DISTRIBUTION OF ORGANIC CARBON AND ORGANIC XENOBIOTICS AMONG DIFFERENT PARTICLE-SIZE FRACTIONS IN SEDIMENTS

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Abstract

The distributions of benzo[a]pyrene, hexachlorobiphenyl, and total organic carbon in a Lake Michigan sediment and a Florissant soil sample were determined and related to the known bioavailability of the compounds. The distribution of organic compounds among small particles (<63 μm diameter) was different from the distribution of the total organic carbon. However, the organic matter remained the major sorbent for these compounds. Changing the fractionation conditions, by performing the fractionation in distilled water instead of natural lake water, altered the distributions for both organic carbon and xenobiotics among the particles. Further, the contaminant distribution relative to organic carbon content differed between particle-size fractions and between contaminants of different compound classes, e.g., PAHs and PCBs. The differential distribution of the contaminants in the particle-size fractions likely contributed to the observed differences in bioavailability of organic contaminants for benthic organisms and may be exacerbated by selective feeding.

Key words: sediment, particle-size distribution, organic carbon, PAHs, PCBs

Introduction

Non-polar organic contaminants, such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs), are bound by particles in the water and tend to accumulate in sediments. The partitioning of non-polar organic xenobiotics between water and sediment or soil has been found to be linearly related to the organic content in both phases. Partitioning of organic contaminants between the two phases has also been correlated with clay content of the sediment, where the highest partitioning has been reported to occur in the clay fraction. In most cases, the partition coefficient is demonstrated to increase with the increasing hydrophobicity of the xenobiotics and amount of organic matter in sediment (Karickhoff et al., 1979; Means et al., 1980; Schwarzenbach & Westall, 1981). However, the role of the structural properties of the organic matter associated with the sediment particles has not been
thoroughly evaluated. In the case of dissolved organic matter, changes in the structure can alter the observed partition coefficient even on a carbon normalized basis (Chiou et al., 1986; Gauthier et al., 1987; Kukkonen et al. 1990; Kukkonen & Oikari, 1991). In soil systems, some studies have demonstrated that partitioning varies with soil organic matter composition. For instance, the organic carbon normalized partition coefficient decreases for a particular compound with increases in the soil organic matter polarity expressed as the (O + N)/C ratio (Rutherford et al., 1992).

Benthic organisms living in a contaminated sediment and ingesting sediment particles may accumulate high body burdens and thus, return xenobiotics to active circulation in food webs. Accumulation of sediment-associated contaminants may occur either via the aqueous phase, i.e., passively through direct contact with pore water, or through ingestion of contaminated sediment particles. The importance of these routes to contaminant accumulation depends on the ecology and feeding behaviour of the organism and characteristics of the sediment and chemicals. There is evidence that assimilation from ingested material can be a significant accumulation route for lipophilic compounds (Landrum, 1989; Boese et al., 1990; Harkey et al., 1994). Further, accumulation via particle ingestion depends on the feeding rate of the organism, assimilation efficiency, and contaminant concentration in the ingested food particles, which may be significantly different than the concentration in the bulk sediment (Lee et al., 1990; Lydy & Landrum, 1993).

Selective-feeding benthic organisms consume particles with higher organic carbon concentration and smaller size than non-selective feeders (McMurthy et al., 1983; Klump et al., 1987). For example, Diporeia spp., a benthic amphipod in the Great Lakes, accumulates the majority of its PAH body burden from the fine-grain sediments (< 63 μm) (Eadie et al., 1985). Diporeia is an extremely selective feeder and can selectively ingest particles enriched in one hydrophobic contaminant over another relative to the particle organic carbon content (Harkey et al., 1994).

In order to evaluate the importance of particle ingestion in the accumulation process, it is necessary to determine the partitioning of the xenobiotics to different particle size fractions. There are several methods to fractionate soil or sediment samples (Stockham & Fochtman, 1977; Christensen, 1992). Traditional analysis of particle-size distribution in soil or sediments involves removal of the organic material and chemical dispersion of the remaining solids (Day, 1965). The result can differ considerably from the actual particle-size distribution due to aggregation of particles under natural conditions (Wall et al., 1978; Walling & Moorehead, 1989). The procedure is therefore not applicable to a study of the partitioning of xenobiotics to "natural" sediment particle-size fractions. For example, Walling & Moorehead (1989) used the terms "ultimate particle-size" for the sediment particle-size fractions obtained by the methods with chemical dispersion and "effective particle-size" for the fractions obtained from sediment dispersed in the natural water. To relate the xenobiotic distributions to the exposure conditions of the benthic organisms, the fractionation should be performed under as undisturbed conditions as possible.

The objectives of the study were: (1) to demonstrate that the settling velocity method can be used for measuring the xenobiotic distribution among sediment particles; (2) to measure the effect of water quality (lake water versus distilled water) on the distribution of particles, organic carbon, and xenobiotics in two different sediments; and (3) to examine the sorption behaviour of two different xenobiotics (one PAH and one PCB) of similar hydrophobicity to help account for previously observed differences in bioavailability.
Material and Methods

Sediments

Lake Michigan sediment (organic carbon 0.5% of sediment dry weight) was obtained by PONAR grab at 45 m depth about 8 km southwest of Grand Haven, MI. The sediment was sieved at 1 mm to remove animals and large debris and kept in the dark at 4°C. This sediment has a low background concentration of PAHs (Eadie et al., 1982).

The other material used as a sediment is characterized as a silt loam soil. It was obtained from Florissant, MO. This material was selected because its low carbonate content permitted simplification of organic carbon analysis. It is also used as a sediment in some studies (Lydy & Landrum, 1993; Harkey et al., 1994) and has been used as a reference material in previous sediment bioassays (Ingersoll & Nelson, 1990). The Florissant soil was wet-sieved through a #230 standard testing screen with Lake Michigan water to obtain a material particle-size < 63 μm for use in the experiment. Water used throughout the work was Lake Michigan surface water stored in the dark at 4°C prior to use.

Chemicals

³H-benzo(a)pyrene (BaP, specific activity 69 Ci/mmol, Amersham Corp.) and C-2,2',4,4',5,5'-hexachlorobiphenyl (HCBP, 12.2 mCi mmol⁻¹, Sigma Chemical Co.) were dissolved in acetone, and radiopurity was determined using thin layer chromatography (TLC) and liquid scintillation counting (LSC) (Landrum, 1989). The radiopurity of both compounds was >98 percent.

Sediment dosing

Four different sediment treatments were prepared: Lake Michigan sediment with BaP and HCBP, Lake Michigan sediment with BaP alone, Florissant soil with BaP and HCBP and Florissant soil with HCBP alone. The dosed sediment samples were prepared by adding 20 to 100 microlitre of the dosing solution dropwise to sediment slurry (1:1 (vol:vol) wet sediment to lake water) in a beaker while the mixture was stirred vigorously at room temperature. The water-sediment mixtures were stirred at room temperature for four hours and kept at 4°C overnight. The overlying water was decanted, and the sediments were mixed with fresh lake water again and allowed to stand in the dark at 4°C under lake water for one to two months. The small amount of possible remaining water-soluble carrier used should have only a minimal effect on the partitioning of the compounds to the sediment (Nkedi-Kissa et al., 1985).

Sediment fractionation and analysis

Sediment particle-size distribution was determined by a modified sedimentation technique (Day, 1965; Royse, 1970; Siebert, 1977). Approximately 40 g wet Lake Michigan sediment was first wet-sieved using filtered (0.3 μm; Gelman Sciences, glass fiber, type A/E) Lake Michigan water through 420, 105, and 63 μm standard sieves. Materials remaining on the sieves were collected in beakers. Triplicate samples were taken for LSC, and the
remained was dried to constant weight at 90°C for mass and sediment organic carbon (SOC) analyses. Material still in the water or about 20 g wet sediment was mixed with either 1.0 litre filtered Lake Michigan water or 1.0 litre distilled water in a graduated cylinder at room temperature. Samples (25 ml) from the sediment suspension were taken at 20 cm depth at 0, 120, 240, and 600 seconds after mixing. After 1200 and 4600 seconds, water samples were taken at a depth of 10 cm. The sampling times and depths were calculated by Stoke's law:

\[ v = \frac{h}{t} = \frac{x^2 g (\rho_s - \rho_l)}{18\eta} \]

where: \( v \) = particle settling velocity (cm s\(^{-1}\)), \( t \) = time (s) required for particles to fall through fixed distance \( h \) (cm), \( x \) = diameter of the particle (cm), \( g \) = acceleration induced by gravity = 980.7 cm s\(^{-2}\), \( \rho_s \) = density of particles ~2.6 g cm\(^{-3}\) (Royse, 1970), \( \rho_l \) = density of water at 20°C = 0.998 g cm\(^{-3}\) (Weast & Astle, 1982), \( \eta \) = viscosity of water at 20°C = 0.01002 g cm\(^{-1}\) s\(^{-1}\) (Weast & Astle, 1982)

The given time points yield particle-size classes smaller than 63 \( \mu \)m (0 s), all the particles in the sample), < 43 \( \mu \)m (120 s), < 31 \( \mu \)m (240 s), < 20 \( \mu \)m (600 s), < 10 (1200 s), and < 5 \( \mu \)m (4600 s). From each sample taken, three 2 ml aliquot were analyzed via LSC. The rest of the sample (19 ml) was dried to constant weight at 90°C for mass and SOC determinations. The samples obtained by this technique always contain all the remaining fractions i.e., the dry weight, organic carbon content, or xenobiotic concentrations in each fraction were calculated by subtracting the content of the next sample from the previous one. The fractionation was conducted twice in lake water for each sediment sample and once in distilled water for Lake Michigan sediment and Florissant soil with HCBP.

Dosed wet bulk sediment samples were taken in triplicate for determination of contaminant concentration, dry-to-wet weight ratios, and SOC. The dry-to-wet weight ratios were determined by weighing a wet sediment sample and drying at 90°C to constant weight. Contaminant concentration in sediment was determined by placing approximately 100 mg wet sediment into 12 ml LSC cocktail (Research Products International, 3a70B) and sonicating (Tekmar high intensity sonic disrupter) for two minutes to maximize the extraction of the compounds. The activity of the compounds was counted after two days with an LKB 1217 liquid scintillation counter. The data were corrected for quench using the external standards ratio method after subtracting background. Samples from one Lake Michigan sediment fractionation were analyzed by Coulter Counter to check the calculated nominal particle-size obtained by pipet analysis (Vanderploeg, 1981).

The SOC content was determined by drying sediment samples, treating 100 mg dry sediment with 1 N HCl to remove carbonates, redrying, and analyzing organic carbon on a Perkin-Elmer 2400 CHN Elemental Analyzer.

Results

The measured particle-size and sediment organic carbon (SOC) distributions show differences for separations performed in lake water and distilled water for Lake Michigan sediment (Figure 1) and Florissant soil (Figure 2). In
the fractionation procedure, the recovery of dry weight varied from 93 to 99 % for Lake Michigan sediment and from 89 to 98 % for Florissant soil. The recovery of SOC varied from 92 to 98 % and from 97 to 105 % for Lake Michigan sediment and Florissant soil, respectively. To verify the particle-size fractions obtained by settling technique, samples from one Lake Michigan sediment fractionation with lake water were analyzed by a Coulter Counter® technique. The mass (dry weight) distribution obtained by settling technique and the particle volume distribution analyzed from the first pipet sample (< 63 μm) by the Coulter Counter® appear different (Figure 3). However, when each of the pipetted samples were analyzed using the Coulter Counter®, only a few percent of the particles for any size fraction were larger than the calculated particle-size (Table 1). This result confirms that the size fractions obtained by the settling technique are very close to the calculated values. The factor creating the difference between the techniques may have to do with comparison of a volume distribution to a mass distribution and the potential change in the particle density with changes in particle-sizes.
Fig. 3. Comparison of the panicle dry mass and particle volume distributions in the less than 63 μm particle-size fractions of Lake Michigan sediment. The particle dry mass distribution was analyzed by the settling technique using lake water; volume distribution was analyzed by the Coulter Counter®.

Table 1. Percent volume of particles measured by Coulter Counter® in each fraction that are larger than those calculated using Stoke's law for samples taken during settling experiments.

<table>
<thead>
<tr>
<th>Calculated Size</th>
<th>% Particles larger than calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 63 μm</td>
<td>0.8</td>
</tr>
<tr>
<td>&lt; 43 μm</td>
<td>2.7</td>
</tr>
<tr>
<td>&lt; 31 μm</td>
<td>2.4</td>
</tr>
<tr>
<td>&lt; 20 μm</td>
<td>3.4</td>
</tr>
<tr>
<td>&lt; 10 μm</td>
<td>6.7</td>
</tr>
<tr>
<td>&lt; 5 μm</td>
<td>18.4*</td>
</tr>
</tbody>
</table>

*Coulter Counter® analysis indicated that 12.7% of the particles in the fraction ranged from 5.04 to 6.35 μm.

When fractionation was performed in the lake water, there were no differences in the mass or SOC distributions for the Lake Michigan sediment treated with BaP and HCBP together, with BaP alone, or among the Florissant soil samples treated with BaP and HCBP together and with HCBP alone. Therefore, the results within each sediment type could be combined.

The Lake Michigan sediment was dominated by particle sizes ranging from 420 μm to 43 μm, accounting for 80% of the total sediment dry weight (Figure 1A). The type of water used for the fractionation affected the observed particle-size distribution. The percent dry weight of the three coarse fractions remained the same for fractionation performed in both water types. However, when the fractionation was performed in distilled water, the percentage of 63 μm to 43 μm fraction decreased from 26% to 17%, while the four finest fractions doubled in percent mass compared to fractionation performed in lake water (Figure 1A). The distribution of SOC differed from the particle-size distribution. For fractionation performed in lake water, over 70% of SOC resided with the fine particles smaller than 63 μm, and 50% of the total SOC was in particles between 63 μm and 31 μm (Figure 1B). The fractionation made in the distilled water resulted in a different SOC distribution. As with the mass distribution, the amount of SOC in coarse fractions remained the same for both procedures, while a clear change occurred in the finer fractions. The amount of SOC in the fractions between 63 μm and 31 μm decreased from 50% in lake water down to 24% in distilled water, while the SOC content of the finest fraction (≤5 μm) increased from 8% in lake water to 33% in distilled water (Figure 1B, Table 2).

The Florissant soil sample, of which 91 ± 0.8% (n=6) of the total mass is ≤63 μm, was presieved through a 63 μm sieve. When fractionation was performed in lake water, 46% of total dry weight was found in the 31 to 20 μm fraction. In distilled water, the 31 to 20 μm fraction decreased to 24% with a subsequent increase in the finest fraction (≤5 μm) to 21% from 5% in lake water (Figure 2A). The SOC distribution in lake water was slightly
Table 2. Organic carbon content (% dry weight) in each particle-size fraction of Lake Michigan sediment. Fractionation was performed either in Lake Michigan water or in distilled water. The OC content in the bulk sediment and three coarse fractions were analyzed from the original samples (n=4). OC content in the fine fractions was calculated from the samples obtained by the sedimenting technique.

<table>
<thead>
<tr>
<th>Size Fraction (μm)</th>
<th>Lake Water</th>
<th>Distilled Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk Sediment</td>
<td>0.45 ± 0.04</td>
<td>0.54 ± 0.05</td>
</tr>
<tr>
<td>&gt;420</td>
<td>0.22 ± 0.08</td>
<td>0.33 ± 0.06</td>
</tr>
<tr>
<td>420 - 105</td>
<td>0.27 ± 0.08</td>
<td>0.30 ± 0.02</td>
</tr>
<tr>
<td>105 - 63</td>
<td>0.16 ± 0.02</td>
<td>0.18 ± 0.03</td>
</tr>
<tr>
<td>63 - 43</td>
<td>0.54</td>
<td>0.45</td>
</tr>
<tr>
<td>43 - 31</td>
<td>1.69</td>
<td>1.12</td>
</tr>
<tr>
<td>31 - 20</td>
<td>0.81</td>
<td>0.59</td>
</tr>
<tr>
<td>20 - 10</td>
<td>1.02</td>
<td>0.67</td>
</tr>
<tr>
<td>10 - 5</td>
<td>0.99</td>
<td>0.88</td>
</tr>
<tr>
<td>&lt;5</td>
<td>1.08</td>
<td>2.46</td>
</tr>
</tbody>
</table>

Table 3. Organic carbon content (% dry weight) in each particle-size fraction of Florissant soil. Fractionation was performed either in Lake Michigan water or in distilled water. The OC content in the bulk sediment and three coarse fractions were analyzed from the original samples (n=4). OC content in the fine fractions was calculated from the samples obtained by the sedimenting technique.

<table>
<thead>
<tr>
<th>Size Fraction (μm)</th>
<th>Lake Water</th>
<th>Distilled Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk Sediment</td>
<td>1.18 ± 0.05</td>
<td>1.12 ± 0.03</td>
</tr>
<tr>
<td>63 - 43</td>
<td>0.40</td>
<td>0.36</td>
</tr>
<tr>
<td>43 - 31</td>
<td>0.47</td>
<td>0.74</td>
</tr>
<tr>
<td>31 - 20</td>
<td>1.13</td>
<td>0.24</td>
</tr>
<tr>
<td>20 - 10</td>
<td>1.90</td>
<td>0.65</td>
</tr>
<tr>
<td>10 - 5</td>
<td>2.58</td>
<td>1.09</td>
</tr>
<tr>
<td>&lt;5</td>
<td>2.09</td>
<td>3.35</td>
</tr>
</tbody>
</table>

different than that of the dry particle distribution (Figure 2B). The use of distilled water for the settling significantly affected the SOC distribution. Compared to the separation in lake water, the SOC dropped in the fractions between 31 μm and 5 μm and increased in the finest fraction to 64 % (Figure 2B, Table 3).

When the fractionation was performed in lake water, the distributions of BaP and HCBP in the Lake Michigan sediment were clearly different than the particle mass distribution or SOC distribution (Figure 4A). About 60 to 70 % of the mass of the compounds was associated with particles in the 63 μm to 31 μm range. The coarse fractions (>63 μm) did not bind much BaP or HCBP, although the percentage of dry sediment mass was high in these-fractions. Further, these two compounds were differently distributed among the sediment particles. HCBP was more associated with the 63 μm to 43 μm fraction (53 ± 5 %, n=4) than BaP (44 ± 9 %, n=2). BaP was more associated with the small particles sizes (Figure 4A). The use of distilled water in the fractionation made a clear difference in the distribution patterns of these compounds. In the distilled water, over 40 % of both compounds was found in the finest
Fig. 4. Distribution of benzo(a)pyrene (BaP) and 2,2',4,4',5,5'-hexachlorobiphenyl (HCBP) among the particle-size fractions in Lake Michigan sediment. Fractionation was performed either in Lake Michigan water (n=4 for BaP and n=2 for HCBP) [A] or in distilled water (n=1) [B].

Fig. 5. Distribution of benzo(a)pyrene (BaP) and 2,2',4,4',5,5'-hexachlorobiphenyl (HCBP) among the particle-size fractions in the Florissant soil. Fractionation was performed either in Lake Michigan water (n=2 for BaP and n=4 for HCBP) [A] or in distilled water (n=1) [B].

fraction, and the amount of the compounds associated with the particles between 63 μm and 31 μm decreased about 20% (Figure 4B). Xenobiotic distributions in Florissant soil suggest, more strongly than in Lake Michigan sediment, that BaP and HCBP distribute differently among the particle-size fractions (Figure 5A). HCBP tended to associate more with the mid-size (from 31 to 10 μm) particles, while BaP had more even distribution across particles smaller than 31 μm. HCBP (43 ± 5%, n=4) resided in the particle-size fraction between 31 μm and 20 μm, while only 28 ± 2% (n=2) of BaP resides on these particles. The particle-size fractions 10 μm to 5 μm and smaller than 5 μm contained 35 ± 6% and 15 ± 3% of the BaP and 22 ± 4% and 6 ± 0.6% of the HCBP, respectively (Figure 5A).

The settling technique was very useful for the concurrent analyses of the distributions of total mass, organic carbon, and xenobiotics among sediment particles. In these experiments, the recovery of BaP was from 98 to 112% and the recovery of HCBP was 95 to 101% in the Lake Michigan sediment. Similarly, the recovery of BaP was 99
Fig. 6. The relative concentrations (concentration in the fractions divided by the concentration in the whole sediment) [A] and organic carbon normalized relative concentrations (org. carbon normalized concentration in the fraction divided by the org. carbon normalized concentration in the whole sediment) [B] of benzo(a)pyrene (BaP) and 2,2',4,4',5,5'-hexachlorobiphenyl (HCBP) in the particle size-fractions of Lake Michigan sediment. Comparison of fractionations conducted in lake water (LW) and in distilled water (DW).

Fig. 7. The relative concentrations (concentration in the fractions divided by the concentration in the whole sediment) [A] and organic carbon normalized relative concentrations (org. carbon normalized concentration in the fraction divided by the org. carbon normalized concentration in the whole sediment) [B] of benzo(a)pyrene (BaP) and 2,2',4,4',5,5'-hexachlorobiphenyl (HCBP) in the particle-size fractions of Florissant soil sample. Comparison of fractionations conducted in lake water (LW) and in distilled water (DW; HCBP only).

to 112 % and the recovery of HCBP was 94 to 105 % in Florissant soil. The recovery is calculated using the activity measured in the bulk sediment and comparing it to the sum of the activities measured in each fraction.

The concentrations of BaP and HCBP in different sediment particle-size fractions can be better compared using relative concentrations (xenobiotic concentration in the fraction divided by the xenobiotic concentration in the bulk sediment). Further, the influence of different organic carbon concentrations in the different fractions can be accounted for by normalizing to the relative organic carbon content of the fractions. If all organic matter binds the compounds in a similar manner, the relative concentration after carbon normalization should be one. In Lake
Michigan sediment, the relative concentrations of BaP and HCBP in different fractions, before carbon normalization, suggest that these compounds tend to concentrate on the smaller particles (Figure 6A). The relative BaP and HCBP concentrations were much lower than one in the coarse fractions (>63 μm), and the type of water used for the fractionation did not affect these distributions. Thus, the material in the large particles does not bind xenobiotics as efficiently as in smaller particles. The relative concentrations in the finer material (< 63 μm) were greater than one and depended on the water used in fractionation. Further, some differences in the relative distribution among particles remain, even with carbon normalization (Figure 6B).

There was also a clear difference between the relative concentrations of BaP and HCBP in the different particle-size fractions in Florissant soil (Figure 7A). Further, the large differences in the distributions of the two compounds remained after the organic carbon normalization (Figure 7B).

Discussion

Although basic relationships between particle-size and xenobiotic sorption have been established in laboratory studies (Barber et al. 1992), the relation between sorption, particle-size, and bioavailability is not as clear. One reason for this is that most of the sorption studies using different particle-size fractions have used particles <63 μm as the smallest size fraction. This fractionation is too coarse to relate the particle-size distribution to the bioavailability of compounds to benthic organisms.

Besides the size, the physical-chemical characteristics of inorganic particles dictates the adsorption of natural organic material as well as xenobiotics onto the particles. A sediment particle can be viewed as an inorganic base that contains one or more minerals and is coated with the natural organic molecules, for example, humic substances (Figure 8). Each of the mineral types has a characteristic surface charge (Sposito, 1992), and this charge influences the nature and extent of the interaction between natural dissolved organic matter and mineral surfaces (Davis, 1980, 1982; Tipping, 1981a, 1981b). Also, the nature of dissolved organic matter as well as the characteristics of the aqueous phase affect the adsorption (Zhou et al., 1994). Finally, this particle-associated organic matter largely controls the sorption of non-polar organic xenobiotics onto the sediment particles.

Increasing the ionic strength of the aqueous phase increases the adsorption of natural dissolved organic matter to various particles (Rashid et al. 1972; Zhou et al., 1994). The desorption of organic matter in distilled water depends on the chemical nature of organic molecules (Zhou et al., 1994). Thus, when sediment particles are suspended in a media that has a lower ionic strength than the original solution from which the particles were isolated, some of the sorbed natural organic matter can desorb and some of the particles can disaggregate. This apparently happened in the fractionation conducted in the distilled water and resulted in different organic carbon and xenobiotic distributions compared to lake water fractionation (Figures 1, 2, 4 and 5). Based on these results, we recommend that sediment fractionation studies be conducted in water originating from the same location as the sediment or, if this is not possible, in an artificial water that resembles the original water composition as closely as possible.

Even when the fractionation is performed in lake water, the organic carbon distribution differs from the dry
Fig. 8. A conceptual model of sediment particles where dissolved organic matter (DOM) forms a coating on the inorganic base particle with the subsequent binding of an organic xenobiotic, mainly to the organic coating.

particle mass distribution (Figures 1 and 2) with most of the organic matter residing with the small particle-size fractions (Table 2 and 3). This relative distribution has been reported previously (Schwarzenbach & Westall, 1981; Barber, 1994). This distribution difference is explained by differences in the mineralogical composition of different particle-size fractions, which affect the amount and type of natural organic matter sorbing on the particles (Barber, 1994). In addition, if different types of natural organic matter are bound by particles of differing size and composition, it is possible that the differing organic matter would have different affinities for different classes of xenobiotics. This, in fact, has been observed with dissolved organic matter in natural waters (Kukkonen et al., 1990; Kukkonen & Oikari, 1991).

Thus, molecular structure, the amount of surface area, and the organic matter composition may all influence the sorption of non-polar organic compounds to particles and, therefore, the bioavailability (Word et al., 1987). The differential bioavailability seen among sediments possessing the same organic carbon content but obtained from different sources (Word et al., 1987; DeWitt et al., 1992; Suedel et al., 1993) points heavily to the influence of the sediment composition components on exposure. Not only does the partitioning apparently vary with the organic carbon content and composition, but compounds of different chemical classes apparently bind to different portions of the organic matter. Some studies also suggest that bacterial flora on the particles may affect the binding of the xenobiotics (Rao, et al., 1993), and this may also affect the bioavailability of the compounds, especially in the case of selective feeders.

Recently, the distribution of several non-polar organic compounds among sediment particles was examined with respect to the organic matter content. In these studies, the distribution of pyrene, benzo(a)pyrene, and hexachlorobiphenyl differed from the organic carbon distribution for particles <63 μm in diameter (Harkey et al., 1994; Kukkonen & Landrum, 1994). The distributions among small particles also differed significantly, even
between compound classes (Harkey et al., 1994) and when the contaminant concentration changed (Kukkonen & Landrum, 1994; Landrum et al., 1994). These relative distributions were directly attributed to bioavailability differences of these sediment-associated contaminants observed in *Diporeia*, a very selective feeder, and *Lumbricus variegatus*, a relatively nonselective feeder (Harkey et al., 1994; Kukkonen & Landrum, 1994, 1995a; Landrum et al., 1994).

Selective feeding behavior is one of a number of biological characteristics affecting contaminant bioavailability. In *Diporeia* spp., this selectivity, along with differential binding, is suggested as a major reason for the differential accumulation of chlorinated hydrocarbons as opposed to polycyclic aromatic hydrocarbons from sediments (Landrum, 1989; Landrum & Faust, 1991; Harkey et al., 1994). When the relative distribution among sediment particles is large, such selectivity is readily assumed (Harkey et al., 1994). However, when the chemically measured differences in distribution are small, the picture is much more uncertain (Kukkonen & Landrum, 1995b). The relative strength of contaminant association to particles may be equally as important as selective feeding.

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