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FINAL REPORT

BIOACCUMULATION OF SEDIMENT-ASSOCIATED HYDROPHOBIC CONTAMINANTS: BIOLOGICAL AND CHEMICAL FACTORS CONTROLLING ASSIMILATION

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EXECUTIVE SUMMARY

The ability to predict accumulation levels of sediment-sorbed hydrophobic organic contaminants (HOC) by deposit-feeding organisms based on sediment concentrations is limited in part by an incomplete understanding of the chemistry controlling assimilation efficiency. This project included a combination of controlled laboratory bioaccumulation, desorption, and assimilation efficiency studies. A field study which compared *in situ* BSF values of PCBs and PAHs to the desorption of those compounds was also conducted. As a result of this work, better pictures are evolving concerning the importance of gut surfactants in controlling the assimilation of HOC by deposit-feeders, the chemical availability of sediment-sorbed HOC in urban harbor sediments, and the likely role of soot on the chemical and biological availability of PAH in sediments.

The prepondorance of results presented in this report derived from the doctoral research projects of grduate students Elizabeth Lamoureux and Michael Ahrens. Both of these students have recently initiated the process of writing their dissertations; thus a range of completeness of interpretation is presented in the sections that follow.

The report is divided into five parts:

(1) Part I constitutes a published manuscript (Lamoureux EM, and Brownawell BJ. 1999. *Environ. Toxicol. Chem.* 18, 1733-1741.), in which the desorption behavior from NY Harbor sediments of three classes of HOC (PCBs, PAHs, and superhydrophobic LABs) are compared to model predictions and to the accumulation of these HOC by the clam *Yodia limatula*. The rate and extent of desorption of the most hydrophobic HOC (LABs and PCBs with log $K_{ow} > 6.3$) was well described by an intra-particle diffusion model proposed by Wu and Gschwend (1988). Less hydrophobic PCBs desorbed at a slower than predicted rate and a greater desorption resistent fraction remained after one month of sorption in many cases. The greater than predicted resistence to desorption may be related to smaller PCB molecules being able to access nm-scale pores/sorption volumes or the possibility that more soluble, easily desorbed PCBs may be lost during sediment transport processes, leaving behind only the more resistant sorbed pools for the lower chlorinated congeners. The PAHs were all desorbed much slower (one to four orders of magnitude) than that predicted by the Wu and Gschwend model that is based on organic matter partitioning. This is consistent with many observations of reduced bioavailability and pore water

concentrations of PAHs in sediments. Explanations for the reduced chemical availability include a greater tendency to bind to carbonaceous soot particles as well as to mechanisms postulated for the lower chlorinated PCBs.

The fraction PAHs, and LABs desorbed after 48 hours correlated well with measured biota-sediment factors (BSF) in *Yoldia limatula* exposed to the same sediments, consistent with desorption rate-limited assimilation that we had hypothesized. The correlation between desorption kinetics and BSF for PCBs was much less good, but may have been complicated by PCB body burdens present in the clams before the start of bioaccumulation studies. Other laboratory and field studies presented elsewhere in the report suggest that desorption of chlorinated HOCs, including PCBs, does not predict well the assimilation or bioaccumulation of that occurs in the guts of at least some deposit-feeding invertebrates. Several studies, including this one, have related field BSFs with log K_{ow} and observed a maximum at intermediate K_{ow}s (~6.0-6.5). This maximum may be due to predictably slow desorption of high K_{ow} compounds and lower than predicted rates and extent of desorption of the low K_{ow} compounds due to association with resistant phases.

The desorption and bioaccumulation of HOC was compared from three sediment depths from the Governor's Island sediment cores. This site is a known deposistional area, and deeper sediments have most likely been in-place in the bed for longer periods of time. No significant effect of sediment depth was found either for desorption or for bioaccumulation, suggesting that down-core variation in sediment redox conditions and sediment age had little effect on HOC chemical or biological availability.

(2) Part II describes a manipulative laboratory experiment in which the effect of soot on the desorption and bioavailability of HOC was investigated. The soot derived from the tailpipes of diesel buses and treated with hexane to partially remove oily residues. The desorption rates of the PAHs naphthalene (NAP)and benzo(a)pyrene (BAP) were affected greatly be amending harbor sediment with soot, and the behavior was consistent with that observed in experiments conducted only with soot. On the other hand, relatively high additions of soot had no significant effect on the desorption of hexachlorobenze (HCB). The lack of effect for the highly chlorinated HCB is attributed to the role that bulky chlorine substituents have in blocking p-pi interactions with soot sorption sites. PAH desorption could be reasonable well described by a two-component (fast and slow) desorption kinetic model. Interestingly the PAH desorption rates for the slow compartment

were similar to rates observed with field aged sediments, a result consistent with the possible role of soot in controlling the chemical and biological availability of PAHs in urban harbor sediments.

Assimilation efficiencies (AE) of sediments and soot particles ingested by the worm Nereis succinea were also measured in lab studies. The AE values for HCB were not significantly affected by the soot amendments, but BAP AE values in the presence of soot and soot-amended sediment were significantly lower than that measured with spiked control sediments. However, the AE values were higher than the amount of radiolabeled HOC that desorbed over 24 hours. Furthermore, the effect of soot on AE was far less than the effect that it had on desorption rate or extent. We hypothesize that aqueous desorption rates and extents may correlate with the general biological availability of soot-associated PAH ingested by sediments, but that other processes in the gut (most likely solubilization by gut surfactants) control the actual magnitude of the assimilation.

(3) Part III of the report is an initial description of experiments that were conducted to address possible effects of diagenetic processes on the chemical and biological availability of sediment-sorbed HOC. Sediments are viewed in mathematical and conceptual models of contaminant desorption as inert surfaces coated with inert organic matter. Two types of experiments were conducted, both with biologically stable HCB (log K_{ow} = 5.5) and hexachlorobiphenyl (HCBP; log K_{ow} = 7.3). In the first experiment, HOC were equilibrated and then desorbed under four types of conditions (surficial oxic sediment incubated under oxic conditions, oxic incubated under reducing conditions; deeper anoxic sediment incubated under reducing conditions, and anoxic sediment incubated under oxic conditions). Subtle differences in the rate or extent of desorption were observed; the results are consistent with modeling efforts based solely on organic matter content of the sedments. More hydrophobic HCBP desorbed more slowly than HCB, but not by as large a factor as would be predicted by its much higher hydrophobicity. AE experiments showed no significant effect of redox conditions on the bioavailability of sorbed HCB or HCBP, consistent with the sediment depth studies presented in Part I. Interestingly, the AE values of HCBP were actually higher than that of HCBC, opposite to the expectation from desorption experiments. This result casts further doubt on the ability of desorption into clean seawater to mimic bioavailability of chlorinated hydrocarbons to deposit-feeding invertebrates.

A second experiment involving the effect of organic matter mineralization and diagenesis on the chemical and biological availability was carried out but the results have yet to be analyzed.

Radiolabeled HCB and HCBP were incubated with both fresh and decomposed remains of the green algae *Dunaliella tertiolecta*. After additional incubation in unpoisoned systems, the desorption and assimilation by *Nereis* of the two HOC were monitored.

(4) Part IV of this report may be the most significant. This section describes most of the laboratory studies that were conducted to determine factors that affect assimilation efficiencies of sediment-sorbed HOC by deposit-feeders. Most of the experiments were also conducted with Nereis succinea, but useful comparisons were made with three other species. AE values of spike HCB, tetrachlorobipheny (TCB), and BAP were relatively high (over 30%) under all conditions tested; however, we were able to document several factors that do and do not seem to exert controls over HOC bioaccumulation.

Several experiments with surfical sediments and with deeper sediments containing less labile organic matter showed that HOC AE values were much greater than that for the organic carbon that serves as the primary sorption matrix for HOC of the sediment. This result confirmed our hypothesis that HOC assimilation be deposit-feeders was likely to be controlled by processes that release or desorb HOC in the gut, and not be co-assimilation with sediment organic matter. However, much greater desorption rates of HCB than for TCB were not reflected in comparison of the measured AE values that showed no effect of HOC structure.

The effect of contaminant aging on sediments had only a modest effect on AE; HCB and TCB aged on sediments for over one year was assimilated as well as from sediments aged for one week; these results are not consistent with decreases desorbability that is typically found for aging HOC for that time period. Greater AE of TCB than for BAP was mirrored by similar differences in contaminant desorbability, but the values of AE were higher than could be explained by only aqeuous desorption during a gut passage.

The AE values determined for Nereis were higher than those found for three other species: *Pectanaria gouldii*, *Yoldia limatula*, and *Haploscoloplos sp,* which varied in feeding style and gut residence time from each other. There was a positive, albeit relatively weak, correlation observed between AE and *Nereis* body size, despite a much longer gut residence time for larger adult *Nereis*. Manipulative experiments with Yoldia in which some animals were starved following ingestion of radiolabeled sediment, also showed no effects of gut residence time on AE. In addition, there was

no relationship between AE and gut residence time when the results from different species were compared.

Many of the results from the experiments above begin to make sense when the effect of gut surfactants in intestinal fluid is considered. In this work it was shown that the gut fluids of Nereis and Pectanaria were able to rapidly (minute timescale) solubilize a large fraction of sediment sorbed HOC. The greater solubilization by Nereis than of Pectanaria matched the differences in gut surfactancy estimated by surface contact angle measurements. A dramatic result was that the fraction of sediment associated HOC desorbed by gut juice at a level that plateued over approximately a 45 minute window was identical to the measured assimilation effieciencies of HOC by both species. These initial results are consistent with the work and hypotheses of Mayer, Weston, and colleagues who have argued that gut juice solubilization of HOC is a good indicator of bioavailability; our work comparing the rate of solubilization to the measured AE values provides an important test of this hypothesis. Our work shows that aqueous desorption (without surfactant) of chlorinated often does not correlate with bioavailability of HOC in organism gut, and is probably too slow to account for the high AE values measured. There appears to be a better correlation between aqueous desorption rates and extents with the bioavailability of PAH and highly hydrophobic LABs, but more work is required to compare the aqeuous phase and gut juice desorption. Initial experiments were conducted to see if the dissolution by gut juice could be mimicked by that of detergent solutions of various concentrations. Results presented show that the dissolution of HOC by gut juice is more rapid than in the presence of SDS.

(5) In Part V is presented some of the results from field collected biota and sediments. The desorption rates of PCBs and PAHs varied significantly between different sites around the Harbor complex. General features of the desorbability of these HOC match that observed in Part I, and uncertainties in particle aggregate radius may complicate comparison of model predictions with measured desorption rates of PCBs. An interesting finding that was that the desorbability of lower chlorinated PCBs from Newark Bay sediments, that contained higher concentrations of those compounds, was faster and closer to predictions that were the rates determined at other sites more removed in space from nearby sources of low molecular weight PCBs. These results are consistent with water column partitioning results found along the axis of the Hudson River. More soluble PCBs are more chemically available for desorption closer to sources, and as weathering proceeds

during transport partition coefficients increase and the desorbability of residual PCBs increases. PAHs desorbed much more slowly than predictions based on organic carbon partitioning models, but did not correlate well with the amounts of soot carbon measured in sediments. Comparison of the compositition of easily desorbable PAHs sometimes showed an enrichment in petrogenic PAHs, suggesting that variation in PAH source (combustion vs petrogenic) may affect desorption if the two pools do not exchange sufficiently rapidly. It is also likely that competetition for soot carbon sorption sites affects the results and might be difficult to account for in hydrocarbon-rich urban harbor sediments.

Comparison of HOC desorption with in-situ BSFs was frought with experiment difficulties caused by the problems with obtaining representative samples of relevent species. However, it is clear that there is little if any correlation between BSFs and aqueous desorption rates or extents for PCBs. There is some evidence that there is a correlation for PAHs and we are continuing to statistically analyze the available data.

PART I:CHEMICAL AND BIOLOGICAL AVAILABILITY OF SEDIMENT-SORBED HYDROPHOBIC ORGANIC CONTAMINANTS: LABORATORY STUDY WITH *Yoldia limatula*

INTRODUCTION

Accumulation of hydrophobic organic contaminants (HOC) by benthic organisms can occur either from the aqueous phase or dietary exposure. As HOC partitioning to sediment increases with increasing octanol-water partition coefficient (K_{ow}), the importance of aqueous (pore water or overlying water) exposure pathways decrease relative to sediment ingestion. Sediment ingestion has been shown to be a significant or primary route of uptake to several species of deposit-feeding organisms exposed to HOC with log K_{ow} values $\geq$ 5.5 (Fowler et al., 1978; Klump et al., 1987). An equilibrium partitioning model, which predicts bioaccumulation levels that are independent of the route of uptake, has been proposed for the protection of benthic organisms (DiToro et al., 1991). However, field and laboratory studies have shown that organism body burdens sometimes depart significantly from equilibrium conditions. For example, accumulation of polycyclic aromatic hydrocarbons (PAH) have been reported at levels lower than predicted by equilibrium partitioning calculations (Paine et al., 1996). Conversely, accumulation of polychlorinated biphenyl (PCB) congener mixtures by deposit-feeders are often higher than equilibrium partitioning predictions (Lake et al., 1990).

Kinetic bioaccumulation models typically consider organism ingestion, growth, chemical uptake from water, chemical elimination, chemical transformation within the organism, and assimilation of contaminant from the diet (Thomann et al., 1992). Under conditions where sediment ingestion is the dominant exposure pathway, contaminant assimilation efficiency is one of the largest sources of uncertainty when modeling body burdens of contaminants. Contaminant assimilation efficiencies determined through short-term laboratory exposures for deposit-feeding invertebrates are relatively high. For example, hexachlorobiphenyl assimilation efficiencies of 16.1-46.4% have been reported for oligochaetes (Klump et al., 1987); fluoranthene assimilation efficiencies of 56% and 22.4-46.0% have been measured for *Capitella sp.* I (Forbes et al., 1996) and for *hydrobia* (Forbes and Forbes, 1997), respectively. However, assimilation of sediment organic matter (SOM) by deposit-feeders is limited; typically only 5-30% of the total is in a bioavailable form (Mayer, 1989). Assuming that HOC is uniformly distributed throughout the

organic matter pool, high contaminant and low SOM assimilation efficiencies implicate the rate and/or extent of desorptive release of contaminant from sediment during gut passage as a potential limiting mechanism. Assessment of the extent of desorption in the guts of deposit-feeding organisms is problematic. For some species desorptive release into clean seawater may approximate the gut environment. For other species, desorptive release is likely enhanced by the presence of surfactants (Mayer et al., 1996). Weston and Mayer (1998) have shown that absorption of PAH solubilized by the gut fluids of the polycheate *Arenicola brasiliensis* is nearly 100%, highlighting the importance of desorption extent on contaminant assimilation efficiencies. Although it is largely untested, it is possible that the processes that affect the relative desorption of various contaminants from sediments into clean seawater also limit HOC desorption when sediments are exposed to gut fluids.

HOC sediment desorption studies have demonstrated that an increase in HOC hydrophobicity generally leads to a decrease in the rate of sorption. Furthermore, the rate of desorption often decreases during the progression of a desorption experiment (Karickhoff, 1980; Pignatello and Xing, 1995). The fraction of chemical that desorbs at a slower rate is often said to reside in a resistant phase. In short-term laboratory experiments, this resistant phase has been modeled by considering a combination of intra-aggregate diffusion and heterogeneity of sediment aggregate size (Wu and Gschwend, 1988). Other experimental data, collected under conditions where HOC has aged for long periods in the lab or field, show very slow desorption that can not be easily described by intra-aggregate pore diffusion models (Pignatello et al., 1993; Carroll et al., 1994). It has been argued that such slow desorption might be the result of slow diffusion through more crystalline ("glassy") organic geopolymer phases (Carroll et al., 1994; Brusseau and Rao, 1989; Weber et al., 1992; Xing et al., 1996). However, Holmén and Gschwend (1997) point out that there is a strong inverse dependence of diffusivity on hydrophobicity in glassy-type polymers. Hence, an assumption of glassy-type organic matter resulted in a range of PAH diffusivities which was too large to explain the sorption variation of PAH observed in their study. Another potential explanation for limited desorption is association of the organic contaminant with soot or coal matrices. Gustafsson and coworkers (1997) were able to account for higher than predicted partition coefficients of PAHs observed in Boston Harbor (McGroddy and Farrington, 1995) and Mystic Lake by quantifying the fraction of soot in these sediments and calculating a soot-phase partition

coefficient. Regardless of the mechanism, it is clear that under some environmental conditions, a fraction of sediment associated contaminants becomes more resistant to desorption.

The objective of this study has been to compare the rate and extent of desorption of HOC into seawater with the extent to which these contaminants are accumulated by a deposit-feeding bivalve. Three HOC classes which differ in structure and likely matrix associations were measured: polychlorinated biphenyls (PCB), linear alkylbenzenes (LAB), and polynuclear aromatic hydrocarbons (PAH). Desorption and bioaccumulation experiments were conducted on surficial and deeper sediments collected from a single site in New York Harbor to assess any effects of sediment depth on chemical and biological availability. Desorption experiments determined the maximum rate of desorption into seawater by use of a polymer resin with excess sorbent capacity (Carroll et al., 1994). Bioavailability experiments were conducted by incubating the subsurface-deposit feeding bivalve, *Yoldia limatula,* with sediments from the different core sections. Slow desorption as a potential mechanism which may limit the bioavailability of certain HOC is discussed.

EXPERIMENTAL APPROACH

Sediment collection

Sediments were collected in May 1995 from a site located near Governors Island in New York Harbor at a water depth of 11.6 meters (m). The site is in a high sediment deposition area with sediment accumulation rates on the order of several cm/yr (Olsen et al., 1981). Subsurface maxima in the concentrations of a variety of contaminants have been measured at this and other high deposition sites in New York Harbor, reflecting a drop in contaminant inputs over the past couple of decades (Bopp and Simpson, 1989). Two Soutar-type box cores (0.6 m^2), deployed from the research vessel *Onrust*, were sectioned into three intervals: 0-4 cm, 5-9 cm, and 10-14 cm, and identical intervals were combined and homogenized. Due to the high sediment accumulation, these sediments intervals reflect historical deposition of less than ten years time at the site. However, it would be difficult to assess the length of time contaminants may have been associated with sediment particles because of the dynamic cycling of sediments between bedded deposits and overlying waters in high energy environments such as the Hudson Estuary/New York Harbor system. After collecting samples for HOC analysis, the remainder of the sediment sections were sieved on site with a 500 μm mesh screen and a minimal amount of seawater in order to remove

detritus and biota. Sieved sediments were placed in acid-washed Nalgene® bottles and stored at 4° C for one month until the initiation of the bioavailability and desorption experiments. All sediments to be used in the desorption and bioavailability experiments were further sieved in the lab with a 63 μm mesh screen, using no more than a 2:1 ratio of seawater to sediment.

Desorption experiments

Desorption experiments were conducted utilizing the method of Carroll and coworkers (1994). XAD-4 resin (Aldrich) was prepared by first rinsing with deionized water and then refluxing successively with methanol, acetone/hexane (50/50), and methanol in a Soxhlet apparatus for 24 hours. The resin was then rinsed with deionized water, placed in a clean jar, filled with deionized water and refrigerated until use to prevent dehydration. Approximately 7 grams (g) wet (1.5-2 g dry) sediment, 10 milliliters (ml) of seawater, and approximately 2 g wet XAD-4 resin were placed in solvent rinsed 25 ml vials. The vials were placed in a rotating shaker (150 rpm) and kept at 25° C. Vials were removed at 2, 5, 12, 48, 158, and 480 hours after initiation of the experiment and 0.5 g of potassium carbonate was added to enhance phase separation. The XAD-4 and sediments were separated by low speed centrifugation and both phases were frozen until analysis.

Bioavailability experiments

Three 10-liter aquarium tanks, one for each of the three sediment intervals, were filled with seawater and five 16-ounce jars, each containing approximately 300 g of wet sediment (5 cm deep), were placed in the tanks. Exposures were conducted at room temperature (21° C) and the salinity of the water was 30 parts per thousand (ppt). Three pre-weighed *Yoldia limitula*, purchased from the Woods Hole Marine Biological Laboratory, were placed in each jar. Within one hour puffs of suspended sediment were visible indicating the *Yoldia* were actively feeding. The tanks were aerated and pH and salinity were monitored. The seawater in the tanks was replaced weekly. At each time point organisms from one of the jars were removed, placed in clean sediment and allowed to depurate for 24 hours. Approximately 6 g of wet sediment was added to the remaining jars to replenish sediment displaced by *Yoldia* feeding activity. The clams were then weighed, shucked, placed in pre-weighed centrifuge tubes, homogenized with a Virtus Tissue Homogenizer, and frozen until extraction.

Analytical procedures

The extraction of PCB, PAH and LAB from sediment, tissue, and XAD-4 resin samples followed a modification of the method described in (Lamoureux, 1995). Wet sediment and tissue samples were placed in centrifuge tubes, 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. 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 XAD-4 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 for lipid weight analysis on a Cahn microbalance. 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).

PCBs were analyzed on a Hewlett Packard 5890 gas chromatograph equipped with a 30-m DB-5 capillary column (J&W Scientific) and an electron capture detector. 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). 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 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%. Procedural blanks were subtracted from all samples and were generally less than 10% of sample PCB concentrations.

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 and corrected for recovery. 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. Total LAB concentrations were obtained by summing the individual alkylbenzene concentrations and subtracting blank values, which fell below 10% of sample concentrations.

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, acenapthene, 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, subtracted from all samples, were well below 10% of all sample PAH concentrations.

Total organic carbon (TOC) was measured on a Carlo Erba EA1108 CHN Analyzer. Measurements were made relative to a sulphanilamide standard after removal of inorganic carbon with dilute hydrochloric acid. Disaggregated grain size analysis was measured on a Sedigraph in a sodium metaphosphate solution after prior removal of organic carbon with hydrogen peroxide (Coakley and Syvitski, 1991) while aggregated grain size was determined through pipette analysis (Folk, 1968) without organic carbon removal.

Calculation of predicted and measured desorption rates

The rates and extent of desorption measured in these experiments were compared to predictions of the Wu and Gschwend radial intra-particle diffusion model (Wu and Gschwend, 1988). The advantages of this mechanistic-based model is that it provides a priori predictions of desorption based on measurable sediment and HOC properties. It describes sorption as a reversible

process which includes aqueous phase diffusion of HOC through the pores of aggregated particles that is retarded by rapid partitioning between intra-particle fluid and organic matter. The numerical solution to this model can simulate multi-compartment sorption kinetic behavior first described well by Karickhoff (1980). The model has come under scrutiny in recent years because it can not describe the very slow sorption observed in some experiments and because it ignores possible slow diffusion of HOC through natural organic matter (Pignatello and Xing, 1995). We have compared our data to this model to both test the application of the model to marine sediments across a wide range of HOC and to examine under what conditions there are gross departures from the predictions of this simple model. For example, measured desorption rates much lower than predicted by the model would be consistent either with very strong sorption (e.g., adsorption to soot carbon) or with incorporation into resistant phases (e.g., low permeability geopolymers or protection by small pores or mineral coatings).

The radial diffusion coefficient employs a sorption rate constant (k) which is estimated from an average radius (r) of the particle aggregates and the effective diffusivity (D_{eff}):

$k = \alpha D_{eff} / r^2$

where α is a constant and D_{eff} is the effective (sorption-impeded) intra-particle diffusion coefficient (cm^2/s) (Wu and Gschwend, 1988). In this study, we have used the relationship from Karickhoff et al. (1979) to estimate the sediment-water distribution coefficient (K_d) that is used in the calculation of D_{eff} from the fraction organic carbon of the sediment (f_{oc}) and the K_{ow} of the sorbate: $\log K_d = \log f_{oc} + \log K_{ow} - 0.21$. The K_{ow} values for PCBs (Hawker and Connell, 1988), PAHs (Schwarzenbach et al., 1993), and LABs (Sherblom et al., 1990) were taken from the literature. An average particle diameter of 20 μm, used in the D_{eff} calculation, corresponds to a value intermediate between the mean aggregated and disaggregated diameters measured for each sediment (see Table 1).

The numerical solution to the Wu and Gschwend model provides desorption kinetic results that distinctly depart from first-order kinetic behavior, even when only a single particle radius is used. Much of the desorption kinetic data that we provide below also seem to show desorption behavior where the rate constant decreases over time. On the other hand, the desorption kinetics that we observed could be reasonably well described by a first-order model (r^2 =0.76-1.0) for the majority of HOC that we examined. The small number of time points (6) in our study precludes

sophisticated kinetic treatments or robust comparisons between kinetic models. Therefore in order to compare our results to Wu and Gschwend model predictions three exercises were performed:

1. For HOC desorption results that could be reasonably described by first-order desorption kinetic behavior (ln C_s versus time, where C_s is the sorbed HOC concentration), we compared observed first-order rate constant measurements to first-order rate constant estimates calibrated to the numerical solution of the Wu and Gschwend model when 50% of HOC has desorbed (when t~0.03 r^2/D_{eff} or when α=22.7 for the condition when there is diminishingly low fraction of chemical sorbed at equilibrium) (Wu and Gschwend, 1988).

2. For many of the lower molecular weight PCBs, the plots of ln C_s versus time could not be approximated by a first-order model, and instead were fit to a two-compartment model (Karickhoff, 1980) using JMP version 3.1.6.2 (SAS Institute, Cary, NC, USA). The parameters k_{fast}, k_{slow}, and the f_{fast} were determined, where f_{fast} (f_{slow} = 1 - f_{fast}) is the fraction of the sorbed HOC in a pool desorbing with rate constant k_{fast}. In most cases where a two compartment model was clearly needed to describe the data, the k_{fast} was slower than that predicted by the Wu and Gschwend model; thus k_{slow} departed from the intra-particle diffusion model by and even greater extent. As so few data determined the three adjustable parameters in the two-compartment model we place little statistical confidence on the values of k (especially k_{slow}). However, the values of k_{fast} do provide better than order of magnitude estimates of initial desorption to compare to intra-particle diffusion model predictions.

3. A stricter comparison of our data to the numerical solution of the Wu and Gschwend model was conducted by comparing the extent of desorption measured at a given time to model prediction by use of graphical solutions provided in Wu and Gschwend (1988).

RESULTS

Sediment Characterization

Total concentrations for each compound class increase slightly with depth (Table 1). The organic carbon content of the sediment decreases slightly with depth while the median diameter of

both aggregated and disaggregated measurements of the <63 μm fractions remains more constant over the sampling interval.

In addition to total PAH concentrations, methyl-phenanthrene to phenanthrene ratios (mp/p) ratios are reported on Table 1. This ratio, defined as the ratio of the sum 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 as PAHs that derive from petrogenic sources are known to contain a greater abundance of alkylated homologues than those that derive from pyrogenic sources (Prahl et al., 1984). An mp/p ratio of 0.5-1 is indicative of combustion-derived sources of PAH (Prahl et al., 1984) 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, the low mp/p values measured in these New York Harbor sediments suggest that pyrogenic sources dominate the PAH signature that is preserved.

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 et al., 1994). 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 relative to commercial surfactant mixtures. I/E values reported on Table 1 are greater than 1, indicating some degree of degradation has occurred. The similarity of the I/E ratios calculated for the 0-4 and 10-14 cm sediment intervals suggests that little degradation has occurred 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, bioavailability and metabolism within an LAB homologue group.

HOC Desorption

The rate and extent of desorption of all compound classes is similar for all three depth intervals indicating the effect of the sediment aging following deposition and burial has not significantly hindered desorption of the contaminants in the deeper sediments (Figure 1). PCB show the least impedance to desorption, with 20-40% remaining in the sediment after 480 hours. The total PAH desorption rate and extent was less than that of the total PCBs with 30- 60%

remaining in the sediments at the end of the experiments. Total LAB desorption was the most limited with 55 - 60% of the initial concentration remaining in the sediment.

While total compound class desorption patterns are useful for comparison, more can be learned from looking at the desorption rate of individual compounds. The desorption of PCB congeners 52, 101, 138, and 180 over time are shown on Figure 2a. as examples of the relative desorption of a tetra-, penta-, hexa-, and heptachlorobiphenyls. Interestingly, the least hydrophobic congener 52 (log K_{ow} = 5.84), has the most desorption resistant fraction and appears to exhibit the fastest shift from a fast to a slow desorption rate. The desorption rates of the most hydrophobic congeners 138 and 180 (log K_{ow} = 6.83 and 7.36, respectively) appear to be initially slower than the other two congeners and do not show a pronounced shift indicating that the desorption resistant fraction of these congeners are small or the time course of desorption has not been followed long enough. Note that 88 and 86 percent of congeners 138 and 180 have desorbed after 20 days. The low molecular weight congeners fit well to a two compartment model, however, as shown on Figure 2c.

Differences in individual PAH compound desorption kinetics do not appear to be a simple function of K_{ow} (Figure 2b). Benz(a)anthracene (log K_{ow} = 5.91) and phenanthrene (log K_{ow} = 4.57) desorb at similar rates while the overall desorption rate of 2-methylphenanthrene is slower (log K_{ow} = 5.01). Benzo(a)pyrene (log K_{ow} = 6.50) did not desorb over the time course of the experiment despite having a K_{ow} value lower than PCB congener 138.

The desorption kinetics of the LAB compounds plotted on Figure 2d are much slower (note the change of scale) and more predictable in terms of hydrophobicity than the desorption kinetics of the representative PCB and PAH compounds; LAB desorption rates increase with increasing chain length and hydrophobicity. The estimated K_{ow} values of LAB for a given chain length increase with increasing distance of the phenyl substitution position from the center of the chain (Sherblom et al., 1990). The desorption patterns of these LAB compounds are consistent with their K_{ow} values in that the external (most hydrophobic) compounds desorb slower than the internal (less hydrophobic) LAB.

Bioaccumulation

The total compound class BSFs (ng/g organism lipids/ ng/g sediment organic carbon) observed in *Yoldia limitula* over time are plotted on Figure 3. Significant PCB levels were

measured in *Yoldia* prior to initiation of the experiment as indicated by the y-intercept value. The lipid content of *Yoldia* declined over the time course of the experiment (percent lipid (wet weight)=0.48-0.012t, t=days), however, the mean lipid contents at the beginning and the end of the experiment were not statistically different ($P>0.05$). Little difference in bioaccumulation rate and extent was seen between the sediment intervals. PCB, the compound class for which desorption was the greatest, also attained the highest levels of bioaccumulation in *Yoldia*. Although LAB exhibited the slowest desorption kinetics, they appeared to accumulate to a greater extent in *Yoldia* than the PAH.

DISCUSSION

Comparison of measured and predicted desorption kinetics

The desorption patterns of the individual PCB, PAH, and LAB compounds plotted on Figure 2 are typical for each compound class in that the PAH, LAB, and highest molecular weight PCB desorb at relatively constant rates while the majority of the PCBs conform to a two-compartment model with initially fast and then slow desorbing components. For comparison with the retarded/radial diffusion model predictions, desorption rate constants (k) for the PAH, LAB, and the high molecular weight PCB compounds were calculated from a first-order kinetic model that approximates the observed desorption behavior (Desorption rate constants and correlation coefficients are given on Table 2). The desorption kinetics of the remainder of the PCB were fit to a two-box model in order to obtain desorption rate constants for a labile pool (k_{fast}) and a more resistant pool (k_{slow}). For this comparison k_{fast} is used for PCB with log K_{ow} values less than 6.7. Measured log k values are plotted against the log k values predicted from the retarded/radial diffusion model on Figure 4a and relevant kinetic parameters for select HOC are given in Table 2. Measured and predicted rate constants are in close agreement in both magnitude and dependence on K_{ow} for the LAB and approximately half of the PCB. The PCB which show close agreement are the most hydrophobic PCB with log K_{ow} values that are greater than 6.2. The PCB for which measured k values fall below predicted values are congeners which possess log K_{ow} values that are less than 6.2. Note that for the lower K_{ow} PCB k_{slow} departs from $k_{predicted}$ by an even greater amount than Figure 4a indicates (for examples see Figure 2). The measured PAH rate constants are far below model predictions.

The k_{slow} calculated from this study of field-contaminated sediments (sorption timescales of years to decades) for congener 49, a tetrachlorobiphenyl (2,2',4,5'-CB), is 3.5 x 10^{-4}/hr (Table 2) which is slower than available literature k_{slow} values measured for tetrachlorobiphenyls derived from studies using laboratory spiked sediments (sorption timescales of days to weeks); 1.72-2.54 x 10^{-3}/hr for congener 65 (2,3,5,6-CB) [35] and 0.8-5 x 10^{-3}/hr for congener 54 (2,2',6,6'-CB) (Coates and Elzerman, 1985). In contrast, the measured k_{slow} for congener 118, a pentachlorobiphenyl (2,3',4,4',5-CB), of 5.2 x 10^{-3}/hr is much more comparable to the k_{slow} value of 0.98-2.01 x 10^{-3}/hr reported by Cornelissen and coworkers (1997), suggesting that the rate of slow desorption decreases with increasing time of contaminant association with sediments for lower molecular weight congeners but perhaps not for high molecular weight congeners As can be seen in Figure 2c, little data constrains the estimate of k_{slow} derived from a two-compartment model. However, a comparison of our estimates to those measured in other long-term PCB desorption experiments may suggest differences in the role of aging for low and high molecular weight PCB congener desorption kinetics. Future experiments would need to be done to confirm our k_{slow} estimates.

Possible explanations for the deviation from desorption rate constants predicted by the Wu and Gschwend retarded intra-particle diffusion model for the less hydrophobic compounds and their observed biphasic desorption patterns include: (1) the existence of micropores within the sediment matrix that are available to the smaller compounds but prohibit the penetration of larger compounds on the basis of size and shape, (2) two types of organic matter phases within particle aggregates; "elastomer" and "glassy" in which HOC diffusion is relatively fast and slow, respectively (Pignatello and Xing, 1995; Young and Weber, 1995), and (3) strong partitioning to soot phases within the sediment. The close agreement of the most hydrophobic compounds with the retarded intra-particle diffusion model and the lack of agreement of the least hydrophobic compounds with the model is supported by the first explanation. In this scenario, the labile PCB pool could decrease over time either during transport of contaminated sediment in the water column or following deposition, leaving behind a slowly re-equilibrating resistant pool. The smaller, less hydrophobic congeners, being more soluble may have been removed from the labile pool faster, leaving a greater fraction in the resistant phase.

The low molecular weight PCB desorption behavior also may be explained by the intra-organic matter diffusion model; the observed multiphasic desorption behavior could be due to desorption from both elastomer (fast) and condensed (slow) sedimentary organic matter phases