

COMPARISON OF THE RELATIVE DESORPTION AND
BIOAVAILABILITY OF POLYCHLORINATED BIPHENYLS,
POLYCYCLIC AROMATIC HYDROCARBONS, AND
LINEAR ALKYL BENZENES FROM HUDSON RIVER SEDIMENTS

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ABSTRACT

Laboratory-based desorption and bioavailability experiments, using contaminated sediments collected from a site in New York Harbor near Governor's Island, were conducted during the summer of 1995. Experiments were designed to: (1) investigate the probable correlation of desorption of sediment-associated contaminants into an aqueous media with their bioaccumulation, and (2) determine whether a sediment process known as "aging" affects the relative desorption and bioavailability of sediment-associated nonionic organic contaminants by comparing the desorption and bioaccumulation of contaminants collected from different core intervals. The desorption and uptake of polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and linear alkylbenzenes (LABs) were measured in order to compare these three compound classes which possess similar physico-chemical properties but differ in likely matrix associations. A slightly greater fraction of contaminants desorbed from the surface sediments but the difference was not great enough to conclude that the aging process is responsible for impeding desorption from the deeper sediments. Biota sediment factors for *Yoldia limatula* (ng/g organism lipid/ng/g sediment organic carbon) were 7, 2, and 3 for PCBs, PAHs, and LABs, respectively, and no difference was seen between surface and deeper sediments. The patterns of PCB and LAB desorption and bioaccumulation are similar, indicating similar processes control their mass transfer. Patterns of PAH desorption and bioaccumulation differed; however, several compounds neither desorbed nor were taken up, suggesting association with a soot or coal matrix. The isomeric composition of the bioaccumulated LABs are radically different than that of the sediments. Slow desorption of the less branched LAB isomers, coupled with preferential metabolism, could promote such fractionation.

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Introduction

Several studies have demonstrated that sediments are the primary source of hydrophobic organic contaminants to benthic organisms in estuarine and coastal systems (e.g., Fowler et al. 1978, Varanasi et al. 1985, Long and Morgan 1990). An equilibrium partitioning model has been proposed to predict the bioavailability of nonionic organic contaminants to benthic organisms (DiToro et al. 1991). However, nonequilibrium conditions between benthic organisms and sediments can exist indefinitely in a system where the kinetics of the rate-limiting mechanism controlling biouptake of an organic contaminant is slower than the time required for removal processes such as biotransformation or transport. Limited biodegradation of organic contaminants in sediment systems has been well-documented (Ogram et al. 1985, Mihelcic et al. 1993, Hatzinger and Alexander 1995) and is evidence of the existence of such a rate-limiting process. Uptake of a hydrophobic organic contaminant by benthic organisms can occur either directly from pore-water or indirectly by sediment ingestion. Hydrophobic organic contaminants have much higher concentrations in sediments than in pore water, and studies have shown that sediment ingestion is a significant or primary route of uptake for sorbed hydrophobic contaminants (Fowler et al. 1978, Klump et al. 1991, Kukkonen and Landrum, 1995, Boese et al. 1995). The extent to which a sediment-associated organic contaminant is assimilated by benthic organisms is likely to be controlled by a number of biological and chemical processes. We hypothesize that one of these processes is the release of the contaminant into an aqueous media in the gut. The rate of desorption of an organic contaminant into water from its sediment matrix, therefore, could be correlated with its bioavailability. The focus of this study has been to investigate this relationship.

Sediment-sorbed organic compounds often include both a fraction that is reversible, or desorbs at a rate similar to its sorption rate, and a fraction that is

resistant to desorption (e.g., Karickhoff 1980, DiToro and Horzempa 1982, Carroll et al., 1994). Limited desorption could either be due to the matrix an organic contaminant is associated with prior to deposition (e.g., coal and soot) or to deep penetration into the sediment matrix which may increase with time through a process known as chemical "aging" (Hatzinger and Alexander 1995). This "aging" process is poorly understood but may be a result of a number of microbial and chemical processes associated with the diagenetic alteration of sediments. Mineral deposition or microbial exudation resulting from these processes might coat particle surfaces and mesopores and thus impede desorption by effectively increasing the length scale of diffusion or by preventing equilibrium of the interior of a matrix from being reached with its surface. This irreversible fraction would also be less bioavailable for reasons stated above.

In the summer of 1995 laboratory-based desorption and bioavailability experiments, designed to study the effects of chemical and biological alteration of the associated matrices of hydrophobic organic contaminants, were conducted using sediment samples from different core sections collected from a site in the Hudson River Estuary known to be contaminated. Desorption experiments, designed to simulate gut release, employed the use of a polymer that acts as an infinite reservoir for sediment-associated hydrophobic contaminants to diffuse into (Carroll et al., 1994). Bioavailability experiments were conducted by incubating the subsurface-deposit feeding bivalve *Yoldia limatula* with sediments from the different core sections. These experiments measured the desorption and biouptake of three nonionic organic contaminant classes which differ in structure and likely matrix associations, but possess similar physico-chemical properties; polychlorinated biphenyls (PCBs), linear alkylbenzenes (LABs), and polynuclear aromatic hydrocarbons (PAHs) over time.

The New York Harbor of the Hudson River ecosystem is an excellent system to study the effects of matrix associations on bioavailability of PCBs because contaminant signatures are well above background and their spatial and temporal distribution has been well characterized (Bopp 1982). Additionally, preliminary results

from the Environmental Protection Agency's Regional Environmental Monitoring and Assessment Program (R-EMAP) study of New York Harbor include the finding that 50% of the Harbor Area is toxic as defined by Microtox Toxicity. The total PCB concentration exceeded its Effects Range-Median level (ER-M) in 78% of the toxic area whereas the ER-M for a number of PAH compounds was exceeded for only 9% of the area (Darvene Adams, personal communication). Atmospheric PAHs, which are often associated with products of incomplete combustion such as fly ash and coal particles, deriving from New York City (NYC) and other urban centers most likely contribute a significant fraction of the PAH contamination in the Hudson River Estuary, thus enabling the investigation of the bioavailability of PAHs associated with this matrix. The large inputs of sewage effluent to the estuary contribute hydrophobic organic contaminants including LABs which are specific to this waste stream and have a known time input.

Biota Sediment Factors

The extent to which a hydrophobic organic compound is bioaccumulated by an organism from sediment or water has been shown to be largely dependent on the fugacity capacity of the compound in the organism and its fugacity in the environment (Mackay 1979, Mackay and Paterson 1981 1982). The relevant biotic phase for most hydrophobic organic contaminants is the organism lipids (Connolly and Pedersen 1988). The partitioning of a compound between the water and lipid phases is well predicted by its octanol-water partition coefficient (K_{ow}).

Similarly, the hydrophobicity of an organic contaminant is the driving force that causes it to partition to the nonaqueous phase (Karickhoff et al. 1979, Means et al. 1980, Chio et al. 1979, Schwarzenbach and Westall 1981). When the total organic carbon (TOC) content of the sediment is greater than 0.1 percent, it is this phase that is responsible for the sorption of hydrophobic organic contaminants from water (Schwarzenbach and Westall 1981). The organic carbon-water partition coefficient

(K_{oc}) is related to the sediment water partition coefficient (K_d) as follows:

$$K_d = f_{oc} K_{oc}$$

The sediment organic carbon partition coefficient K_{oc} can also be related to the octanol-water partition coefficient K_{ow} :

$$\log K_{oc} = a \log K_{ow} + b$$

where a and b are empirically derived.

Under equilibrium conditions, which assumes there is low phase transfer resistance or chemical transformation, the partitioning of a hydrophobic organic compound between lipids and TOC is described as (Thomann et al. 1992):

$$BSF = C_l / C_{oc}$$

where

BSF = biota sediment factor,

C_l = contaminant lipid-normalized tissue concentration (ng/g lipids)

C_{oc} = contaminant organic-carbon normalized sediment concentration (ng/g TOC)

Experimental Methods

Sediments were collected on May 23, 1995 from a site located near Governor's Island in the New York Harbor portion of the lower Hudson River Estuary (Figure 1) at a water depth of 11.6 meters (m). Two box cores, deployed from The Onrust, the Marine Sciences Research Center's vessel, were sectioned into three intervals: 0-4 cm, 5-9 cm, and 10-14 centimeters (cm), and identical intervals were combined and homogenized. The 0-4 cm, 5-9 cm, 10-14 cm sections were

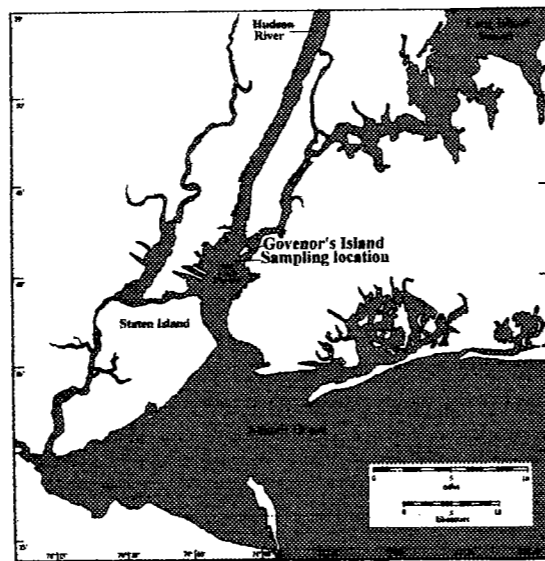


Figure 1. Sampling location.

light brown, grey, and black, respectively.

Samples for total sediment chemistry were taken from each section and placed in acetone, methylene chloride, and hexane-rinsed glass jars and frozen until analysis. The remainder of the sediment sections were sieved on site with a 500 micrometer (μ m) mesh screen and a minimal amount of seawater in order to remove detritus and biota. Sieved sediments were placed in clean Nalgene[®] bottles and stored at 4° Celsius (C) until the initiation of the bioavailability and desorption experiments. Comparison sediments, as well as the polychaetes *Spio setosa* and *Streblospio benedicti* to be used in the bioavailability experiments (not reported on in this paper), were collected from Flax Pond, a tidal wetland located on the southern shore of Long Island Sound. These sediments were also sieved with a 500 μ m mesh screen, placed in clean jars and refrigerated until the onset of the experiments. The polychaetes were obtained by wet sieving large quantities of surface sediments that had noticeable fecal pellet accumulation with a 300 μ m mesh screen. The material retained on the screen was placed in trays and the worms were identified and collected under a dissecting scope.

All sediments to be used in the desorption and bioavailability experiments were further sieved in the lab with a 63 μ m mesh screen and minimal amounts of seawater (to reduce variability between sediment sections and between Hudson River sediments and the Flax Pond sediments). Desorption experiments were conducted by placing approximately 7 grams (g) wet (1.5-2 g dry) sediment, 10 milliliters (ml) of seawater, and approximately 2 g wet XAD-4 resin in solvent rinsed 25 ml vials. The XAD-4 resin had been cleaned by first rinsing with deionized water and then refluxing with methanol, acetone/hexane (50/50), and methanol in a Soxhlet apparatus for 24 hours (8 hours for each solvent). The resin was then rinsed with deionized water, placed in a clean jar, filled with deionized water and refrigerated until use to prevent dehydration (Carroll et al. 1994). Desorption experiments were conducted by placing the vials in a rotating shaker (150 rpm) and kept at 25° C. At each time point vials were removed and 0.5 g of potassium carbonate was added to the vial to enhance phase separation

(Carroll et al. 1994). The vials were centrifuged and the XAD-4 resin was removed from the vial with a pipette, and placed in clean vials until extraction. The resin and the sediment remaining in the vials were frozen until analysis. Two time-point sediments from each depth interval were analyzed in addition to the XAD-4 resin in order to obtain a mass balance.

Bioavailability experiments were conducted by incubating *Yoldia limitula*, purchased from Woods Hole Biological Supply, with Hudson River sediments from each depth interval as well as the control reference sediment. Four 10-liter aquarium tanks, one for each of the three sediment intervals as well as one for the control reference, were filled with seawater and five 16-ounce jars (three for the control reference) filled with approximately 300 g of wet sediment (5 cm deep) were placed in the tanks. The pH of the seawater in the tanks was approximately neutral, the temperature was 21° C and the salinity was 30 parts per thousand (ppt). Pre-weighed *Yoldia* were placed in each jar, three for the first two time points and two for the remaining three time points, and observed to make sure they borrowed. Within an hour, all time points had noticeable "puffing" action indicating the *Yoldia* were active. The tanks were aerated and conditions were monitored. The seawater in the tanks was replaced and approximately 6 g of sediment was added to each time point once a week to replenish sediment displaced by the puffing action of the *Yoldia*. In addition to the clams, three jars, containing approximately 75 polychaetes (*Spio setosa* and *Streblospio benedicti*) each, were placed in the 0-4 cm aquarium. At each time point organisms were removed from the sediment, placed in clean sediment and allowed to depurate for 24 hours. The clams were then weighed, shucked, placed in a preweighed centrifuge tube, and a wet weight was obtained. Whole organisms were homogenized with a Virtus Tissue Homogenizer and frozen until extraction.

The extraction of PCBs, PAHs and LABs from sediment, tissue, and XAD-4 resin samples followed a modification of the method described by Takada et al. (1994). Wet sediment or tissue was placed in a centrifuge tube, and recovery standards were added for each compound class: 1-C9 alkylbenzene (AB), 1-C12AB,

1-C14AB (n-CmAB: n refers to the position of the alkyl chain to which the benzene ring is attached, and m refers to the chain length), PCBs 29 and 143, and p-terphenyl. These compounds were used as recovery standards because they do not occur appreciably in the natural environment. Sediments and tissues were extracted sequentially with acetone, 1:1 acetone:hexane, and 1:1 hexane:dichloromethane using a Cole Parmer 4710 Series, 600-watt ultrasonic probe. After each extraction, samples were centrifuged, and supernatants were decanted and combined. XAD-4 resin was extracted in a Soxhlet apparatus by refluxing with acetone/hexane (1:1) for 24 hours. The organic solvent fraction of each sample was back extracted with water, separated into a hexane phase and concentrated. Sediment and tissue samples were concentrated to approximately 1 ml while organism samples were reduced to approximately 6 ml and two 200 µl portions of the sample extract were removed and placed in a drying tray preweighed on a Cahn microbalance. After the tray was placed in a drying oven set at 40° C for 15 minutes and allowed to cool, the tray was then weighed again in order to determine the percentage of lipids for each organism sample. The remaining tissue extract was reduced to 1 ml under a stream of nitrogen.

The sample matrix was cleaned with a 1 cm i.d. column containing 7 g of silica gel (5% deactivated with water). The first fraction, eluted with 25 ml of hexane/dichloromethane (3:1), contained the LABs, PCBs, and PAH. This fraction was analyzed for PCBs on a Hewlett Packard 5890 gas chromatograph equipped with a 30-m DB-5 capillary column (J&W Scientific) and an electron capture detector with conditions as listed in Table 1. After PCB analysis, the sample was further concentrated under a stream of nitrogen for LAB and PAH analysis. The LABs and PAHs were analyzed on a Hewlett Packard 5890 gas chromatograph (GC) equipped with a Hewlett Packard 5970A mass selective detector (MSD) and a 30-m DB-5 capillary column (J&W Scientific). Conditions are shown in Table 1. LAB samples and standards were monitored in the selective ion mode for mass-to-charge ratios 91 and 105. PAH samples and standards were monitored in the selective ion mode for

the following mass to charge ratios: 128, 142, 152, 156, 166, 170, 178, 190, 192, 202, 206, 228, 230, 252, and 276.

	PCB analysis	LAB analysis	PAH analysis
Detector:	Electron Capture	Mass Spectrometer	Mass Spectrometer
Injection Port Temperature:	275° C	275° C	275° C
Detector Temperature:	300° C	300° C	300° C
Column Flow Rate:	3 mls/min	3 mls/min	3 mls/min
Carrier Gas:	Hydrogen	Helium	Helium
Analytical Column:	30 m DB-5, 37 um ID, 25 mm film thickness	30 m DB-5, 37 um ID, 25 mm film thickness	30 m DB-5, 37 um ID, 25 mm film thickness
Temperature Program:	50° C for 2 min., ramp to 120° C @ 30° C/min, 120° C to 240° C @ 2° C/min, 10 min hold	50° C for 2 min, ramp to 120° C @ 30° C/min, to 240° C @ 2° C/min, 10 min hold	50° C for 2 min, ramp to 150° C @ 30° C/min, to 240° C @ 5° C/min, 10 minute hold

PCB standards were prepared by combining Aroclors 1232, 1248 and 1262 (25:18:18) with the recovery standards PCB 29 and 143 in order to obtain response factors. PCBs in samples were quantified relative to PCB 29 and corrected for recovery. Recovery of PCB 29 averaged $87.2\% \pm 14.8\%$ and recovery of PCB 143 averaged $101.2 \pm 18.8\%$. Blanks were subtracted from samples and ranged from 7-18 ng total PCB. XAD-4 blanks, consisting of XAD-4 resin and seawater, had slightly higher levels and averaged 44 ng total PCBs (± 7 , n=3). This value was subtracted from all XAD-4 samples.

The LAB reference standard was prepared by combining a commercial mixture of all secondary isomers with linear alkyl chain lengths of 10, 11, 12, 13, and 14 (courtesy of R. Eganhouse), 26 isomers total, along with four 1-phenylalkanes (1-C9AB, 1-C10AB, 1-C12AB, and 1-C14AB). The masses of each component were estimated for the standard based on GC/FID response of 1-phenyldecane. Individual LAB peaks in samples were calculated by comparing their response to that of 1-C10AB, which was added as an internal standard prior to injection. Mean recoveries were $83.0\% \pm 12.4\%$ for 1-C9AB, $91.7 \pm 14.3\%$ for 1-C12AB and $92.6\% \pm 20.2\%$ for 1-C14AB. The C10ABs and C11ABs were corrected for recovery relative to 1-

C9AB, the C12ABs and C13ABs were corrected for recovery relative to 1-C12AB, and the few C14ABs measured were corrected relative to 1-C14AB. Total LAB concentrations were obtained by summing the individual alkylbenzene concentrations and subtracting blank values (18-30 ng total LABs) determined on the same batch of samples. The XAD-4 blank fell within the same range.

Individual PAH concentrations were determined by comparing their peak area response to that of p-terphenyl. Total PAH concentrations include the following PAHs: naphthalene, 1- and 2-methylnaphthalenes, 2,6-dimethylnaphthalene, acenaphthylene, acenaphthene, 2,3,5-trimethylnaphthalene, fluorene, phenanthrene, anthracene, 1-,2-,3-, and 9-methylphenanthrenes, 3,6-dimethylphenathrenes, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzofluoranthenes, benz(e)pyrene, benz(a)pyrene, perylene, indeno(1,2,3-cd)pyrene, dibenzanthracene and benzo(ghi)perylene. Identification was made by comparing peak retention times to those in standards injected on the same day. The recovery of p-terphenyl was $77.8\% \pm 17.9\%$. Procedural blanks, including XAD-4 resin blanks, were subtracted from samples and contained 10-30 ng total PAH.

Total organic carbon (TOC) was measured a Carlo Erba EA1108 CHN Analyzer. Measurements were made relative to a sulphanilamide standard.

Experimental Results

Sediment analysis results are reported on Table 2. All contaminant concentrations are an order of magnitude lower in Flax Pond sediments in comparison with Hudson River sediments. The similar concentrations reported for unseived sediments frozen immediately after collection in the field in comparison with seived sediments indicate that the seived sediments did not undergo biological alteration or accumulate contaminants during storage (sieved sediments were analyzed immediately following the commencement of experiments).

Table 2. Total PCB, PAH, LAB and TOC concentrations in Hudson River and Flax Pond sediments

	Total PCB	Total PAH	Total LAB		TOC	
	ng/g	ng/g	mp/p*	ng/g	I/E [^]	
Governor's Island 0-4 cm						
Initial Sediment	375.3	4409	-	1618	2.0	4.04
<63 um	412.1	5887	0.69	1282	1.8	3.62
Bio t3	423.6	4814	1.8	1154	2.2	3.44
Bio t5	394.1	4443	1.3	932	2.2	3.28
Desorp t3	305.4	4320	1.6	1220	2.0	3.75
Desorp t6	117.4	987	1.2	571	1.9	3.35
Governor's Island 10-14 cm						
Initial Sediment	481.6	5119	-	2141	1.9	3.72
<63 um	490.2	6297	0.89	1777	1.6	3.31
Bio t3	510.3	6503	1.5	1891	2.1	3.17
Bio t5	464.3	7983	1.3	1683	2.0	2.99
Desorp t3	430.8	6104	1.7	1859	1.8	3.11
Desorp t6	118.5	1235	1.5	1076	1.7	3.01
Flax Pond						
Initial Sediment	14.7	576	-	67.1	1.5	2.9
<63 um	18.2	555	2.5	55.4	1.4	3.1

* mp/p is defined as the ratio of 1-, 2-, 3-, and 9-methyl
[^] I/E is the ratio of 4-, 3-, and 2-C12AB to 5- and 6-C12AB
- indicates ratio could not be calculated due to interference

The total PCB concentrations are within the range of measurements made by our lab at this site (~ 0.3-1 µg/g) and confirm predictions made by Bopp (1989) who had measured total PCBs at 0.8 ppm (ppm~µg/g) at a depth in a New York Harbor core (mp -1.65) corresponding to 1986, and estimated a value of 0.5-0.7 ppm total PCB in surface sediments. Bopp attributed this "residual level" to inputs from the New York Metropolitan area. PCB concentrations in metropolitan waste streams such as sewage treatment plant effluent have been dropping; this should result in lower average PCB concentrations in the Harbor.

The National Status and Trends Program of the National Oceanic and Atmospheric Administration (NOAA) recently reported surface sediment concentrations of total PAH ranging from 1.4 - 9.2 µg/g at sites just north and south of our sampling site in New York Harbor (Long et al. 1995). Our total PAH values of 4.4 and 5.1 µg/g fall within this range. In addition to total PAH concentrations, methyl-phenanthrene to phenanthrene ratios (mp/p) ratios are reported on Table 2.

This ratio defined as the ratio of 1-, 2-, 3-, and 9-methylphenanthrene to phenanthrene, offers a means of estimating the relative abundance of PAHs deriving from petrogenic (e.g., oil) and pyrogenic (combustion) sources. PAHs that derive from petrogenic sources are known to contain a greater abundance of alkylated homologues than those that derive from pyrogenic sources (Blumer 1976). An mp/p ratio of 0.5-1 is indicative of combustion-derived sources of PAH (Prah et al. 1984, National Research Council 1985) whereas ratios of 3.14 and 2.36 have been measured in New York City sewage sludge (Takada et al. 1994) reflecting the significant amount of petroleum-derived inputs. As shown, mp/p values measured in the Hudson River sediments suggest that pyrogenic sources dominate the PAH signature.

Due to the fact that LABs have just recently come to the attention of the environmental community and they are not yet considered to be of environmental concern, there are few measurements available for comparison. However, concentrations reported for New York Harbor sediments, as shown on Table 2, are within the same range as those reported for Tokyo Bay (Ishiwatari et al. 1983) and offshore from a major sewage outfall in southern California (Eganhouse et al. 1983). The relative distribution of internal (phenyl substitution position toward the middle of the chain) to external (phenyl substitution position toward the end of the chain) LAB isomers has been identified as a measure of the degree of degradation of the LAB mixture after it has entered the environment (Takada and Ishiwatari 1990). Values greater than 1 for this internal to external ratio (I/E), defined as the ratio of 5- and 6-C12AB to 4-, 3-, and 2-C12AB, indicate some degree of degradation (Takada and Ishiwatari 1990). I/E values reported on Table 2 indicate some degree of degradation has occurred. The similarity of the I/E ratios calculated for the 0-4 and 10-14 cm sediment intervals indicate that little degradation occurs after incorporation into the sediment bed. Our primary purpose in measuring this ratio in the sediments, however, is to use it as a baseline value for our experiments. Increases or decreases in this ratio can be used to investigate the effect of structure on isomer specific desorption and bioavailability within a compound class.

Contaminant concentrations in test sediments remained relatively constant during the bioavailability experiments. The percentage of TOC, however, did decrease slightly in both bioavailability experiments. The decrease in the contaminant levels in the desorption experiments is explained by comparing them to the increase in the XAD-4 resin concentrations reported on Table 3. These concentrations are reported as concentrations of the incubation sediment for direct comparison. Despite initial variability of the first few time points, levels of all contaminants in the XAD-4 resin fraction increased with time. Contrary to our expectations, the change in mp/p ratios with time does not indicate preferential desorption of petrogenic PAHs. However, several PAH compounds that are associated with combustion sources which were measured in the sediments at levels comparable with other PAHs, were not measured in the XAD-4 resin. These include anthracene, benzofluoranthenes, and benzo(e)pyrene.

It is interesting to note the change in the LAB I/E ratio with time (Table 3). High values are measured in the middle of both experiments and then decrease toward

Table 3. XAD-4 Total PCB, PAH, and LAB concentrations (expressed per dry gram of incubation sediment) over time

Sediment	Hour	Total PCB ng/g	Total PAH ng/g	mp/p*	Total LAB ng/g	I/E [^]
Governor's Island 0-4 cm	2	64.9	421.0	0.73	0.2	‡
	5	34.9	1234.0	0.74	0.3	‡
	12	60.8	1187.0	0.66	38.1	2.6
	48	184.1	949.0	0.68	136.4	3.8
	168	255.0	2830.0	0.70	455.5	2.1
	480	337.2	4341.0	0.73	630.1	2.1
Governor's Island 10-14 cm	2	25.2	427.0	1.08	19.9	1.0
	5	110.6	484.0	0.87	2.6	‡
	12	34.5	549.0	1.10	47.1	1.5
	48	180.3	1659.0	0.91	136.4	3.2
	168	269.6	2378.0	0.77	453.9	1.9
	480	312.1	2746.0	0.79	710.6	2.0
Flax Pond	5	<1.0	64.0	‡	NA	
	168	18.3	124.0	‡	NA	
	480	16.7	NA		NA	

‡ Denominator is zero
* mp/p is defined as the ratio of 1-, 2-, 3-, and 9-methyl phenanthrenes to phenanthrene
[^] I/E is the ratio of 4-, 3-, and 2-C12AB to 5- and 6-C12AB
NA: not analyzed

the end of the experiment to levels approaching those calculated for the original sediment. This indicates that although the internal isomers desorb faster than the external isomers, the external isomers eventually do desorb when the sediment-associated LAB mixture is closer to complete desorption.

Contaminant concentrations and lipid contents of the test organisms are presented in Table 4. Significant contaminant levels were measured in *Yoldia limatula* prior to the initiation of the experiments, complicating attempts to model uptake kinetics. These attempts are further complicated due to the fact that steady-state conditions were apparently not reached over the duration of the experiment as indicated by increasing contaminant levels at the last time point. Additionally, the lipid contents of the organisms did drop during the time course of the experiments,

Table 4. Total PCBs, PAHs, and LAB wet weight (ww) concentrations and %Lipids in *Yoldia limatula* over time

Exposure	Day	Total PCB ng/g	Total PAH ng/g	mp/p*	Total LAB ng/g	I/E [^]	Lipids % ww
Governor's Island 0-4 cm	0	67.0	102.0	0.50	43.3	2.1	0.48
	2	114.2	455.0	0.57	136.8	4.9	0.61
	5	124.2	383.0	1.54	111.9	10.3	0.63
	10	62.1	180.0	0.43	67.9	1.6	0.31
	20	171.4	342.0	1.28	133.2	‡	0.24
	35	114.8	342.0	0.89	147.0	9.7	0.15
Governor's Island 10-14 cm	2	144.6	374.0	0.85	93.9	4.6	0.75
	5	148.6	117.0	0.87	103.7	5.6	1.03
	10	67.0	198.0	0.50			0.29
	20	290.1	548.0	1.02	188.5	16.5	0.41
	35	235.7	707.0	0.92	329.7	4.7	0.25
Flax Pond	2	67.5	165.0	‡	NA		0.20
	10	84.1	NA		NA		0.32
	35	132.5	230.0	1.40	NA		0.61

‡ Denominator is zero
* mp/p is defined as the ratio of 1-, 2-, 3-, and 9-methyl phenanthrenes to phenanthrene
[^] I/E is the ratio of 4-, 3-, and 2-C12AB to 5- and 6-C12AB
NA: Not Analyzed

for both New York Harbor sediment exposures, suggesting that these organisms were stressed. However, we can not rule out variability in clam lipid contents at the beginning of the experiment. As described in the experimental section, conditions remained constant during the time course of the experiment. If the organisms were stressed, it was not indicated by their activity, which was periodically monitored by observing their puffing rate. Loss of lipid weights were seen in a similar experiment which involved exposing Macoma natusa to PCB and hexachlorobenzene spiked sediments (Boese et al. 1995). The authors reported having observed lipid loss during the first month of exposure in previous experiments, with levels stabilizing toward the end of the month. Reasons for these lipid losses are unknown. Nonetheless, concentrations of all contaminants did increase with time and are useful for comparison with the desorption experiments.

The organism mp/p ratios are generally higher than the same ratios calculated for the XAD-4 resin fraction in the desorption experiments, but have no discernable pattern upon which conclusions can be drawn. The I/E ratios, calculated from LAB concentrations measured in the test organisms (Table 4), increase during the time course of the experiment. This could indicate that either preferential assimilation of the internal isomers and/or selective metabolism of the external isomers has occurred. Limited desorption of the external isomers noted in the desorption experiments, supports preferential assimilation of the internal isomers. However, the I/E ratios for test organisms are much higher than measured during the desorption experiments, suggesting that the LABs have either been metabolized or degraded by enteric bacteria during the course of the experiment. It is possible, however, that rapid gut residence times permitted only limited desorption, and hence assimilation of the external isomers, and the depletion of external LAB isomers relative to internal isomers was further enhanced by preferential metabolism.

Discussion

The desorption of total PCBs, PAHs, and LABs, is depicted graphically in Figures 2a, 2b, and 2c, respectively. The desorption of all compound classes is greater from the surface than from the deeper sediment. However, the difference is not significant enough to conclude that the aging process has hindered desorption of the contaminants in the deeper sediments.

PCBs show the least impedance to desorption, with 60-80% of the sediment concentrations measured in the XAD-4 resin at the last time point. Carroll and coworkers (1994) reported 60% desorption in short term (160 hrs.) and 90% in long term (months) experiments, of PCBs from highly (25-205 mg/kg) contaminated Hudson River sediments. This experiment demonstrates that comparable fractions of PCBs can desorb from sediments that are orders of magnitude less contaminated.

The desorbed fraction of PAH was greater than expected but still less than the PCB desorption. This is in agreement with the findings of McGroddy and Farrington (1995) who reported porewater concentrations of PCBs in accordance with equilibrium predictions from PCB sediment concentrations, while porewater PAH concentrations were below equilibrium-predicted levels. The authors attributed limited-PAH desorption to association with combustion-derived particles.

The LABs showed the least availability for desorption. To our knowledge this is the first investigation of the desorption potential of LABs from sediments. LABs have been shown to rapidly degrade in oxic systems (Bayona and Albaiges 1986, Takada and Ishiwatari 1987, Holt and Bernstein 1992). However, strong associations with sediments could result in accumulation of LABs over time. As mentioned above, similar I/E ratios calculated in surface and deeper sediments indicate that degradation of LABs does not occur after incorporation into the sediment bed.

The sorption/desorption of organic chemicals by sediments is best explained by a radial/retarded intraparticle diffusion model (Wu and Gschwend 1986, Brusseau et al. 1991). This model describes a sorptive process which includes aqueous-phase

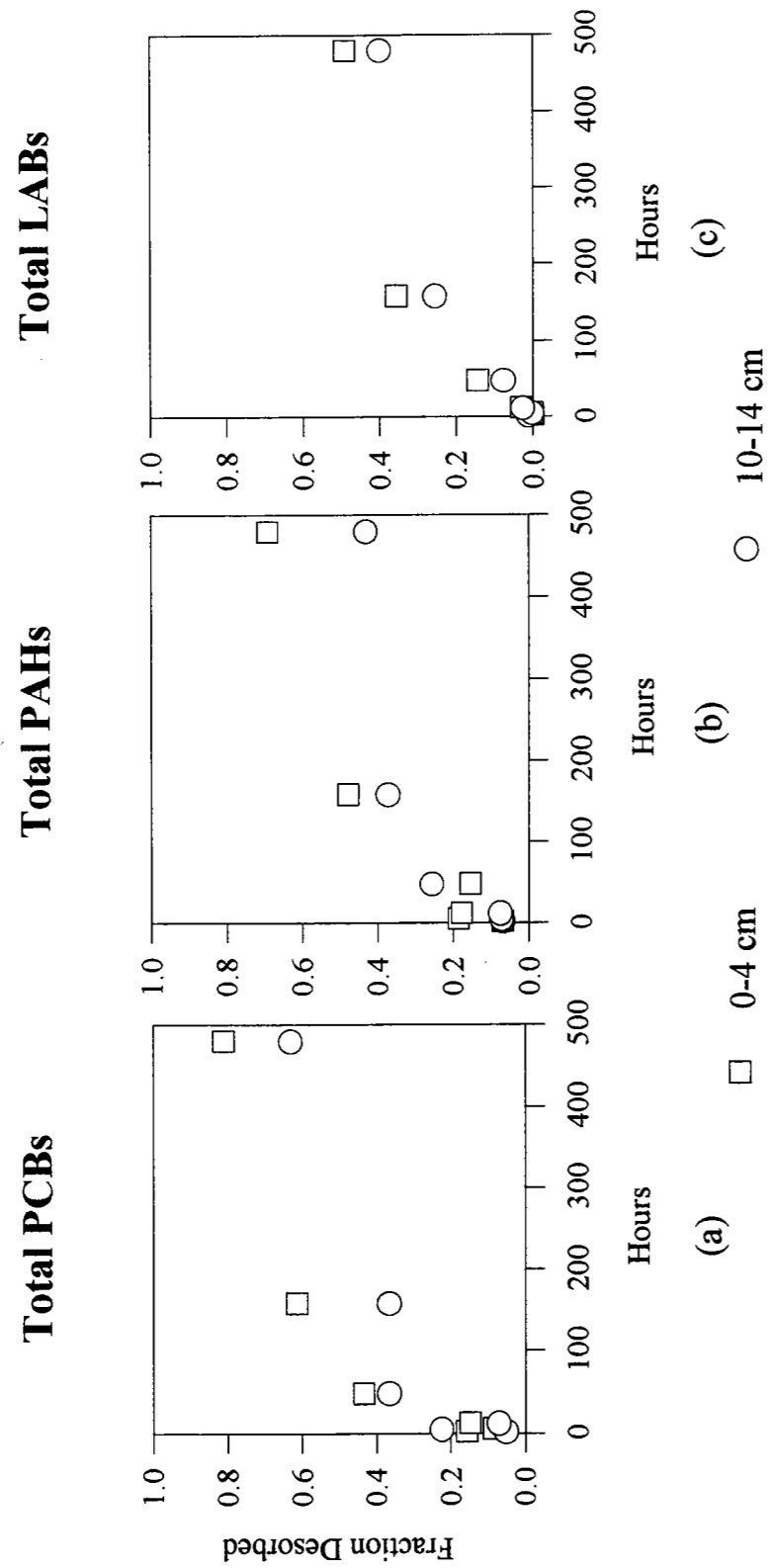
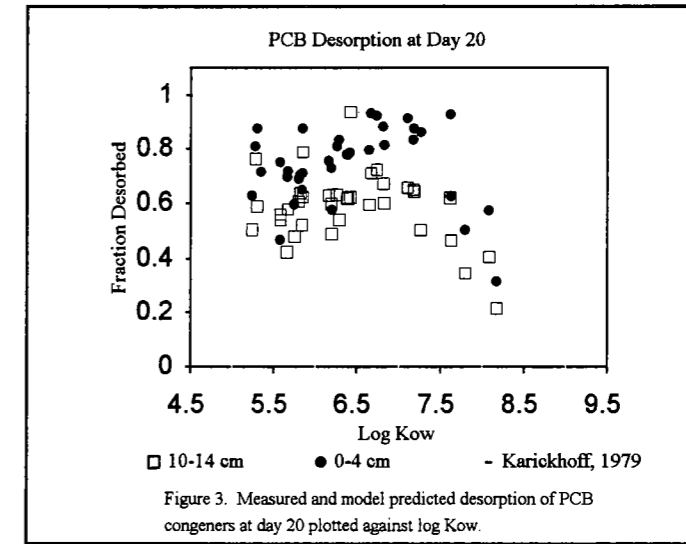


Figure 2. The fraction of total PCBs (a), PAHs (b), and LABs (c) desorbed from New York Harbor surface (0-4 cm) and deeper (10-14) sediments over time.

diffusion of a compound into the micropores of particle aggregates that is retarded by instantaneous sorption to pore walls (Brusseau and Rao 1989). A two-box model was first introduced to describe this process (Karickhoff 1980) but this model is dependent upon empirically-derived constants and therefore its use as a predictive tool is limited. The retarded/radial diffusion model employs a sorptive rate constant which is estimated based on the average radial distance of the particle aggregate and the effective diffusivity of the solute. The effective diffusivity is impeded by sorption. Sorption is described by a partition coefficient which is calculated from the K_{ow} of an organic contaminant and the fraction of organic carbon in the sediment. The sorption rate constant can be used to estimate sorption/desorption at a given time. At the sixth time point of our experiment (480 hours), using partition coefficients estimated by Karickhoff and coworkers (1979), this model predicts that 100% of the PCBs with $\log K_{ow}$ values less than 7 will be desorbed, while higher molecular weight PCB congeners will be resistant to desorption. Model predictions and our data for individual PCB congeners are plotted against their $\log K_{ow}$ on Figure 3. The higher molecular weight congeners ($\log K_{ow} > 7.5$) generally conform to this model but the lower molecular weight congeners are less desorbed than predicted. Although the fraction is small, a desorption-resistant fraction of PCBs exists in these sediments in accordance with what has been seen in previous studies of PCB desorption (DiToro and Horzempa 1982, Coates and Elzerman 1986, and Carroll et al. 1994).



The desorbed fraction of individual LAB and PAH compounds for both depth intervals for our last experimental time point is plotted against their log K_{ow} s on

Figures 4 and 5. The X axis scale is expanded for direct comparison with the fraction of PCBs desorbed (Figure 3). The similarity in the shape of the LAB and PCB desorption with increasing log K_{ow} suggests that hydrophobicity is important in controlling the desorption of high molecular weight compounds. However,

similar plots of LAB desorption for earlier time points (not shown) show a number of external LAB isomers which have not desorbed to a great extent or at all, exemplifying the importance of structure in controlling the rate of desorption. PAH desorption, however, has no regular pattern with increasing log K_{ow} .

Reasons for this anomalous behavior could be due to their associated matrix, however,

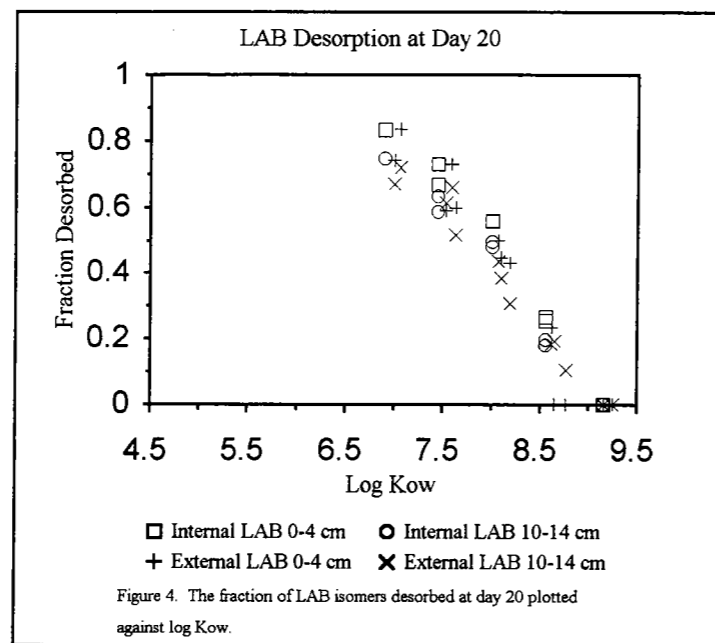


Figure 4. The fraction of LAB isomers desorbed at day 20 plotted against log K_{ow} .

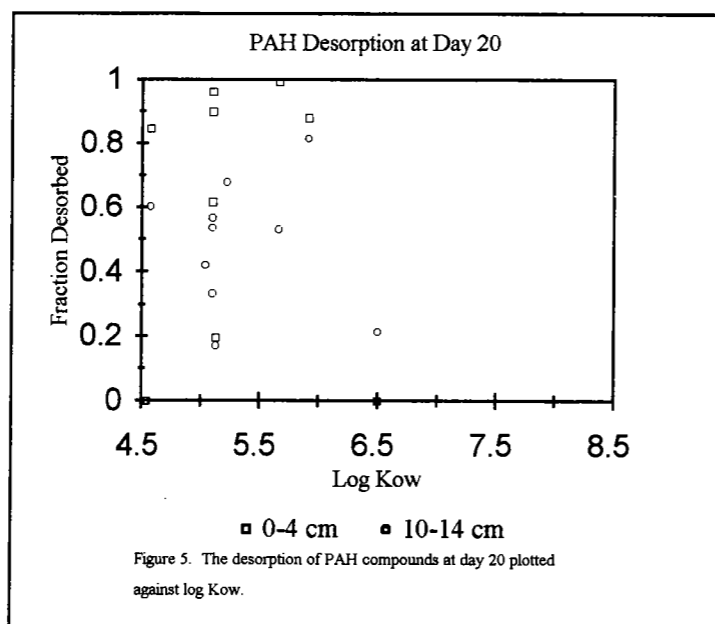


Figure 5. The desorption of PAH compounds at day 20 plotted against log K_{ow} .

further analysis of individual congeners and the matrices within the sediment are required before any conclusions can be drawn.

The contaminant BSFs over time are shown in Figures 6a, b, and c.

Accumulation was greatest for PCBs with final time point total PCB BSFs of 6-8. Lake and coworkers (1990) compared PCB accumulation in several frequently used test organisms including *Yoldia* for field and laboratory experiments with different concentrations of PCBs. The highest accumulation reported was for a laboratory study which exposed *Yoldia* to sediment with low levels of contamination (A-1254 <48.3 ng/g). This study reported A-1254 Accumulation Factors (AFs, equivalent to our BSFs) of 13.1 (C.V.= 2.7%, n=2) for *Yoldia* (Rubinstein et al. 1987). The remaining studies, which include both high (A-1254 >3000 ng/g) and low sediment contamination levels conducted both in the field and laboratory reported a much lower range of AFs (3.61-4.92; Lake et al., 1987, Rubinstein, 1987, Lake et al. 1990). Our final total PCB BSFs are slightly higher than the latter range but much lower than the first study. Final LAB and PAH BSFs in *Yoldia limatula* were much lower than the final PCB BSFs. Final LAB BSFs are slightly higher than the final PAH BSFs, in contrast to the desorption experiments, indicating a separate mechanism is playing a role in the accumulation of these contaminants.

The individual congener BSFs for PCBs and LABs are plotted against their log K_{ow} s on Figures 7 and 8, respectively. The pattern of accumulation for these

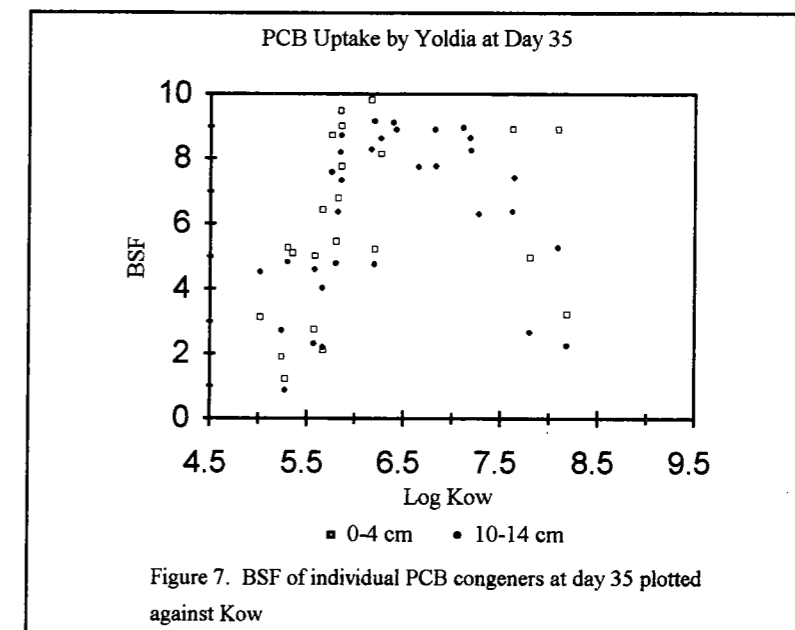


Figure 7. BSF of individual PCB congeners at day 35 plotted against K_{ow}

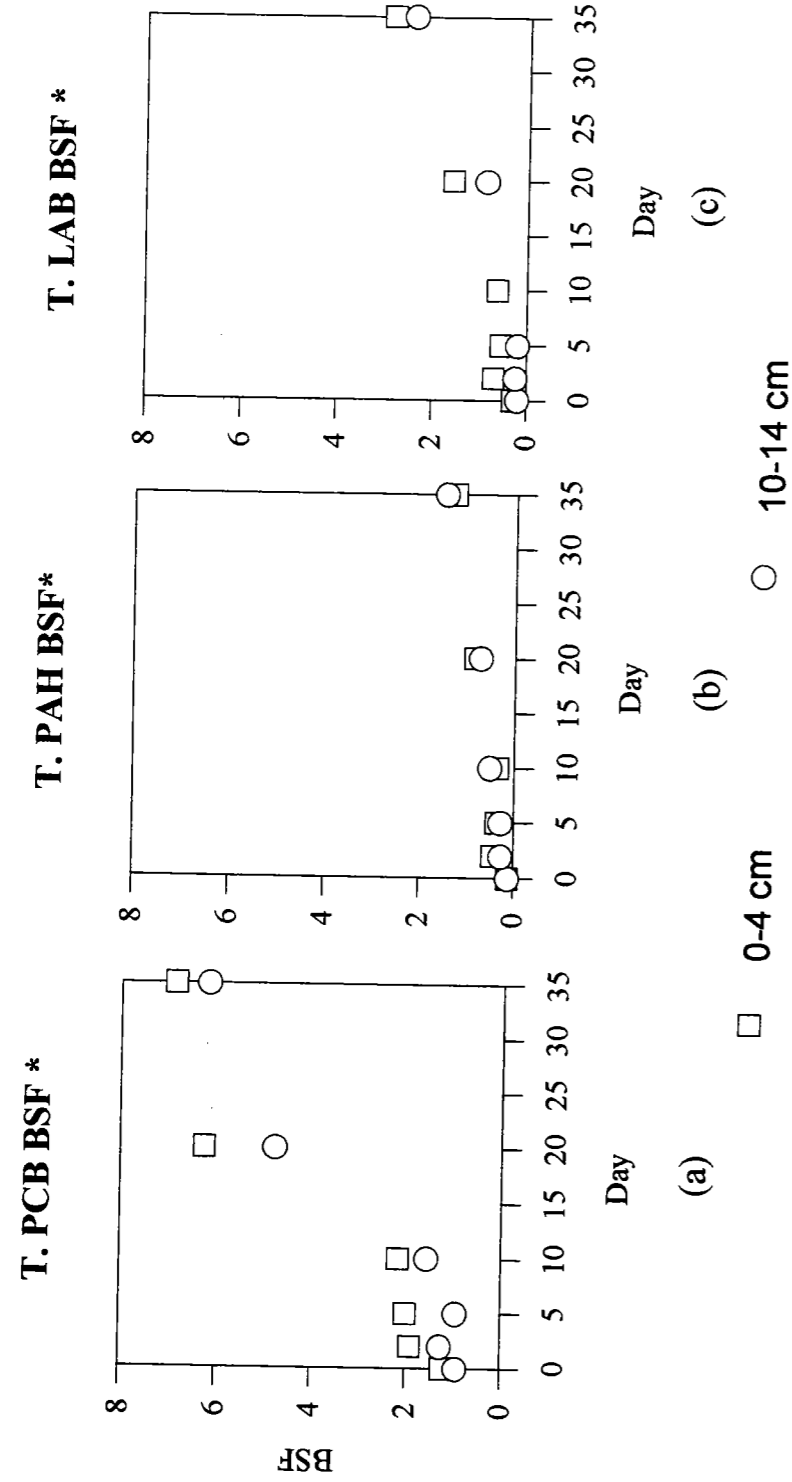
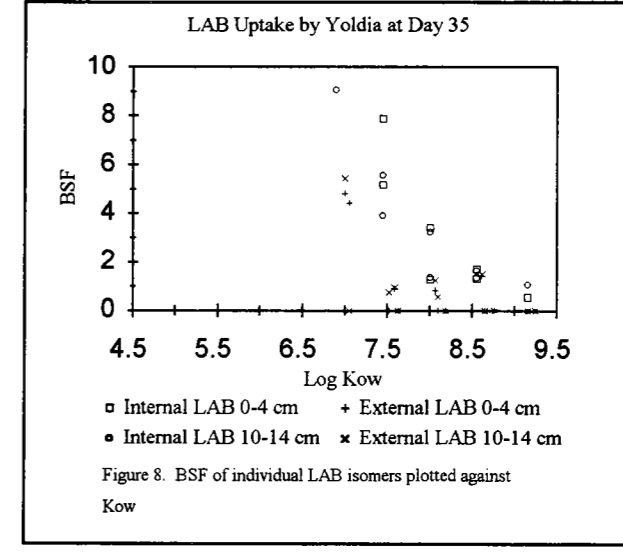


Figure 6. Total PCB (a), PAH (b), and LAB (c) BSF for *Yoldia limatula* from surface (0-4 cm) and deeper (10-14 cm) sediments

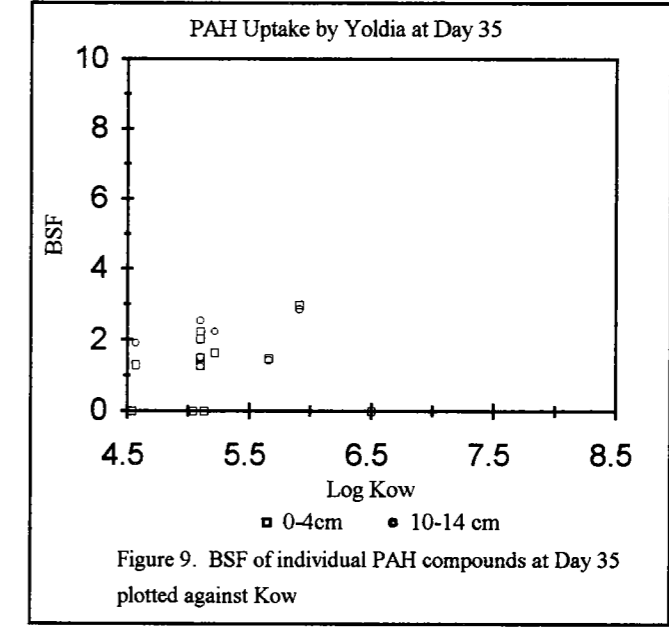
*BSF=contaminant organic-carbon normalized tissue concentration (ng/g)/contaminant organic-carbon normalized sediment concentration (ng/g total organic carbon)

two compound classes is similar to their desorption pattern shown on Figures 3 and 4. The primary difference is with the external isomers of LABs, which have low to undetectable BSFs. As previously discussed, this could be due to a combination of slow release and degradation. Figure 8 also



shows that the total LAB BSF is dominated by a few less hydrophobic, internal isomers. The pattern of PAH uptake, shown on Figure 9, does not show a clear correlation with PAH

desorption. However, the same compounds which were not desorbed, anthracene, the benzo(a)fluoranthenes, and benzo(e)pyrene were not bioaccumulated. Further information can be gained by the modeling of individual compound behavior, which is underway.



Similar desorption and bioaccumulation patterns of

organic contaminants from sediments suggests similar processes are responsible for their release from sediment into water and *Yoldia*. The day 35 BSFs of individual congeners show a positive relationship with the desorbed fraction at 48 hours as shown

on Figures 10a, b and c. The number of compounds which have not been either bioaccumulated or desorbed is indicated on the Figures. As mentioned previously, the PAH compounds which have neither desorbed or bioaccumulated may be associated with a coal or soot matrix, inhibiting their ability to desorb. The LAB isomers which have neither desorbed or bioaccumulated include several external isomers, due to their structure, and the C-14 internal and external isomers, due to their hydrophobicity.

Conclusions

Although there was less desorption of contaminants from sediments collected at depth relative to those collected from the surface, the difference is not great enough to distinguish an aging effect. Significant fractions of sediment-associated PCB, PAH, and LAB both desorbed into an aqueous media and were bioaccumulated by *Yoldia limatula* in separate desorption and bioavailability experiments. The PCBs proved to be the most bioavailable and had the greatest ability to desorb. In fact, the relative desorption of each compound class was similar to the degree of bioaccumulation. This, coupled with the similarity of isomer patterns of uptake and desorption of PCBs and LABs suggest that desorption into an aqueous media in the gut is an important mechanism controlling bioavailability. Differences in isomeric composition between the desorbed fraction of LABs and those bioaccumulated may be due to metabolism of external isomers enhanced by slow desorption. PAH compounds that were neither bioaccumulated or desorbed may be associated with a strong matrix such as coal or soot.



Figure 10. Individual PCB (a), PAH (b), and LAB (c) compound BSF at 35 days plotted against the fraction desorbed at 48 hours.

Recommendations for Future Work

These experiments demonstrate that the potential for bioaccumulation is strongly associated with the ability of a compound to desorb into an aqueous media. Sediment Quality Criteria are established based on the fraction of organic carbon of a sediment and the hydrophobicity of a contaminant. Three compound classes with similar K_{ow} s did not have similar BSFs, suggesting the importance of matrix associations. Further investigation into the nature of these matrices is necessary, in order to develop predictive models of desorption, which can also be used to predict bioavailability. Further interpretation of this data may offer some information in this regard. We have one more desorption time point (45 day) which will be analyzed to determine if additional contaminants desorbed from the sediments. A desorption rate constant will be calculated from the time course release for specific contaminants. We plan to relate the desorption rate to BSF and the bioaccumulation uptake rate. By modelling the behavior of individual compounds in both the desorption and bioavailability experiments we will be able to further elucidate the relative importance of individual processes in controlling their bioaccumulation.

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