carbon content (4–6%). Water-side mass transfer

resistances may thus be important for strongly sorbing compounds even in relatively rapid flowing streams. In lakes and impoundments stirred by wind-driven circulations, the water-side mass transfer resistance may be important for less strongly sorbing compounds. The mobile fraction of most metals in sediments exhibits a partition coefficient much less than this, suggesting that their release from stable sediments is controlled by sediment-side processes.

21.5 ANALYSIS OF SEDIMENT BED FATE AND TRANSPORT MECHANISMS

Fate and transport processes are examined separately to determine the most important mechanisms influencing contamination mobility in sediment. Fate and transport mechanisms are separated into two categories: those operating in stable, immobile beds and those operating 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.

21.5.1 Passive Sediment Fate and Transport Processes

Sediment fate and transport involve the following passive processes:

21.5.1.1 Molecular Diffusion Molecular diffusion is a ubiquitous chemical transport process within a sediment bed. 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 contaminants. The net result is the movement of contaminant 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 contaminant flux is

$$F^{\text{diff}} = -D_{sw} \frac{\partial C_w}{\partial z} \quad (21-24)$$

F^{diff} is quantified by Fick's first law and couples the concentration gradient to the diffusion coefficient.

The effective diffusion coefficient in the porous medium, D_{sw} , is less than the diffusion coefficient in water due to the porosity and tortuosity of the sediment. Often a constitutive relationship similar to that proposed by Millington and Quirk (1961) is used to relate the diffusion coefficient in the sediment to that in water, $D_{sw} = D_w \epsilon^{4/3}$. Here ϵ represents the sediment porosity and D_w is the molecular diffusion coefficient of the contaminant in water, typically on the order of $10^{-5} \text{ cm}^2/\text{s}$.

Field investigations in sediment beds typically involve analytical measurements 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 rarely measured. Available concentration profile data usually are limited to a snapshot in time and seldom reflect trends over time. Typically, only single measurements for a particular year are available for hydrophobic organics and metals. These measurements are not very useful in assessing the influence of diffusion, which is manifested over long time periods and may only influence concentration profiles in thin layers. In addition, diffusion normally occurs at significant rates only within the pore-water phase, and bulk sediment concentrations may not reflect the mobile fraction of contaminants. For metals, in particular, total sediment concentration measurements are not very useful in defining the rates of passive transport processes.

A better approach to 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 contaminant dissolved in the pore water is identified. By discrimination between soluble and insoluble fractions of metals, a much better assessment of potential adverse effects can be made. High-resolution coring makes possible comparison to detailed mathematical models and can be very useful in identifying the most important transport processes. For example, diffusional processes give rise to concentration profiles that are quite different from those produced by advective transport.

21.5.1.2 Adsorption and Desorption Equilibrium between the Solid Surface and Pore Water Organic compounds that are hydrophobic by nature are capable of being adsorbed onto the organoclay fractions of the sediment. Thus, an adsorption-desorption equilibrium exists at the sediment and pore-water interface. In the case of transport into clean sediment, adsorption on the particles retards the movement of a concentration front due to transient accumulation of material in the sorbed phase. Adsorption slows transient pore-water processes (including diffusion) according to a retardation factor, R_f , that is essentially the ratio of the total concentration in the sediment to the concentration in the mobile pore-water phase:

$$R_f = \frac{\text{Total concentration}}{\text{Mobile phase concentration}} = \epsilon + \rho_s K_{sw} \quad (21-25)$$

Here ϵ is the void fraction (porosity) of the sediment bed, ρ_s is the bulk (dry) sediment density, and K_{sw} is the effective sediment water-partition coefficient. Many authors define the retardation factor as R_f/ϵ , where R_f is as defined by Eq. (21-25). Care must be taken to define the retardation factors and the conservation equations in which they arise in a consistent manner.

A simple estimate of the time required for attenuation of a contaminant in the sediments as a result of retardation is the product of R_f and the time required for the attenuation to occur by diffusion assuming no retardation. The

effect of retardation can be quite large. For a compound such as pyrene ($K_{oc} = 10^5$ L/kg), assuming 1% organic carbon, $\rho_s = 1$ kg/L, and $K_{sw} = K_{oc} f_{oc}$, the retardation factor is about 1,000. As described earlier, a significant fraction of the contaminants may not readily desorb. Under such conditions the partition coefficients used in Eq. (21-25) must be measured via desorption experiments and not simply assumed to be given by $K_{oc} f_{oc}$. It is also important to recognize that retardation affects only transient processes. Under steady contaminant transport, there is no further accumulation of contaminants in the sorbed phase and, therefore, there is 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 elimination of active processes, contaminant release and exposure are generally negligible. The time for diffusion to reduce 50% and 95% of the contaminant within a layer, h , is defined by

$$\begin{aligned}\tau_{0.5}^{\text{diff}} &= \frac{1.94}{\pi^2} \frac{h^2 R_f}{D_{sw}} \\ \tau_{0.05}^{\text{diff}} &= \frac{11.2}{\pi^2} \frac{h^2 R_f}{D_{sw}}\end{aligned}\quad (21-26)$$

This assumes no migration of contaminants into the layer from below and assumes that the overlying water provides no resistance to mass transfer.

Although sorption onto an immobile phase can retard contaminant 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 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 (DOM). DOM is generally operationally defined as the organic fraction that passes a 0.45- μm filter and consists of humic and fulvic acids, among other things. Colloidal matter is composed of groups of these fulvic and humic acid molecules that form large-diameter suspensions in water. The suspensions typically have a negative electrical surface charge and the stability is dependent on the structure of the electrical double layer formed, van der Waals forces, hydration phenomena, and the effects of adsorbed substances. Organic colloids represent a sink for hydrophobic organic contaminants in the water. They effectively increase the solubility by increasing the mass of contaminants that can partition into the mobile phase containing both water and colloidal material. In this manner, the mobility of organic contaminants can be enhanced. Colloids can enhance the effective

solubility of metal and ionic contaminants. Various metals and metal complexes also form colloidal species.

The net effect of the increased effective solubility of a contaminant is a change in the retardation factor (Reible et al. 1991; Thoma et al. 1991),

$$R_f = \frac{\text{Total}}{\text{Mobile}} = \frac{\varepsilon + \rho_b K_{sw} + K_{cw} C_c}{1 + K_{cw} C_c} \quad (21-27)$$

Here

C_c = concentration of colloidal particles in the water and
 K_{cw} = partition coefficient between the colloids and the water.

The effective retardation factor represented by Eq. (21-27) assumes that the colloidal particles are transported through the sediment pore water at the same rate as the water molecules themselves. This may not be a good assumption, due to filtration or preferential retention or exclusion of the polar colloidal molecules. A commonly used but approximate estimate of the partitioning of an organic contaminant 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 example for 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 pyrene-contaminated sediment layer by a factor of 2 to 10.

21.5.1.3 Chemical Reaction and Biodegradation A stable sedimentary environment does not lend itself to rapid degradation dynamics. Many organic compounds of concern in sediments are persistent and not subject to rapid degradation by either abiotic or biological processes. Only the upper few cm of a fine-grained sediment may be aerobic; the remainder of the sediment column is generally anaerobic. Organic compounds that are subject to microbial degradation generally degrade more slowly under anaerobic conditions. Although degradation may be slow, the persistence of contaminants over decades or centuries may be of interest. Unfortunately, very little information exists about the persistence of sediment contaminants over these time-scales.

Hughes et al. (1997) have reviewed the potential for PAH degradation in sediments and identified some of the limitations in achieving significant degradation in the field. PAHs degrade most rapidly under aerobic conditions, but some degradation under anaerobic conditions has also been observed (Zhang and Young, 1997). Anaerobic conditions are important for biotransformation of chlorinated organic compounds. Chlorine can interfere with the action of oxygenating enzymes, meaning that reductive dechlorination is often necessary before aerobic transformation can proceed. For example, reductive dehalogenation under reducing conditions converts dichlorodiphenyltrichloroethane (DDT) to dichlorodiphenyldichloroethene (DDE) and lindane to benzene. Pesticides such as toxaphene have

been known to be anaerobically degraded in soils and salt marsh sediments. Anaerobic dechlorination of PCBs can also occur (Tiedge et al. 1993) and has been observed under field conditions (Brown et al. 1984). Dechlorination of highly chlorinated PCBs encourages subsequent aerobic degradation of the less chlorinated PCB or biphenyl (NRC 2001).

In the absence of site-specific quantitative information on the rates of these reactions, the conservative assumption of negligible degradation rates is normally applied. With no degradation, attenuation of contaminant concentrations can only result from transport processes.

21.5.2 Active Sediment-Transport Processes

Diffusion, sorption, and reactions were considered in the absence of sediment or bulk pore-water movement. If sediment or pore water is moving, an advective flux generally dominates any diffusive flux. Mechanisms resulting in advective transport in sediments and their implications for contaminant transport are discussed below. The focus of this discussion remains on stable sediments and slowly moving dunes and ripples (i.e., complete scouring of the sediment bed is not considered). The situation of high suspended-sediment loads was discussed previously while the influence of resuspended sediment on water-column concentrations and exposures was examined. Sediment-transport processes emphasized here are such that the basic character of the sediment bed remains largely intact and the resulting changes in contaminant 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.

21.5.2.1 Deposition or Erosion Sediment deposition or erosion rates are likely to vary significantly over space and time (see Chapters 2 and 4). On average, or in specific locations, however, it may be possible to characterize erosion or deposition by an average velocity $U = D/\rho_s$ or $U = E/\rho_s$, where E and D are the erosion and deposition rates defined by Eqs. (21-5) and (21-7), respectively. The growth of the sediment bed by deposition of clean sediment causes burial of contaminated sediment from the surficial mixed layer at a rate $\langle W_s \rangle D/\rho_s$. Similarly, the process of erosion removes contaminated sediment from the surficial sediment layer at a rate $\langle W_s \rangle E/\rho_s$. In either case, processes such as bioturbation mix the entire depth of the surface layer so that Eq. (21-19) applies as long as the rate of erosion or deposition is low compared to the rate of surficial layer mixing. If the contamination is initially limited to a uniformly mixed depth h , the times to 50% and 95% reduction in concentration in the layer for deposition or erosion at an average velocity U are given by

$$\tau_{0.5}^{\text{ero}} = 0.693 \frac{h}{U} \quad \tau_{0.05}^{\text{ero}} = 3 \frac{h}{U} \quad (21-28)$$

Deposition rates can sometimes be measured by sediment traps placed at the sediment-water interface, although these may not indicate net deposition rates, because they do not allow erosion. Thus sediment traps would track only the deposition portion of a deposition-and-erosion cycle driven, for example, by diurnal tidal variations. Deposition rates can also be estimated by the depth of burial of certain radionuclides, such as ^{210}Pb and ^{137}Cs : γ spectroscopy can be used to measure activities of excess ^{210}Pb (source: U-series, $t_{1/2} = 22$ yrs, 46.5-KeV peak), and ^{137}Cs (source: nuclear fallout and reactors, $t_{1/2} = 31$ yr, 661.6-KeV peak). The presence of a particular radionuclide can be used to date a layer in an undisturbed sediment core, and the location of this layer relative to the sediment surface defines the amount of deposition that has occurred. ^{137}Cs was introduced into the atmosphere as a result of above-ground nuclear testing in 1954 and peaked in 1964. ^{210}Pb decreases to background in surficial sediments, with the decrease indicating age since deposition. Changes in the geochemical character of depositing sediment and sediment erosion and mixing patterns, however, can greatly complicate the interpretation of profiles of these radionuclides.

21.5.2.2 Dune Formation and Transport by Bed Load In the previous section, deposition and erosion were assumed to occur at a uniform rate from an essentially flat surface. While this may be valid under low water velocity or in a low-energy environment in an estuary, this view of erosion and deposition does not hold under high-energy or high-velocity conditions. Under high-energy conditions, dunelike structures are formed that generally progress downstream by erosion on the upstream face and deposition on the downstream face, as shown in Fig. 21-2. During this overturn and migration process, sediment particles are exposed and either scoured or reburied by other sediment particles (see Chapter 2). During exposure to the stream water, contaminants sorbed to the sediment particles can be desorbed and contaminants in the adjacent pore water diluted mixed into the water column.

To quantify the rate of transport of sorbed and dissolved contaminants 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. Savant-Malhiet and Reible (1993) developed a model of contaminant dynamics under these conditions that provides a means of estimating sediment recovery rates by bed-load transport of noncohesive sediment. The model is beyond the scope of the present paper, but results emphasize that bed turnover and contaminant release can be rapid (compared to processes such as diffusion) even under relatively low sediment-migration rates.

21.5.2.3 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 the water level relative to the adjacent

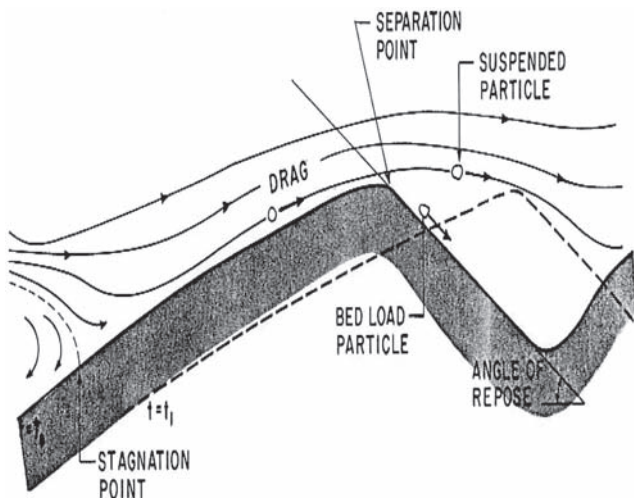


Fig. 21-2. Depiction of bed-load sediment flow over dunelike sediment structures.

water table. The bulk flow through the sediment can result in an advective flux of contaminant that complements the diffusive flux described above. The relative magnitudes of advective and diffusive transport can be quantified with a Peclet number,

$$P_{pe} = \frac{Vh}{D_{sw}} \quad (21-29)$$

Here V is the superficial, or Darcy, velocity perpendicular to the contaminated layer of height h . For low values of the Peclet number, the transport is dominated by diffusion and the previous discussion applies. For large values of the Peclet number, advection dominates and the characteristic times for reduction in concentration of a layer of sediment of height h are

$$\tau_{0.5}^{adv} = 0.693 \frac{hR_f}{V} \quad \tau_{0.05}^{adv} = 3 \frac{hR_f}{V} \quad (21-30)$$

Note that the advective processes are assumed to be sufficiently slow so that the upper layer remains mixed by bioturbation or other processes. It is also important to note that the retardation factor arises in Eq. (21-30). Advection is a pore-water process subject to retardation due to accumulation on the immobile solid particles and enhancement by sorption onto mobile fine and dissolved particulate matter.

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, which collect any water that seeps through the sediment) are commonly used. It is particularly important that such measurements reflect the seasonal nature of groundwater flow. Unfortunately, the wide variability in sediment characteristics (e.g., permeability) makes interpretation of such data difficult. In addition, it is difficult to measure seepage

rates of less than about $0.1 \text{ cm}^3/\text{cm}^2/\text{day}$ with typically available meters. An alternative means of detecting slow vertical transport by groundwater flow is through tracers, such as described by Cornett (1989). The groundwater flow in the surrounding aquifer can also be a useful measure 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.

21.5.2.4 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 on the order of 100 to $1,000 \text{ N/m}^2$ can be observed between the upstream and downstream faces of the triangular-shaped dunelike sediment structures that typically form at the sediment-water interface. Figure 21-2 includes a depiction of the basic character of the flow over these dunes. The flow is a simple turbulent shearing flow on most of the upstream face and a recirculating wake on the downstream face which also influences a portion of the subsequent sediment dune. It is the weak and poorly organized flow in the wake that results in the leeward deposition of 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 advective 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, as shown in Fig. 21-3. The experiments and modeling indicated that the induced in-bed flow could extend as much as four to five dune heights into the sediment. Elliot and Brooks (1997a, 1997b) also analyzed this mechanism and achieved similar results. This mechanism likely is important mostly in sediment beds subject to significant organism burrowing activity and in permeable, sandy sediments such as might be observed on the continental shelf of the coastal United States. Note that pressure differences in bends and under other flow irregularities may also cause advective flow in the adjacent sediments.

21.5.2.5 Bioturbation-Induced Transport The previous discussion largely considered sediment as a collection of 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 pref-

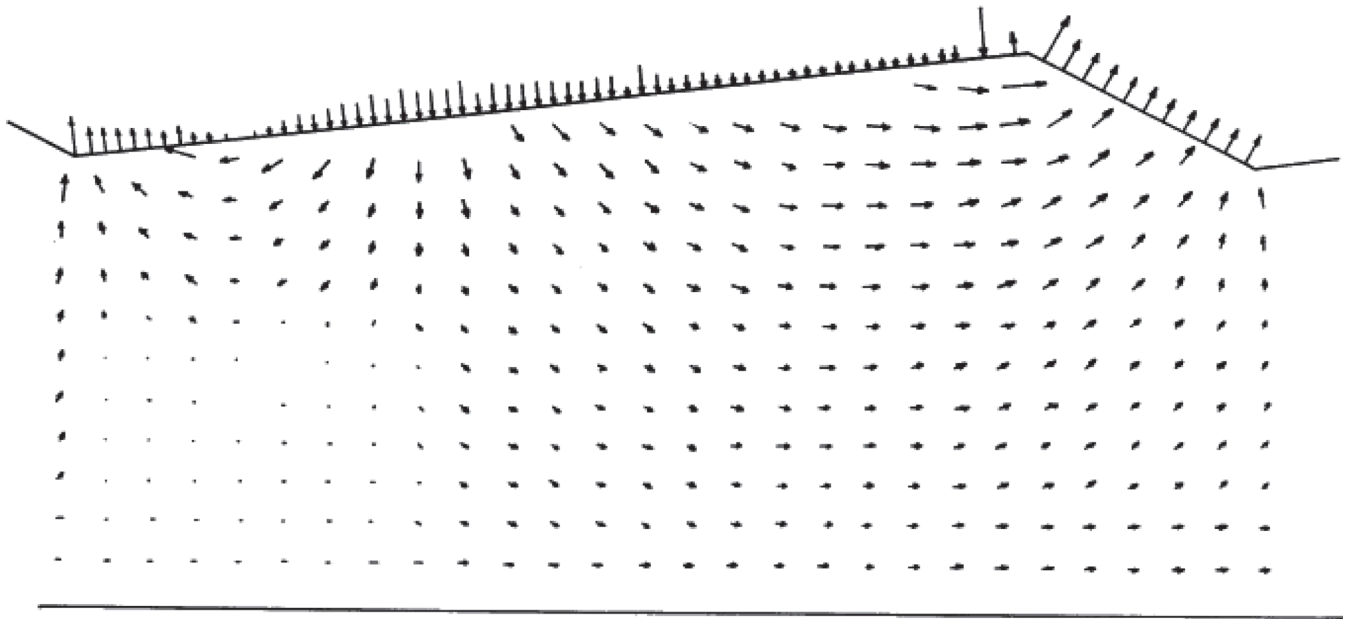


Fig. 21-3. Numeric simulation of the in-bed flow due to pressure variations on the surface of a dune (after Savant 1987).

erential water flow and contaminant transport. Even more important, 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 and defecation, tube building, and biodeposition. Taken together, these processes are termed bioturbation; a depiction of the type of animals that can be present and the interaction with sediments is provided in Fig. 21-4. The net result of bioturbation is the vertical and horizontal movement of sediment particles and pore water. Contaminants on the particles or in the pore spaces likewise are transported in the bioturbation process, which is especially important in the transport of hydrophobic contaminants that are heavily retarded by sorption in pore-water processes.

The possibility of bioturbation as a transport mechanism has long been recognized. Boudreaux (1986a) cites work on the effect of biological activity on sediment composition and properties as old as Davison (1891). A wide variety of animal organisms live on and in the upper sediment layer and interact with sediments in a variety of ways. If the scale of the individual organism mixing 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 has 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

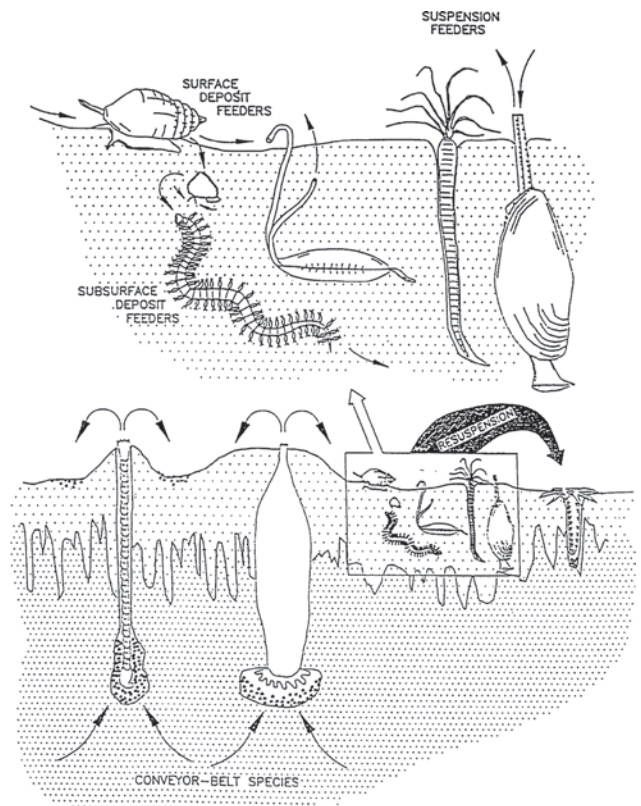


Fig. 21-4. Illustration of the variety of benthic organisms that interact with the sediments and solids associated contaminants (after Rhoads 1974).

depth-dependent biodiffusion coefficient is appropriate. However, as Boudreaux (1986b) noted, it is often difficult to differentiate between a constant and a depth-dependent biodiffusion coefficient on the basis of available data.

If the scale of the individual organism-related mixing is not sufficiently small so that the appearance of a random, diffusive process is achieved, other models must be postulated. For example, worm tubes and other macroscopic animal burrows can significantly enhance the contaminant transport rate across the sediment-water interface on larger scales. In addition, some marine and freshwater worms ingest sediment at depth and deposit the fecal matter at 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 a diffusive process. However, even nonlocal (i.e., macroscale) mixing events of this sort often give rise to contaminant profiles that have 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 contaminant 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/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 salt-water conditions suggest an effective particle diffusion coefficient of 0.3 to 30 cm²/yr. This can be restated as effective mass transfer coefficients of 0.03 to 3 cm/yr using an average effective layer depth h_{bio} of 10 cm. 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 times and amounts of the release of particular radionuclides and the current distribution within sediment allow estimation 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, $k_{\text{bio}} \sim D_{\text{bio}}/h$, equivalent to 1 to 10 cm²/yr for tubificid worms at field densities in freshwater sediments. Tubificid worms are typically found at very high densities and often represent the bulk of the biomass in sediment bioassays (e.g., USEPA 1993a). These

worms are head-down deposit feeders capable of processing 10 or more times their own weight in sediment every day. The high density of these organisms, along with the ability to process large amounts of sediment, leads to relatively high mass-transfer rates. Some organisms may also degrade certain contaminants, further speeding the attenuation of contaminant concentrations.

Focusing specifically on the transport effect of bioturbation, the diffusive models discussed previously can be applied. The time required for 50% and 95% reduction in concentration in a surface layer of depth h due solely to bioturbation at an effective particle reworking diffusion coefficient, D_{bio} , is given by

$$\tau_{0.5}^{\text{bio}} = \frac{1.94}{\pi^2} \frac{h^2}{D_{\text{bio}}} \quad \tau_{0.05}^{\text{bio}} = \frac{11.2}{\pi^2} \frac{h^2}{D_{\text{bio}}} \quad (21-31)$$

Because biodiffusion typically involves particle movement, there is no effect of retardation by sorption onto an immobile phase. Therefore, for a hydrophobic contaminant 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 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 contaminant such as pyrene, however, bioturbation is expected to control contaminant migration in the upper layers of a stable sediment bed. In general, bioturbation is the primary migration mechanism of strongly sorbing contaminants in stable surficial sediments unless the physical character of the sediment or its level of contamination precludes significant colonization by benthic organisms.

21.6 ENGINEERING MANAGEMENT OF CONTAMINATED SEDIMENTS

The goal of remedial efforts at a contaminated sediment site is to manage the risks that they pose. The processes already described define the rate of natural attenuation of contaminants in the surficial sediment layer but also define the attenuation of any residual remaining from more active remediation.

Thus the above discussion of the fate and transport processes provides a basis for the assessment and implementation of natural attenuation. To ensure the effectiveness of natural attenuation as a management option, it is necessary to design a monitoring plan that tests and updates the conceptual model of contaminant release and exposure from the sediments and demonstrates the attenuation of concentration

and risk that is predicted by it. The design of such a monitoring plan is beyond the scope of this chapter, but the general approach must be consistent with the most important process or processes that influence contaminant behavior.

Engineered efforts to control exposure and risk beyond natural attenuation can be placed into two broad categories:

1. Containment and/or treatment in situ;
2. Removal and ex situ treatment or disposal.

The feasibility of sediment or dredged material treatment approaches is strongly dependent on the contaminants and the characteristics of the sediment and the environmental setting. Evaluation and the presentation of design approaches for treatment processes are beyond the scope of this work. The initial step in applying any treatment approach, however, is either containment by capping with clean sediments or removal by dredging. In some cases, the body of water can be diverted or contained, allowing removal by dry excavation. Dry excavation will not be considered here because of its similarity to conventional soil removal. Instead, the basic features and key design constraints of capping and wet dredging will be discussed.

21.6.1 Contaminated Sediment Containment by in Situ Capping

Capping is the placement of clean sediment or similar materials over contaminated sediment. For ease of placement, sand or other coarse media are normally used as capping material. Geomembrane material may be used beneath a cap in soft sediments to aid in the support of the cap, and stones or other large material may be employed as armoring on top of the cap to reduce cap resuspension and erosion. The purpose of a cap is to contain the contaminated sediment physically, separate the contaminants from organisms living at the sediment-water interface, or isolate the chemical contaminants from the overlying water by reducing flux. The design of a cap to meet each of these goals is discussed below.

21.6.1.1 Containment of Contaminated Sediment The goal of sediment containment is to armor the sediment bed and eliminate the resuspension and erosion that may control contaminant release. Contaminants tend to be associated with fine-grained sediments that are often cohesive and exhibit low shear strength or load-bearing capacity. A more coarse-grained cap can provide significant stabilization if placement can be achieved. In addition, since such a cap is generally composed of granular, noncohesive sediment, for which erosion properties are well known, uncertainties associated with the stability of the underlying cohesive sediment become irrelevant.

The ability to place a cap over a sediment with low load-bearing capacity can be estimated by considering local shear failure (Palermo et al. 1998). The thickness of a cap that can be supported for a certain strength sediment is given by

$$h_{\text{cap}} = (2 + \pi) \frac{2}{3} \frac{C_{\mu}}{\gamma} \quad (21-32)$$

where

C_{μ} = the shear strength of the sediments and
 γ = the specific weight of the cap materials.

If the cap is made of sand with a specific weight of 5 kN/m³ and the sediments are at the liquid limit ($C_{\mu} \sim 2.5$ kN/m²; Das 1979), a load of almost 1.7 m or 5.6 ft may be placed without local shear failure of the sediment. A thinner cap may be required to ensure a factor of safety, or for weaker sediments. A thicker cap may be placed, if desired, by placement in multiple lifts to allow consolidation and strengthening of the sediment prior to placement of the entire cap.

The long-term stability of an armoring cap layer depends upon the erosion characteristics of the cap and the hydraulic forces to which it may be exposed. For simple preliminary design, the Transportation Research Board (1970) established a criterion for the onset of erosion of noncohesive granular media of particle size d_p that is dependent upon bed shear stress, τ_b :

$$\begin{aligned} \tau_b &= 4 d_p \quad (\tau_b \text{ in lbf/ft}^2, \quad d_p \text{ in ft}) \\ \tau_b &= 58.4 d_p \quad (\tau_b \text{ in N/m}^2, \quad d_p \text{ in m}) \end{aligned} \quad (21-33)$$

Another approach, employing flow velocity rather than bed tractive force, may be found in Palermo et al. (1998). Use of Eq. (21-33) or the methods in Palermo et al. (1998) requires specification of a design flow condition. This is typically a major rare flood event such as a 100-yr flood or a maximum design flood. In addition, however, special care must be taken to ensure that such a flood event controls the potential for cap instability. Wind-driven seiche flows, wave action, or ice scouring of the sediments may challenge cap integrity more than a major flood event.

Simple relationships such as Eq. (21-33) do not recognize the spatial variability in shear stresses and the resulting cap erosion. Localized erosion of a cap, however, is unlikely to significantly affect overall cap effectiveness, which is proportional to the total area of sediment capped.

Palermo et al. (1998) also includes approaches to the evaluation of a stable grain size when a body of water is subjected to commercial or recreational navigation traffic. Regular exposure to high-powered traffic, especially in relatively shallow water, may limit the feasibility of capping as a management alternative. However, irregular recreational boat traffic outside of dock and marina areas, may not pose a significant challenge to cap integrity because any cap erosion may be localized.

Eq. (21-33) assumes that the cap grain size is uniform. Other criteria on cap materials may be required to ensure stability and eliminate the potential for fine-grained material to be lost through the cap, including (Palermo et al. 1998)

- A nonuniform particle-size distribution, e.g., $d_{85}/d_{15} \sim 4$;
- Angular shapes for coarse-grained particles such as gravel and cobbles;
- A maximum particle size of not more than $2 d_{50}$ (USBR 1973);
- A minimum particle size of not less than $0.05 d_{50}$ (USBR 1973);
- A minimum layer thickness of approximately $1.5 d_{50}$;
- Maintaining a ratio of particle sizes between upper and lower layers of a multilayered cap such that $d_{15}^{\text{upper}}/d_{85}^{\text{lower}} \leq 5$ (this criteria also defines an upper bound for the ratio of particle sizes in the cap layer immediately adjacent to the sediment layer desired to be contained); and
- Limiting placed cap slope to the stable angle of repose of the cap material (Palermo et al. 1998 suggested a vertical to horizontal slope of 1:1.88 for clean sand, although a factor of safety of 2 to 3 might be applied).

21.6.1.2 Separate Benthic Organisms from Contaminated Sediment The adequacy of a cap to physically separate organisms from contaminated sediment depends upon the thickness of the cap and the depth of penetration of the organisms. The depth and intensity of interaction of organisms with sediments is strongly dependent upon the type of organism and environmental characteristics such as sediment texture. Freshwater benthos, for example, may only populate the upper 5 to 10 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. Deposit feeders typically prefer fine-grained sediment high in organic carbon content, whereas burrowing filter feeders may prefer coarse-grained sandy sediment. More than 90% of the 240 observations of bioturbation mixing depths in both fresh and salt water reported by Thoms et al. (1995), however, were 15 cm or less and more than 80% were 10 cm or less. Almost all of these estimates were based upon measurements of the vertical distribution of various radionuclides, which have proven to be very useful tools in identifying the degree of mixing within the upper layers of sediment. Short-term mixing in this regard can be effectively assessed with beryllium (^7Be , cosmogenic source, $t_{1/2} = 52$ days, 477 KeV peak), which is mixed downward from the water column by the benthic organisms.

Certain organisms may penetrate significantly deeper than 15 cm. The importance of these penetrations at the population level depends upon the density and intensity of organism behavior at the deeper levels. As indicated by the measurements reported by Thoms et al. (1995), however, 90% of the observations showed minimal mixing below 15 cm, leading to the conclusion that population-level impacts are generally limited to that depth. Deeper penetrations by individual organisms, however, may be important in particular environmental settings or when the organisms of concern are those that tend to penetrate more deeply.

If the depth of concern for organism penetration is h_{bio} , and the cap consolidation is given by Δh_{cap} , the depth of cap,

h_{cap} , necessary for separation of benthic organisms and the contaminated sediments is given simply by

$$h_{\text{cap}} > h_{\text{bio}} + \Delta h_{\text{cap}} \quad (21-34)$$

Cap consolidation may be estimated by conventional consolidation measurements and models such as PCDDF (Stark 1991).

21.6.1.3 Reduce Contaminant Flux to the Overlying Water The final objective of a cap is reduction of chemical flux to the overlying water. If the criterion for cap stability is achieved, only pore-water processes are effective below the zone of bioturbation. Thus the pore-water concentration, C_{pw} , controls the driving force for flux to the overlying water. This flux is usually described by a combination of advective and diffusive processes,

$$F_{\text{cap}} = V C_w - D \frac{dC_w}{dz} \quad (21-35)$$

Here V is the superficial or Darcy velocity driven by local or mean hydraulic gradients and D is an effective coefficient including both diffusion (Eq. 21-24) and dispersion. Wang et al. (1991) and Thoma et al. (1993) demonstrated the applicability of flux models of the form of Eq. (21-35) and defined a modeling framework that was later extended by Palermo et al. (1998).

If it is assumed that the cap poses essentially the only mass transfer resistance and the pore-water concentration beneath the cap, C_0 , remains constant, the flux at the top of the effective cap thickness, h_{cap} , is given by

$$F_{\text{cap}} = \frac{C_0 V}{2} \operatorname{erfc} \left\{ \frac{R_f h_{\text{cap}} - V t}{2 \sqrt{R_f D_{sw} t}} \right\} + C_0 \sqrt{\frac{D_{sw} R_f}{\pi t}} \exp \left\{ - \frac{(V t - R_f h_{\text{cap}})^2}{4 R_f D_{sw} t} \right\} \quad (21-36)$$

where R_f is given by Eqs. (21-25) or (21-27) and defined by cap properties. The effective cap thickness is the cap thickness minus allowances for consolidation and bioturbation. The effective cap thickness is the thickness of the chemical isolation layer. For times long compared to $R_f h_{\text{cap}}/V$, the flux through the chemical isolation layer approaches VC_0 . For $V \ll D_{sw}/h_{\text{cap}}$, however, the migration through the cap is diffusion controlled and the flux at the top of the chemical isolation layer is given by

$$F_{\text{cap}} = \frac{C_0 D_{sw}}{h_{\text{cap}}} \left[1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp \left(- \frac{D_{sw} \{n\pi\}^2 t}{R_f h_{\text{cap}}^2} \right) \right] \quad (21-37)$$

For times long compared to $R_f h_{\text{cap}}^2 / (\pi^2 D_{sw})$, the flux through the cap approaches $C_0 D_{sw} / h_{\text{cap}}$.

Both Eqs. (21-36) and (21-37) predict minimal flux through the cap from the time of placement until times approaching

the characteristic time for the advective or diffusion-dominated process that controls migration through the cap. That is, the time until some contaminants have migrated over most of the cap can be estimated by

$$\begin{aligned}\tau_{\text{cap}}^{\text{adv}} &\sim \frac{R_f h_{\text{cap}}}{V} && \text{advective conditions} \\ \tau_{\text{cap}}^{\text{diff}} &\sim \frac{R_f h_{\text{cap}}^2}{\pi^2 D_{\text{sw}}} && \text{diffusive conditions}\end{aligned}\quad (21-38)$$

At times short compared to these characteristic times, the flux through the cap is effectively zero. Note that the flux through the cap, even after these times, may still be significantly less than the flux from the exposed sediment prior to cap placement. The uncapped sediment is typically subject to bioturbation and erosion that a well-designed cap will eliminate. Under diffusive conditions, the cap provides a longer diffusion path that effectively reduces flux even at steady state (long time).

The flux through the chemical isolation layer, defined by Eqs. (21-36) or (21-37), controls the flux through the bioturbation layer as well. This provides a basis for estimating the concentration in the bioturbation layer, which is defined by the balance of the flux in from the chemical isolation layer and out into the overlying water. If k_{bio} is the effective mass transfer coefficient in the bioturbation layer, k_w is the benthic water layer mass transfer coefficient, and V is the seepage velocity, assumed independent of either the bioturbation-layer or benthic-water-layer mass transfer processes, the water-phase concentration in the bioturbation layer is

$$C_{\text{bio}} = F_{\text{cap}} \left(\frac{1}{k_{\text{bio}} R_f + V} + \frac{1}{k_w} \right) \quad (21-39)$$

and the corresponding solid-phase concentration, which can be compared to sediment quality standards, is

$$W_{\text{bio}} = K_{\text{sw}} C_{\text{bio}} \quad (21-40)$$

Examination of Eqs. (21-36) and (21-37) shows that as the effective cap thickness increases, the flux decreases and the time required to achieve the steady state (maximum) flux increases. The cap thickness is initially defined by the placement thickness, h_0 , which is reduced by consolidation of the cap, Δh_{cap} , mixing of the upper layers of the cap by bioturbation, h_{bio} , and consolidation of underlying sediment, Δh_{sed} , which expresses contaminated pore water over a portion of the cap. The contaminants expressed with the pore water due to underlying sediment consolidation, however, are subject to retardation. It is assumed that the time of consolidation and the time for bioturbative mixing of the upper layers of the cap are very small compared to the time required for contaminant transport through the cap. Thus the effective cap thickness for use in Eqs. (21-36) and (21-37) can be written

$$h_{\text{cap}} = h_0 - \Delta h_{\text{cap}} - h_{\text{bio}} - \frac{\Delta h_{\text{sed}}}{R_f} \quad (21-41)$$

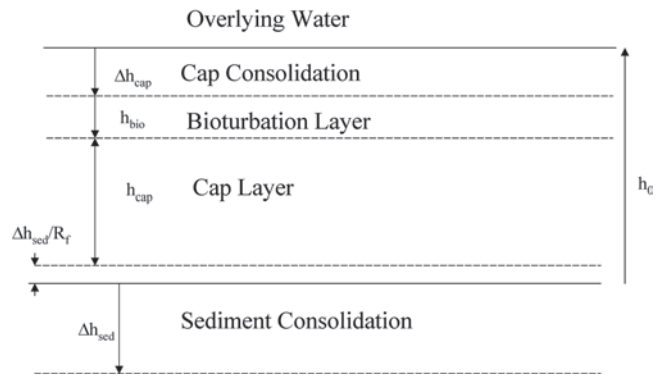


Fig. 21-5. Depiction of the different layers present in a cap as defined by the effective cap thickness.

The relationship of these terms within the cap is shown in Fig. 21-5.

In either the advection-dominated case or the diffusion-dominated case, it is possible to compare this flux to that estimated from the uncapped sediment-water interface to determine the effectiveness of the cap. Alternatively, it may be desired to design a cap by selecting the thickness necessary to achieve a desired reduction in flux or a time until significant migration through a cap might occur.

21.6.2 Dredging Contaminated Sediments

Options that involve removal of contaminated sediments from a water body are significantly more complicated than in situ approaches. Removal options require controls to minimize contaminant loss during sediment removal and transportation, pretreatment of produced dredged material for dewatering and equalization, treatment or transport and disposal of the dredged material, and management of the residual contamination in the sediment and treatment effluents. Thus removal options involve not only dredging but several other component technologies to manage the dredged material.

21.6.2.1 Dredging Technologies Dredges fall into one of two basic categories: hydraulic dredges that primarily use suction and hydraulic action to remove sediments, and mechanical dredges that remove sediments by direct, mechanical action. Hydraulic dredges are generally preferred for high production rates and to minimize sediment resuspension. Solids content of dredge material produced by hydraulic dredging, however, is typically less than 15% and in some environmental dredging operations has been as low as 1%. Hydraulic dredges with a rotating cutterhead or a horizontal auger are commonly used in contaminated-sediment removal. Mechanical dredges, such as a clamshell or cable-arm bucket dredges, are generally preferred for high solids content, low water production, improved performance in the presence of debris and obstructions, and greater accuracy. Close to in situ densities have been generated during mechanical dredging operations. Hybrid dredges have also been used that are predominantly mechanical in action but also withdraw water to control migration of a resuspension plume.

21.6.2.2 Resuspension of Contaminants One of the most significant factors in the selection of dredges for removal of contaminated sediments is the resuspension potential. Sediment characteristics such as grain size largely control resuspension. Fine-grained sediments settle the most slowly and result in the most resuspension in and around a dredgehead. Dredging effectiveness is also limited by residual sediment contamination not targeted or captured by the dredging operation, and by the influences of debris, sediment heterogeneity, and dredge type. In the presence of large debris, certain hydraulic dredges may be ineffective or lead to increased resuspension rates. Hard, consolidated sediment layers, or hardpan, may make dredging overlying contaminated sediments extremely difficult and of limited effectiveness. Sediments also tend to settle back into the cuts of mechanical dredges, leading to increased resuspension rates and residuals in the surface sediments.

Sediment resuspension and associated contaminant loss during dredging operations have been the focus of much attention. Limited data preclude reliable a priori predictions for all except conventional cutterhead and bucket dredges operating under near-normal conditions. Available data for conventional cutterhead and bucket dredges show resuspension rates generally less than 1% of the sediment dredged (Hayes et al. 2000). Whereas available data for smaller dredge types (USACE 1990; Foth and Van Dyke 2000; 2001) show resuspension and contaminant loss rates generally in excess of 1%.

If the contaminant is assumed to be largely associated with the sediment particles, a 1% sediment loss translates directly into a 1% contaminant loss. The mass of contaminant released per unit area of sediment dredged is given by

$$F_{\text{sus}} = f_{\text{sus}} h_{\text{dredge}} W_s \rho_s \quad (21-42)$$

where h_{dredge} is the depth of dredging, ρ_s is the sediment bulk density, W_s is the contaminant concentration, and f_{sus} is the fractional resuspension rate.

21.6.2.3 Residual Sediment Contamination The portion of sediments that remains as a residual contaminated layer may be a more significant source of long-term exposure and risk. Typically, removal of this contaminated residual is attempted by "overdredging," the process of removing an additional layer of less contaminated underlying sediment. Complete removal of the contaminated layer is not possible, however, due to the mixing of this layer with the less contaminated underlying sediment even during overdredging. Removal of the residuals is especially difficult where overdredging is hindered by debris or by "hardpan" or bedrock that limits the depth of the dredging cut.

It is not possible to predict with certainty either the depth or the concentration of the residual contaminated layer or its relationship to sediment and operational variables. Problems posed by residual contaminated sediment from dredging, however, have been demonstrated in a variety of dredging

projects. The dredging of PCBs near a GM facility in Massena, New York required 15–18 dredge passes to reduce sediment concentrations below 500 mg/kg in areas where initial concentrations exceeded 500 mg/kg (BBL 1996). In some areas, a cap was ultimately placed over the residual contamination because repeated dredging passes could not reduce the sediment concentrations below 10 mg/kg. In an area of the Grasse River, also near Massena, removal of as much as 98% of the PCBs from the sediment column reduced the average PCB concentrations in surficial sediments (upper 8 in.) by only 53% (Thibodeaux et al. 1999). Both of these efforts were hindered by the presence of bedrock or hardpan, limiting the extent of overdredging, and by the fact that the highest PCB concentrations were observed at depth rather than at the sediment surface. Demonstration projects in the Lower Fox River of Wisconsin also indicate the potential for residual PCB contamination in the surficial sediments after cessation of dredging (BBL 2000).

Although no definitive approaches to estimating residual contaminant concentrations or residual sediment depths have been developed, mechanical mixing associated with dredging suggests that the residual layer would exhibit a concentration similar to the depth-averaged concentration in the layer being dredged,

$$\bar{W}_s \approx \frac{\int_0^{h_{\text{dredge}}} W_s(z) dz}{h_{\text{dredge}}} \quad (21-43)$$

The thickness of this residual layer is uncertain and dependent upon the presence of hardpan or debris but is likely to be at least 1–4 in. given the significant concentrations typically observed in 4- to 12-in. surficial sediment samples after dredging. Multiple passes can significantly reduce this residual concentration if the dredge is not limited by hardpan or debris.

The attenuation of concentrations in this thin surface layer may be very rapid in that the contaminants may be quickly removed by erosion, or bioturbation may rapidly mix the contaminants over at least the mixed layer of the sediments. A conservative estimate (i.e., an overestimate protective of human health) of the flux immediately after dredging is that the surficial sediment concentration is given by Eq. (21-43). That is, the flux to the overlying water due to the residual contamination immediately after dredging is then

$$F_{\text{res}} = K_s \bar{W}_s \rho_s \quad (21-44)$$

21.6.2.4 Dredged Material Handling In addition to management of resuspension losses and residuals from dredging, the dredged material requires significant handling. The additional required steps include pretreatment of produced dredged material for dewatering and equalization, treatment or transport and disposal of the dredged material,

and management of the residual and treatment effluents. Although it is beyond the scope of this paper to evaluate these steps, the cost and difficulty of onshore management of the contaminated sediments may exceed that in water and should be considered in any comparative analysis of in situ versus ex situ management options for contaminated sediments.

21.7 SUMMARY

Exposure and risk of sediments to higher trophic organisms (e.g., piscivorous birds and mammalian predators) are controlled by the type and extent of the contamination and the relative rates of the various natural fate and transport processes. Contaminants that are buried, sequestered, or degraded pose less risk, whereas contaminants that can be mobilized by natural physical, chemical, and biological processes can pose significant risks. This discussion quantitatively summarizes the most important fate and transport processes that attenuate contaminant levels and exposure in river, estuarine, lacustrine, and marine sediments. The key factors influencing contaminant release and exposure during the application of common remedial approaches, including in situ capping and dredging, were also summarized.

Exposure and risks to fish and higher animals were attributed to one of three contaminant pathways. The first pathway, direct exposure to resuspended sediment, can often be described by assuming chemical equilibrium between the suspended sediment load and water. The rate of resuspension of surficial sediments would then be needed to predict water-column concentrations. The second pathway, indirect exposure to contaminated sediment through the food chain, can often be described by chemical equilibrium between the bed sediment and the benthic organisms that inhabit the sediment-water interface. The rate of predation on these organisms would then indicate the rate of uptake by fish and higher organisms. The third pathway, direct exposure to contaminants released from stable sediments, requires analysis of the fate and transport processes in the sediment.

Although 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 depending upon the rate at which the process can influence contaminant concentrations. Relationships were presented for estimation of the time required to achieve 50 and 95% reductions in contaminant concentrations by the various mechanisms. Processes that exhibit a shorter characteristic time are likely to be the most important transport processes.

In general, active sediment processes in which contaminants are transported by bulk movement of pore water or particles exhibit the shortest characteristic transport times and, therefore, the shortest sediment-concentration attenuation 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. 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 contaminant movement in the upper layer of sediments. It is important to note that each site is different and that only through detailed studies can the dominant process or processes at a particular site be identified and quantified, allowing the evaluation of the effect of these processes on natural attenuation and active remedial options. In all cases, the nature of the physical environment (e.g., sediment texture, water depth and flow velocities, temperature effects, and climatographic effects, as well as sediment chemistry and heterogeneity), the nature of the contaminants (e.g., hydrophilic versus hydrophobic, persistent versus ephemeral), and the biotic elements of the environmental setting all contribute to the fate of the contaminants in sediments.

There are few options for reducing exposure by active intervention rather than passive natural attenuation, largely removal or containment. There are limited in situ treatment options. Both removal and containment leave residual contamination and risks that must be assessed to appropriately select or design either option.

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