

**Sediments:
Chemistry and Toxicity of
In-Place Pollutants**

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CHAPTER 8

Bioavailability of Sediment-Associated Contaminants to Benthic Invertebrates

Peter F. Landrum and John A. Robbins

1.0 INTRODUCTION

Sediment contamination is one of the major end results of pollutant discharges into freshwater and marine aquatic environments. These contaminant discharges have resulted in highly contaminated sediments throughout the world, although the extent of the problem is not yet adequately delineated. In North America, highly contaminated sites have been reported for both coastal marine (NOAA 1988) and freshwater systems such as the Great Lakes (IJC 1987, 1988). For many toxic materials, sediments represent both the primary repository and in many cases the principle source of contamination to the food chain.

Field monitoring studies have shown that changes in portions of the ecosystem, particularly changes in the benthic community structure, are correlated with increased sediment-associated contaminants within the Great Lakes (Nalepa & Landrum 1988). However, developing cause/effect relationships is difficult because other factors such as changes in habitat, nutrient loads, and the amount of suspended materials often occur simultaneously or sequentially with the introduction of pollutants and may themselves alter the functioning of a specific ecosystem. Evidence for the effects of sediment contaminants within ecosystems can be found in monitoring studies that show the presence of the same contaminants in organisms and sediments collected from the same area (NOAA 1987). Furthermore, tumors in bottom-dwelling fish occur with greater than expected frequency in areas where sediments are contaminated with carcinogenic contaminants (Couch & Harshbarger 1985). Perhaps the most direct evidence of the effects of sediment contaminants lies in laboratory bioassays, where sediments collected from contaminated areas have produced toxicity in a wide

range of laboratory bioassay organisms (Swartz 1987, Lamberson & Swartz 1988).

In spite of the evidence that sediment-associated contaminants are entering and affecting biological systems, the processes responsible for the transfer of contaminants from sediments to biota and the physicochemical and environmental factors modifying these processes remain ill-defined. Since sediments are such important potential sources for ecosystem modification and food chain transfer, it is important to characterize and understand the nature of the interaction between this complex medium and its living inhabitants. Our objectives are to review the current state of knowledge on the bioavailability of sediment-associated contaminants and to propose a model to help interpret our current understanding and define areas where data about important factors are missing. The focus of the discussion will be on nonpolar organic contaminants because the variables that influence the contaminant transfer from sediments to biota are best known for these classes of compounds. However, most of the principles described can eventually be applied to other contaminants, polar organics and heavy metals, as specific factors that influence sorption and accumulation become better defined for these materials.

2.0 DEFINING BIOAVAILABILITY

Bioavailability of sediment-associated contaminants can be defined as "the fraction of the total contaminant in the interstitial water and on the sediment particles that is available for bioaccumulation", whereas bioaccumulation is "the accumulation of contaminant via all routes available to the organism". Chemical measures of contaminant concentration in sediment do not always reflect the bioavailable fraction of sediment-associated contaminants (Landrum 1989, Landrum *et al.* 1989); therefore, a simple measure of the sediment residue is insufficient to define the contaminant concentration to which biota are exposed. Further, because feeding by benthic organisms is generally limited to the fine grain material (the material that sorbs most contaminants) the potential exposure would be much greater than would be anticipated from the bulk sediment concentration when ingestion is a significant route of exposure. Therefore, a measure is needed to define the fraction of total contaminant available for biological accumulation.

Two approaches to assess overall bioavailability of sediment-associated organic contaminants are prominent in the literature: (1) comparison of the organism- and sediment-contaminant concentrations, and (2) determination of the uptake clearance of sediment-associated contaminants. The first

approach, a steady-state approach, compares the organism contaminant

concentration to the contaminant concentration in the sediment. An accumulation factor (AF) or preference factor (PF) is calculated as the ratio of the contaminant concentration in the organism normalized to the lipid content divided by the contaminant concentration in sediment normalized to the organic carbon content (McFarland 1984, Lake *et al.* 1987, Foster & Wright 1988, McElroy & Means 1988, Pereira *et al.* 1988). Such normalizations to lipid and organic carbon make the assumption that organic contaminants partition reversibly between the sediment particles and organisms with interstitial water as the exchange medium. Further, the organic contaminants are presumed to partition predominantly to sediment organic carbon and organism lipids and come rapidly to a steady-state condition.

For comparability between studies, the methods to measure lipid content and organic carbon content must be standardized. However, total organic carbon has been measured both as carbon and as total volatile solids content. This methodological difference could result in a factor of four or more difference between reported organic carbon normalized concentrations.

Similarly, various extraction methods have been used to determine total organism lipid content. Most often, the method is a gravimetric determination of the residue from the same extraction used for the extraction of contaminants. The extractions for contaminants are not necessarily the appropriate methods for extracting lipids; thus, a standard lipid-extraction technique should be used to avoid variation between laboratories in the relative values for lipid normalization. It is possible to take a very small aliquot of a sample for total lipid determination using a proven microgravimetric technique (Gardner *et al.* 1985) and reserve the remainder of the sample for contaminant analysis. A standard approach needs to be developed so that comparisons among results obtained in different laboratories are meaningful.

In addition to potential procedural difficulties, other assumptions are required for the PF or AF to be valid. The utility of these factors rests on the assumption that sediment is the only source for the bioaccumulation. Thus, contributions from the overlying water would not be recognized. This assumption may or may not be appropriate, based on the organism and the actual sources involved. If overlying water is a significant contributing contaminant source, the AF would increase significantly over that resulting when sediment-associated contaminant is the only source. In the field, unexpected point discharges or other direct contamination of the overlying water could act as a significant co-source, invalidating the comparison between sediment and organism concentrations.

Further, the AF is likely constant only if contaminant concentrations in organisms are at steady-state with the contaminant concentrations in the sediment. Whether steady-state conditions occur widely in natural systems is not clear, but studies with *Pontoporeia hoyi* and *Hexagenia limbata*

suggest that for some benthic organisms steady-state concentrations only exist during specific times of the year (Eadie *et al.* 1988, Landrum & Poore 1988). Nonetheless, this thermodynamic-based method permits comparisons between extractable residues and the amount of material bioaccumulated. Used in conjunction with laboratory exposures where the source could be controlled, AFs would produce useful comparisons between bioaccumulation and extractable residue.

A second, commonly used approach to define the extent of bioavailable contaminant determines the uptake clearance of sediment-associated contaminants for a specific organism. The uptake clearance is the conditional constant that relates the contaminant flux into the organism to contaminant concentration in the sediment and has units of $\text{g sediment g}^{-1} \text{organism hr}^{-1}$. This approach has been employed for both laboratory and field collected sediments (Landrum *et al.* 1985b, Tatem 1986, Foster *et al.* 1987, Shaw & Connell 1987, Landrum & Poore 1988, Landrum 1989). When measuring kinetics of accumulation from sediment in the laboratory, the contribution from overlying water can be kept at or near zero concentration under flowing-water conditions. The uptake clearance can be used as a measure of the bioavailable fraction and can be compared with the amount of extractable residue. If the elimination kinetics are known, the steady-state contaminant concentration can be calculated as a ratio of the uptake clearance divided by the elimination rate constant. From the calculated steady-state concentration an AF could also be calculated, based on the organism lipid content and the sediment organic carbon content. Kinetic relationships have the advantage that multiple sources can be accommodated in the experimental designs and the fraction of accumulated body burden from each source can be estimated. Further, the incorporation of multiple sources in kinetic calculations permits modeling of field situations where contaminant accumulation results from multiple sources. However, kinetic measurements are much more expensive and time-consuming than the measurements required for an assumed steady-state.

Bioavailability of sediment-associated contaminants can be defined in a general sense; however, no chemical measures currently exist to predict bioavailability of sediment-bound residues. The only approaches available for estimating the bioavailable fraction are comparisons between the accumulation and the sediment chemistry. A better method for defining bioavailability is needed.

3.0 FACTORS AFFECTING BIOAVAILABILITY

Several reviews have outlined major factors affecting the rate or extent of sediment contaminant bioaccumulation, particularly for organic contami-

nants (Neff 1984, Adams 1987, Knezovich *et al.* 1987, Reynoldson 1987, Rodgers *et al.* 1987). These factors can be divided into three general areas: (1) the characteristics of the contaminants, (2) the composition and characteristics of the sediment, and (3) the behavior and physiological characteristics of the organisms. In general, the range of bioaccumulation factors (BAF, the concentration of the contaminant in the organism divided by the concentration in the sediment) for sediment-associated contaminants is 0.1 to about 20 (Neff 1984). Further, previous studies have generally suggested that the accumulation of sediment-associated contaminants occurs via sediment interstitial water.

3.1 Compound Characteristics

For nonpolar organic compounds, the major characteristic which controls bioaccumulation from sediments is the hydrophobicity of the compound, as represented by the octanol-water partition coefficient (K_{ow}). The extent of contaminant accumulation generally decreases with increasing log K_{ow} or decreasing water solubility because of increased partitioning to sediment particles. Other factors that increase the sorption or complexation to sediment particles, such as hydrogen bonding, compound ionization, or chemical reactivity, may also reduce bioavailability (Neff 1984, Adams 1987, Knezovich *et al.* 1987, Reynoldson 1987, Rodgers *et al.* 1987).

Several relationships between K_{ow} and bioavailability have been reported. Some reports show log-linear relationships between K_{ow} and the accumulation of contaminants from sediments (Knezovitch & Harrison 1988, Gobas *et al.* 1989). However, oligochaetes exhibit a maximum BAF at approximately a log K_{ow} of 6 when exposed to chlorinated hydrocarbons covering a range of K_{ow} (Oliver 1984, 1987). The apparent maximum in the BAF seems to result from a combination of pharmacological characteristics, such as the uptake and elimination rates of compounds, and sorption properties of the compounds. Compounds with small K_{ow} are less strongly sorbed and more bioavailable, presumably from both more rapid desorption to interstitial water and increased assimilation efficiency, but are also more rapidly eliminated, which results in relatively low BAF values. Compounds with a very large K_{ow} are more slowly desorbed from sediment and, therefore, less bioavailable, presumably as a result of both decreased desorption rates and lower assimilation efficiency from ingested particles, which also results in a small BAF in spite of the generally high bioconcentration of such compounds from water. Similar relationships were observed for the accumulation of chlorinated hydrocarbons by *Pontoporeia hoyi* (Landrum *et al.* 1989) and for a variety of marine organisms exposed to compounds under field conditions (Pereira *et al.* 1988).

The uptake clearance of polycyclic aromatic hydrocarbons (PAH) from a

single type of sediment was observed to be inversely proportional to the K_{ow} for *P. hoyi* (Landrum 1989). However, the uptake clearance cannot be described by a simple relationship with K_{ow} when the clearances of several classes of compounds are compared. The uptake clearances of chlorinated compounds compared to PAH with similar K_{ow} values are much greater (Landrum 1989, Landrum *et al.* 1989). Thus, the relationship between K_{ow} and accumulation of organic contaminants is not simple, and other factors can significantly influence the accumulation of sediment-associated contaminants.

3.2 Sediment Characteristics

Important sediment properties that enhance sorption, thereby reducing bioavailability, include the organic carbon content, particle size distribution, clay type and content, cation exchange capacity, and pH. Organic carbon is a major factor because it can both sorb organic contaminants and complex metals (Neff 1984, Adams 1987, Knezovich *et al.* 1987, Reynoldson 1987, Rodgers *et al.* 1987, Swindoll & Applehans 1987, Foster & Wright 1988, McElroy & Means 1988). The influence of organic carbon is greater for compounds of greater K_{ow} that sorb primarily to the organic fraction of sediment. Although normalization to organic carbon may help account for the extent of sorption to sediments and, particularly, the fine grain sedimentary material, clays and other fine materials may contribute significantly to sorption, thus reducing contaminant bioavailability (Neff 1984, Adams 1987, Knezovich *et al.* 1987, Reynoldson 1987, Rodgers *et al.* 1987, Swindoll & Applehans 1987).

Under such circumstances, normalization to organic carbon may be invalid and misleading. Sorption of hexachlorobiphenyl to clay, for example, reduces the hexachlorobiphenyl bioavailability (Swindoll & Applehans 1987). Similarly, normalization by organic carbon did not account for all the variability in measured uptake clearances of PAH and PCB congeners by *P. hoyi* from sediments, particularly where the separately dosed fine fraction was compared with sediments dosed in bulk. *P. hoyi* uptake clearances, normalized for organic carbon and measured from sediments with similar bulk organic carbon concentrations, were greatest when the fine fraction of the sediments had been labeled separately (Landrum, unpublished data). Thus, the particle size and not organic carbon content alone is likely an important characteristic which influences bioaccumulation. More efforts are required to account for the sorption to the fine fraction of sediment and to develop the appropriate normalizing factors.

The duration of contact between sediment particles and the contaminant alters both chemical extractability and bioavailability. The increased equilibration time between the contaminant and sediment in laboratory studies

markedly reduces the bioavailability of organic contaminants to benthos (McElroy & Means 1988, Landrum 1989). These changes in bioavailability with increasing contact time are not always reflected in changes in the amount of chemically extractable residue from the sediments. Further, the extent of reduction in chemical residue concentration will not necessarily reflect the extent of reduction in bioavailability. The rate at which contaminants are observed to disappear from a bioavailable pool is approximately inversely proportional to K_{ow} within a single class of contaminants (Landrum 1989). Possible mechanisms driving this reduction include (1) sorption into less bioavailable sediment compartments, (2) removal of the ingestible fraction through packaging of fine material into fecal pellets, and (3) changes in organism behavior.

3.3 Partitioning

Understanding partitioning between sediment particles and interstitial water is important for understanding contaminant bioavailability. In their review of early laboratory studies, Elzerman and Coats (1987) showed that the partitioning of organic contaminants usually fits a Freundlich isotherm. Thus, the partition coefficient can be determined as the slope of the regression line between the contaminant concentration on particles and the concentration of the dissolved contaminant measured at equilibrium for different total contaminant concentrations. In virtually all cases, the experimental designs for determining partitioning followed contaminant adsorption as an approach to equilibrium partitioning. In other words, a contaminant was introduced into the aqueous phase and allowed to adsorb to suspended particles. The concentration in the water and particles is measured until an apparent equilibrium is obtained and a partition coefficient is then calculated. Partition coefficients measured for the same compound with different sediments showed a variability that could be reduced by normalization to sediment organic carbon (Karickhoff *et al.* 1979). The partition coefficient for sediment suspensions often increased as the solids concentration decreased. These increasing partition coefficients generally reach an apparent plateau when the solids concentration is sufficiently small (O'Connor & Connolly 1980, Voice & Weber 1985, DiToro 1985). One explanation for this effect was the presence of a third phase consisting of nonfilterable colloids or dissolved organic matter (DOM) (Voice & Weber 1985, Gschwend & Wu 1985). Such a third phase enhances the apparent solubility of nonpolar organic molecules by maintaining them in solution in a bound form. Binding of contaminants by this third phase also reduces the contaminant bioavailability in the water column (Landrum *et al.* 1985a, 1987, McCarthy & Jimenez 1985, McCarty *et al.* 1985, Black & McCarthy

1988). DOM sorption will also affect bioavailability from interstitial waters that contain large DOM concentrations.

A greater complexity in the partitioning phenomena was observed when the experimental design followed the desorption of contaminants as an approach to equilibrium partitioning. Compounds sorbed to sediments apparently reside in reversible and resistant pools, and the fraction of the total contaminant in each pool changes depending on sorption duration (Karickhoff 1980, DiToro *et al.* 1982, Karickhoff & Morris 1985a). To model this observation, a two-compartment kinetic model was deemed appropriate (Karickhoff & Morris 1985a); since then, additional kinetic models of partitioning have been employed to better describe the variety of complexities involved in partitioning, such as "solids concentration effects" and "multiple sorption sites on particles" (Elzerman & Coats 1987). Mechanistic models identify the sediment particle as a semisolid material and describe the sorption process by diffusion coefficients into the sediment matrix to account for the observed partitioning phenomena (Freeman & Cheung 1981, Wu & Gschwend 1986). These mechanistic models, which require a third phase to describe the overall partitioning, need more development before they can be very useful in bioavailability assessment.

Hysteresis effects exist in the time relations between adsorption and desorption of contaminants to sediment. Nonpolar organic compounds associate rapidly with sedimentary materials but desorb more slowly (Elzerman & Coats 1987, Witkowski *et al.* 1988). A recent quantitative model that examined the sorption and desorption of PCBs showed that the effects on partitioning, such as the solids concentration effect, result from employing equilibrium models instead of kinetic models (Witkowski *et al.* 1988). The importance of a third phase is not ruled out in kinetic models, but in some systems it may not be very important. From the above model, slow desorption relative to adsorption and the relatively slow uptake clearances from sediments (Landrum 1989) suggest small desorption rate constants for sediment sorbed contaminants. Thus, the time required to reach steady-state between the sediment and the interstitial water could be long, and the slow desorption rates will have a significant impact on the bioavailability of organic compounds from sediments.

Focusing on the kinetics, the only existing estimates of the desorption rate constants come from gas stripping experiments employing suspended sediments for some PCB congeners (Coats & Elzerman 1986), other chlorinated hydrocarbon compounds (Oliver 1985), and for certain PAH congeners (Karickhoff 1980, Karickhoff & Morris 1985a). This experimental design maximizes the rate of desorption by maintaining the maximum concentration gradient between the water and the sediment particles through gas purging of the water. These desorption data suggest that it takes months or even years, depending on sediment composition and compound characteris-

tics, to achieve true equilibrium between interstitial water and sediment particles (Karickhoff 1980, Karickhoff & Morris 1985a, Oliver 1985, Coats & Elzerman 1986, Witkowski *et al.* 1988). The desorption rates reported for PAH (Karickhoff & Morris 1985a) were faster than those reported for the chlorinated compounds (Coats & Elzerman 1986), even when the relative K_{ow} s were considered. However, in gas stripping experiments employing humic materials as the sorptive phase, the desorption of PAH congeners was much slower than for chlorinated compounds of similar log K_{ow} (B. J. Eadie, Personal Communication, Great Lakes Environmental Research Laboratory, NOAA, Ann Arbor, MI). Further, the gas stripping of contaminants from humic materials was very dependent on the purge gas flow rate. Thus, comparisons between different results must be interpreted carefully. Based on experiments of desorption from humics with both chlorinated hydrocarbons and PAH under the same conditions, it seems likely that desorption of PAH will be slower and that equilibrium between interstitial water and sediment solids may require much longer contact times than for chlorinated compounds.

Based on a qualitative model (Landrum 1989), these small desorption rate constants help explain the slow rates of contaminant accumulation by benthos. Because of the apparent importance of the desorption constants, more effort to measure them is essential to development of quantitative models for contaminant accumulation from sediments. Further, because the currently measured desorption values are maximum desorption values (as a result of the experimental design), efforts are needed to determine the range of these constants under differing environmental conditions.

3.4 Role of Interstitial Water

From the literature, the dominant route for accumulation of sediment-associated contaminants is suggested to be via interstitial water (Muir *et al.* 1985, Oliver 1987, Shaw & Connell 1987, Knezovitch & Harrison 1988). However, two recent studies suggest that the interstitial water route may not dominate in all systems (Landrum 1989, Landrum *et al.* 1989). The measured partitioning between sediment interstitial water and sediment particles did not reflect the uptake clearances of contaminants belonging to different classes of compounds. The partition coefficient between the sediment interstitial water and sediment particles for benzo(a)pyrene (BaP) was approximately half that for tetrachlorobiphenyl (TCB). The uptake clearance for TCB was nearly ten times greater than for BaP (Landrum *et al.* 1989). The differences between the bioavailability of the two compounds can be better described by their apparent differences in the desorption rates from sediment than by their equilibrium partition coefficient. The significance of interstitial water as a source will be described in more detail below.

3.5 Biological Characteristics

The biological processes and characteristics that influence the transfer of contaminants from sediments include organism behavior, modes and rate of feeding, source of water — interstitial water versus overlying water — for respiration, and organism size (Neff 1984, Adams 1987, Knezovich *et al.* 1987, Reynoldson 1987, Rodgers *et al.* 1987). Critical parameters vary for the species involved; thus, each species must be considered separately.

Feeding behavior is an important feature in the accumulation of sediment-associated contaminants (Varanasi *et al.* 1985, Foster *et al.* 1987, McElroy & Means 1988, Schuyema *et al.* 1988), and in the case of the clam *Macoma nasuta*, the sediment-associated hexachlorobenzene comes almost completely from sediment particle ingestion (Boese *et al.* 1990). Because benthic organisms feed on fine sediment particles rather than bulk sediment and because the partitioning of contaminants is to the fine organic rich particles, the contaminant concentrations on the ingested particles will often be greater than measured bulk concentrations. Even low rates of ingestion or low assimilation efficiencies can result in significant amounts of accumulation via ingestion. This differential sorption between large and small particles must be accounted for before assimilation from ingestion can be determined (Lee *et al.* 1990). The importance of the fine material as a major contaminant source has been demonstrated for benthos in the Great Lakes (Eadie *et al.* 1985) and upper Mississippi River (Bailey & Rada 1984).

Behavioral factors influencing the transfer between sediment and organisms are well illustrated by the clam *Macoma nasuta*. *Macoma* essentially only uses overlying water for respiration (Windsor *et al.* 1990) but feeds on organic detrital material (Boese *et al.* 1990). Thus, its primary source of sediment-associated contaminants is dominated by the ingestion of particles and not by the ventilation of sediment interstitial water (Boese *et al.* 1990). Such discrimination between overlying and interstitial water may be especially important for tube dwellers, such as chironomids, hexagenia, and other organisms, that pump overlying water through their burrows. The extent to which organisms ventilate overlying water will govern the proportion of contaminant derived from interstitial fluids.

Reductions in the exposure of benthos to sediment-associated contaminants through behavioral modification can also occur for infaunal organisms such as oligochaetes. Oligochaetes can modify feeding behavior and even emerge from the sediments if the contaminants can be detected (Keilty *et al.* 1988a), thus modifying their exposure to both sediment interstitial water and to particle-associated contaminants by moving to zones of lesser contamination. In recent work, the oligochaete *Stylodrilus heringianus* was observed to burrow below a layer of fine particles, which presumably contained the greatest concentration of contaminants. This layer of fine sedi-

ments was created by allowing sediments to settle passively and therefore sort according to size. By contrast, in well-mixed sediments the introduced organisms burrowed but returned to the surface, presumably to avoid the toxic contaminants (White & Keilty 1988)

Exposure in natural systems is further modified by "conveyor-belt"-type bioturbation processes through particle-selective feeding, which tends to maintain contaminants in the bioactive layer of sediments (Robbins 1986). These "conveyor-belt" feeders consume particles deeper in the sediments and deposit them on the surface. In laboratory microcosms, oligochaetes have been observed to rework the sediment and enhance the concentration of contaminants in the upper layers with time, which demonstrates particle-selective transport (Karickhoff & Morris 1985b, Keilty *et al.* 1988b, 1988c). Organisms such as chironomids (Wood *et al.* 1987) have been shown to enhance the release of contaminants to overlying water. This release of contaminants from the sediments, which is likely to occur with many of the tube dwellers, would change the concentration to which organisms such as *Macoma* that ventilate overlying water are exposed. Thus, even though *Macoma* does not ventilate interstitial water, the action of the tube dwellers will tend to expose this and other organisms that live near or on the sediment surface to greater concentrations of desorbed contaminants by introducing some interstitial water into the overlying water.

4.0 MODELING BIOAVAILABILITY

In early modeling efforts, accumulation from sediments was treated as a first-order rate process with no definition of the source, sediment particles, or sediment interstitial water. Such models depended on empirical relationships between uptake clearance from sediments, contaminant characteristics, and sediment characteristics. These models provided reasonable initial estimates of the extent of the overall sources, overlying water or sediment-associated contaminants, to the bioaccumulation (Landrum *et al.* 1985b, Eadie *et al.* 1988). The empirical models suggested that features such as assimilation from ingestion and desorption from sediments would be important for mechanistic models. A conceptual framework including such processes has been developed (Landrum 1989).

Because sediment interstitial water has been strongly suggested as the primary source for sediment-associated contaminants (Pavlou & Weston 1984, Adams *et al.* 1985, Muir *et al.* 1985, Oliver 1987, Knezovitch & Harrison 1988), a mass balance box model (Figure 1) was developed that considered sediment as a box containing sediment particles, interstitial water, and organisms. This model, developed for *P. hoyi*, treats contaminant elimination as predominantly fecal, with compounds returning to the

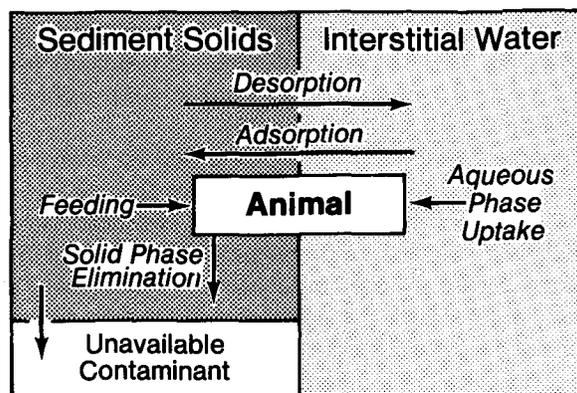


Figure 1. Mass balance box model for the accumulation of organic contaminants for sediments.

sediment reservoir. This assumption was defensible because elimination of PAH is not measurable in the absence of sediment (Landrum 1982). It is not possible to tell, at this time, whether material eliminated via the fecal route is available to the organisms or is removed from the bioavailable pool because *P. hoyi* package their fecal pellets in a peritrophic membrane that essentially makes them large particles. We assumed for this model that the material was equally available after elimination or was such a small fraction of the total sediment that it was an unimportant source. The accumulation by *P. hoyi* comes both from interstitial water and from ingestion of sediment particles. The small pool of material associated with the DOM in the interstitial water can be assumed, for modeling purposes, to be part of the sediment particles. The uptake from interstitial water is considered to be limited by the size of the interstitial water pool to which the organisms are exposed and the desorption rate of contaminants from sediment. The indications of limitations for the interstitial pool size and the desorption rates come from studies of PAH uptake from sediments (Landrum 1989). The amount of compound accumulated from sediment particle ingestion is based on measured ingestion rates (M. A. Quigley, Personal Communication, Great Lakes Environmental Research Laboratory, NOAA, Ann Arbor, MI) and the measured fraction of fine grain material in the sediments. The amount accumulated from sediment ingestion is assumed to originate primarily from contaminants sorbed onto the fine grain sediments preferentially ingested by *P. hoyi*. The accumulation of contaminant from overlying water was ignored in the model because (1) previous studies demonstrated that contaminant dosed to sediments was accumulated with the same uptake clearance whether the accumulation was determined under

static or flow-through conditions and (2) P. hoyi spends less than 10% of its

time above the sediments (M. A. Quigley, Personal Communication, Great Lakes Environmental Research Laboratory, NOAA, Ann Arbor, MI). The quantity of contaminant in the water was allowed to vary through adsorption and desorption kinetics from sediments and the amount accumulated by *P. hoyi* (Equations 1 to 3).

$$dQ_a/dt = (K_a \cdot Q_w) + (K_i \cdot Q_s) - (K_e \cdot Q_a) \quad (1)$$

$$dQ_w/dt = (K_1 \cdot Q_s) - (K_2 \cdot Q_w) - (K_a \cdot Q_w) \quad (2)$$

$$dQ_s/dt = (K_2 \cdot Q_w) - (K_1 \cdot Q_s) + (K_e \cdot Q_a) \quad (3)$$

where Q_a is the mass of contaminant in the organism on a mass per volume of sediment

K_a is the uptake rate constant from sediment for the organism (hr^{-1})

Q_w is the mass of contaminant in the interstitial water on a mass per volume of sediment

K_i is the uptake rate constant from ingestion (hr^{-1})

Q_s is the mass of contaminant per volume of sediment

K_e is the elimination rate constant (hr^{-1})

K_1 is the desorption rate constant from sediment particles (hr^{-1})

K_2 is the adsorption rate constant to sediment particles (hr^{-1})

t is time (hr)

The above equations represent a mass balance model and can be converted into equations with more normally measured concentration-based rate coefficients by the use of the following definitions. The density of organisms in the interstitial water (ρ) is defined as "organism wet weight per volume of interstitial water"; the fraction of interstitial water (ϕ) is "the volume of interstitial water per volume of sediment". Thus, the volume of sediment particles is $\rho_s(1 - \phi)$, where ρ_s is the mean density of sediment particles, $2.5 \pm 0.2 \text{ g mL}^{-1}$ of sediment (Robbins 1980). The mass balance equations are then converted to concentration-based equations (4 to 7). When converting from the mass balance form of the equations to the concentration-based form of the equations, two of the rate constants (K_1 and K_2) do not change. Both constants represent the fractional change in contaminant concentration with time for their respective compartments and retain the units of hr^{-1} . To make their use in the concentration-based equations distinguishable from the mass-based equation and in the case of the elimination to use the more common nomenclature, K_1 is changed to K_{de} to reflect the rate constant for desorption and K_e is changed to K_d to reflect the depuration of the contaminant.

$$dC_a/dt = (K_u \cdot C_w) + (K_r \cdot C_s) - (K_d \cdot C_a) \quad (4)$$

where C_a is the concentration of contaminant in the organism (ng g^{-1}) and equals $Q_a/(\rho \cdot \phi)$

K_u is the uptake clearance constant ($\text{mL g}^{-1} \text{ organism hr}^{-1}$) and equals K_a/ρ

K_f is the uptake clearance from ingestion ($\text{g dry sediment g}^{-1} \text{ animal hr}^{-1}$) and equals the mass-specific feeding rate ($\text{g dry sediment g}^{-1} \text{ organism hr}^{-1}$) times the assimilation efficiency, or $K_i \cdot \rho_s(1 - \phi)/(\rho \cdot \phi)$

C_s is the concentration of contaminant in the sediment (ng g^{-1}) and equals $Q_s/[\rho_s \cdot (1 - \phi)]$

K_d is the elimination rate constant and equals K_e

t is time (hr)

The subsequent equation reflecting the change in interstitial water concentration is as follows:

$$dC_w/dt = [K_{de} \cdot C_s \cdot \rho_s \cdot (1 - \phi)]/\phi - [K_p \cdot K_{de} \cdot C_w \cdot \rho_s \cdot (1 - \phi)]/\phi - (K_u \cdot \rho \cdot C_w) \quad (5)$$

where K_{de} is the desorption rate constant from sediment and is equal to K_1

K_p is the partition coefficient between the sediment and the interstitial water, and the remainder of the constants are as defined above

The substitution for K_2 is found by relating the adsorption and desorption rate at steady state to the partition coefficient (Equation 6).

$$C_s/C_w = K_p = K_2 \cdot \phi/[K_1 \rho_s(1 - \phi)] \quad (6)$$

Finally, the equation for the change in concentration in the sediment with time is described by Equation 7.

$$dC_s/dt = (K_d \cdot \rho \cdot \phi \cdot C_a)/[\rho_s \cdot (1 - \phi)] + K_p \cdot K_{de} \cdot C_w - \{[(K_f \cdot \rho \cdot \phi)/\rho_s \cdot (1 - \phi)] + K_{de}\} \cdot C_s \quad (7)$$

Because laboratory experiments have indicated that the measured contaminant concentrations in sediment do not change, in most cases, or change only slightly (Landrum 1989, Landrum *et al.* 1989) the sediments were assumed to be essentially an infinite source. Therefore, it is not necessary to include Equation 7 in the model. For the cases where the bioavailable concentration in the sediment is known to change, despite the constant or near constant chemically measured sediment concentrations (Landrum 1989), C_s was replaced by $C_s^0 \cdot e^{-\lambda t}$, where C_s^0 is the sediment concentration

Table 1. Parameter Estimates for Modeling the Accumulation of Sediments by *Pontoporeia hoyi*

Parameter	PHE ^a	PY ^b	TCB ^c	HCB ^d
Log K_{ow}	4.4 ^e	5.2 ^e	5.9 ^f	6.7 ^f
K_u (ml g ⁻¹ hr ⁻¹)	129 ^g	199.2 ^g	135 ^g	53.5 ^h
K_f (g sed. g ⁻¹ org. hr ⁻¹)	0.005	0.005	0.004	0.0029
K_d (hr ⁻¹)	0.0046 ^g	0.0012 ^g	0.0001 ⁱ	0.0001 ^h
K_{de} (hr ⁻¹)	0.18 ^k	0.046 ^k	0.005 ^l	0.0024 ^l
ρ_s^m	2.5	2.5	2.5	2.5
ϕ^n	0.698	0.698	0.698	0.698
K_p	273 ⁿ	446 ⁿ	1673 ^l	1900 ^l
λ^o (hr ⁻¹)	0.0055	0.003	0	0
K_s (g sed. g ⁻¹ org. hr ⁻¹)	0.041 ^e	0.019 ^e	0.018 ^f	0.0057 ^e
Assimilation efficiency	0.42 ^o	0.42 ^o	0.3355 ^o	0.24 ^p

^aPHE = phenanthrene.^bPY = pyrene.^cTCB = tetrachlorobiphenyl.^dHCB = hexachlorobiphenyl.^eLandrum (1989).^fLandrum *et al.* (1989).^gLandrum (1988).^hEvans and Landrum (1989).ⁱ K_f = feeding rate (0.012 g sed. g⁻¹ org. hr⁻¹) • assimilation efficiency; feeding rate from Quigley, Personal Communication, Great Lakes Environmental Research Laboratory, NOAA, Ann Arbor, MI.^jEstimated.^kKarickhoff and Morris (1985a).^lCoats and Elzerman (1986).^mRobbins (1980).ⁿLandrum, unpublished data.^oGobas *et al.* (1988).^pKlump *et al.* (1987).

at time equals zero and λ is the rate constant (hr⁻¹) for the apparent reduction in the bioavailable concentration with time.

The model was parameterized with values from the literature (Table 1). The uptake and elimination coefficients, K_u and K_d , were mean values from previous kinetic measurements of uptake from water and elimination in the presence of sediment for the PAH congeners and TCB (Landrum 1988) and for hexachlorobiphenyl (Evans & Landrum 1989). The value for ϕ (Landrum, unpublished data) was calculated from previous experiments designed to measure the uptake from sediments (Landrum 1989). K_{de} estimates for PCB congeners (Coats & Elzerman 1986) and for PAH congeners (Karickhoff 1980) were taken from the literature. The desorption rate constants were for sediments with organic carbon concentrations that were similar (approximately 1%) to that of the sediment used for measuring uptake rates in *P. hoyi*.

Both the feeding rate and the assimilation efficiency must be known to establish estimates for K_p , which is the product of the two terms. The feeding rate for *P. hoyi* was 0.012 g dry sediment g^{-1} organism hr^{-1} , calculated from the gut turnover and the characteristics of the sediment (Landrum 1989). This feeding rate is consistent with feeding rates found for Lake Ontario *P. hoyi* of 0.01 ± 0.002 g dry sediment g^{-1} organism hr^{-1} (Dermott & Corning 1988). In addition to the sediment throughput, the assimilation efficiency must be known to determine the flux of contaminant into the organism from this source.

Two approaches have been used to measure assimilation efficiency for benthic organisms. The first employs a dual radio tracer, ^{51}Cr and a ^{14}C -labeled contaminant. The ^{51}Cr associated with sediment is not well absorbed, while the contaminant will be partially absorbed. With this technique, the assimilation efficiency for 2,4,5,2',4',5'-hexachlorobiphenyl in oligochaetes ranged from 15 to 36% and was inversely proportional to the defecation rate (Klump *et al.* 1987). The second method measured the relative concentration of a radiolabeled contaminant in the food and the fecal pellets normalized to the organic carbon content. The assimilation of natural organic carbon by the organism must be known or measured and the concentration in the fecal matter must be adjusted for this loss. Using this technique, the assimilation efficiency for *Macoma nasuta* ranged from 39 to 57% for hexachlorobenzene (Lee *et al.* 1990).

These assimilation efficiencies are similar to those for other chlorinated compounds in fish, where the contaminants are associated with food (Gobas *et al.* 1988). The regression equation between contaminant $\log K_{ow}$ and assimilation efficiency (Gobas *et al.* 1988) was employed as a first estimate for *P. hoyi* assimilation efficiency from sediments when no other estimate was available.

The partition coefficient for the model was taken from measured partition coefficients between sediment interstitial water and sediment particles for TCB (Landrum *et al.* 1989), phenanthrene, and pyrene (Landrum, unpublished data). Because the partition coefficient had not been measured for hexachlorobiphenyl, it was estimated by multiplying the measured TCB partition coefficient by the ratio K_{ow} for hexachlorobiphenyl divided by K_{ow} for TCB.

With the above independent values to parameterize the model, an estimate of the optimum value of ρ , as determined by a least-squares fit to experimental data, was sought by model simulations based on data from some of the sediment uptake experiments used for kinetics determinations (Figure 2) (Landrum 1989, Landrum *et al.* 1989). In theory, as long as the density of organisms is below some critical value, the value where loading becomes limiting in the experimental design, ρ should be compound independent. For the present, determining ρ through the model will set a lower

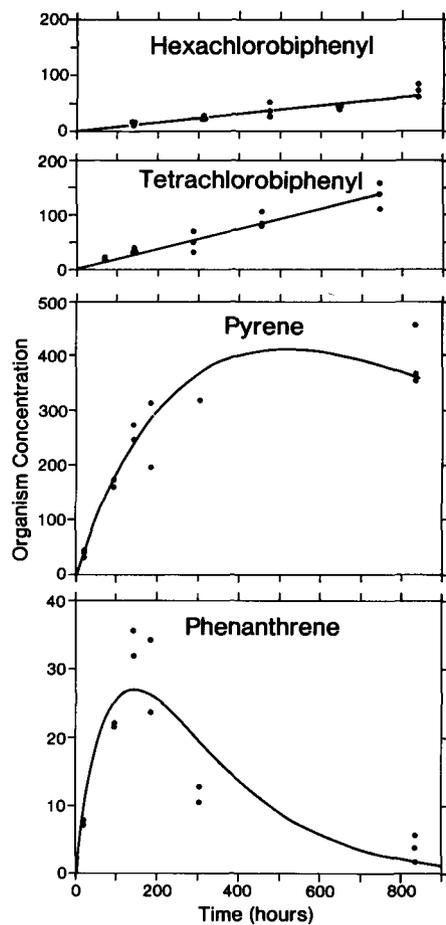


Figure 2. The fit of the model prediction to the experimental data for the using the optimized value of ρ for hexachlorobiphenyl, tetrachlorobiphenyl, pyrene, and phenanthrene.

bound on the amount of interstitial water to which the organism must be exposed to exhibit the measured rate of accumulation. Future efforts should attempt to measure ρ so that the variation in other parameters can be more fully examined.

It is important to begin such optimization with a good estimate; thus, an exact solution for ρ was determined for the steady-state condition by setting both Equations 4 and 5 to zero. The solution includes a required estimate for the organism contaminant concentration at steady state. This estimate

can be obtained from a two-compartment model of accumulation from sediment (Landrum 1989, Landrum *et al.* 1989; Equation 7):

$$dCa/dt = (K_s \cdot C_s) - (K_d \cdot Ca) \quad (7)$$

where K_s is the measured uptake clearance from sediment (g dry sediment g^{-1} organism hr^{-1}) and the other terms are as previously defined.

Thus, the steady-state concentration of contaminant in organisms would be $(K_s \cdot C_s)/K_d$ and could be substituted into the equation to determine ρ . The K_s value used was the average measured sediment uptake clearance (Landrum 1989). With these substitutions, ρ has the following definition in terms of measured variables (Equation 8).

$$\rho = [K_{de} \cdot \rho_s \cdot (1 - \phi)] / \phi \cdot \{ [K_u + (K_p \cdot K_f) - (K_p \cdot K_s)] / K_u \cdot (K_s - K_f) \} \quad (8)$$

While all of the values in the definition of ρ are important, the least well known are the assimilation efficiencies and desorption rate constants. Because ρ is directly proportional to K_{de} , as K_{de} decreases (all other factors remaining constant) the volume of interstitial water required for exposure will increase for a given uptake rate. As the accumulation from feeding becomes greater, the fraction resulting from interstitial water exposure becomes less and the volume of interstitial water required for exposure to maintain a fixed accumulation rate will decrease. For BaP, the model indicates that for *P. hoyi* ρ would be ∞ and the organism would not be obtaining any of its dose from interstitial water, assuming an ingestion rate of $0.012 \text{ g sediment } g^{-1} \text{ hr}^{-1}$ and an assimilation efficiency of 24% — the same as hexachlorobiphenyl, based on the two compounds having similar K_{ow} values. The above scenario, with our best estimates of assimilation efficiency, suggests that our estimates for the assimilation efficiency are inappropriate for BaP.

The optimized values for ρ (Table 2) range over an order of magnitude and the value for each compound depends on some estimates of various parameters for each contaminant, aside from the literature values available, because all of the necessary parameters have not been measured. These optimized values of ρ allowed the model to fit the accumulation data for the various sediment-associated contaminants (Figure 2). The estimated values for each of the contaminants are as follows: For hexachlorobiphenyl, the partitioning between sediments and interstitial water had not been measured but was estimated as described above. For TCB, K_d could not be measured (Landrum 1988) and was assumed to be one order of magnitude smaller than the smallest value previously measured, 0.0001 hr^{-1} . For all of the

Table 2. Estimated Densities of *Pontoporeia hoyi* in Sediment Interstitial Water Based on Rates of Accumulation from Sediment

Compound	ρ (g wet organism mL ⁻¹ porewater)	Interstitial Water ^a Volume/Animal
2,4,5,2',4',5'-Hexachlorobiphenyl	0.736	8.15 μ l
2,4,2',4'-Tetrachlorobiphenyl	0.26	23.1 μ l
Pyrene	3.42	1.75 μ l
Phenanthrene	4.91	1.22 μ l

^aThis estimate assumes a mean organism weight of 6 mg wet weight.

compounds except hexachlorobiphenyl, the assimilation efficiency was estimated from the model of Gobas *et al.* (1988) proposed for fish.

An interesting feature of the ρ values is the implied small volume of interstitial water to which the organisms have to be exposed, based on current estimates of desorption rates, to demonstrate the measured rate of accumulation. At the estimated feeding rate, the organisms only "see" about three times their body mass as a maximum volume of interstitial water. If feeding were turned off, the volume would only be about four times their body mass.

To estimate the relative roles of uptake through interstitial water from direct desorption from particles, the model is run under with the optimum ρ value and all other parameters are held the same, except the K_f term is set at zero. This prevents any accumulation through the ingestion route. Projected organism concentrations obtained under conditions with no uptake from ingestion can be compared with projections where both uptake from ingestion and interstitial water occurred. The ratio of the concentration under the no-ingestion scenario compared to that with both ingestion and interstitial water times 100 gives the percentage of the accumulation attributable to desorption and uptake from interstitial water (Table 3). By the difference from 100%, the percentage of the uptake attributable to ingestion can be calculated from the percentage attributable to interstitial water (Table 3). For BaP, the expected percentage from ingestion was determined by comparing the amount of uptake that would be attributed to ingestion

Table 3. Estimated Contaminant Contribution from Interstitial Water and Sediment Ingestion for *Pontoporeia hoyi*

Compound	Source	
	Interstitial Water	Particle Ingestion
Benzo(a)pyrene	0%	100%
Hexachlorobiphenyl	52%	48%
Tetrachlorobiphenyl	80%	20%
Pyrene	74%	26%
Phenanthrene	88%	12%

with the total uptake observed. The percentage uptake from interstitial water was estimated by the difference from 100% (Table 3). The reason for the different approach for the calculation for BaP compared to the other compounds listed is that no estimate of K_{de} is available for the model.

It should be recognized that the relative percentages of accumulation reflect a balance between the flux due to ingestion and the flux due to uptake from interstitial water. If the desorption rates were greater than those used for parameterizing the model, as suggested by equilibrium partitioning advocates, the organisms would only need to contact a negligible amount of interstitial water to maintain the measured rate of accumulation and the balance of the two terms for the uptake would favor the interstitial water. Because desorption rates are determined by gas stripping, they represent the maximum desorption rates. Under natural conditions it is unlikely that the maximum thermodynamic gradient would be maintained, as occurs in these laboratory experimental conditions; therefore, the rate of desorption actually encountered by the organisms is likely smaller than would be measured under gas stripping. Further, in the sediment matrix, diffusion within the interstitial water may limit transfer of desorbed compounds to the organism. Thus, the volume of interstitial water contacted by the organism is likely larger than estimated above. Alternatively, if the desorption rate constant is infinitely slow, there was no diffusion within interstitial water and the organism could receive its interstitial water dose only by moving to fresh interstitial water, a maximum volume of interstitial water that the organism would need to contact to reach steady-state could be determined. For hexachlorobiphenyl, the volume would need to be about 560 ml, assuming no accumulation from food – admittedly an unlikely scenario. Thus, the bounds on the volume of interstitial water to which *P. hoyi* must be exposed to maintain the observed hexachlorobiphenyl uptake range from 8.2 μ l to 560 ml, depending on the role of feeding and the desorption rate constant.

The model is extremely sensitive to both K_{de} and K_r . While these terms are very uncertain, particularly considering the limited data sets available, it is unlikely that K_{de} will be considerably larger than the values measured by gas stripping experiments. Therefore, accumulation through interstitial water cannot account for the rate of accumulation observed, particularly for the chlorinated biphenyls. To ascertain an accurate measure of the balance between the two routes of accumulation, improved data sets are required.

One approach to test the true limits for ρ could be accomplished through experiments designed to measure uptake clearance as a function of the organism density per gram of sediment. Once ρ was known, estimates for K_{de} under uptake conditions could be calculated. These could be compared with the maximum rate of desorption by gas stripping and could perhaps permit development of relationships between the gas stripping measure-

ments and environmentally relevant desorption rates. Of course such estimates will still depend on gaining a better understanding of the feeding rate and assimilation efficiency.

5.0 SUMMARY

Our model demonstrates that the accumulation of contaminants from sediments is limited by two rate processes: ingestion and desorption from sediment particles. These processes dominate the flux of compound into the organism, depending on their individual magnitudes. For *P. hoyi* the accumulation from ingestion is most important for compounds that sorb most strongly to the sediments and that can account for more than 90% of the accumulation based on our model results. Ingestion of contaminated particles accounts for only approximately 12% of the accumulated phenanthrene. The model demonstrates that instantaneous equilibrium is not appropriate for estimating the amount of contaminant that is bioavailable or for determining the extent of accumulation of organic contaminants in organisms. More study is required to determine which process, desorption or ingestion, is most rate-limiting and to determine whether these processes are so limiting that the possible steady-state concentrations in organisms are kinetically limited.

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