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Bioavailability and Toxicokinetics of Polycyclic Aromatic Hydrocarbons Sorbed to Sediments for the Amphipod *Pontoporeia hoyi*†

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■ The accumulation kinetics, by the benthic amphipod, *Pontoporeia hoyi*, were measured for sediment-associated, selected polycyclic aromatic hydrocarbons (PAHs) and 2,4,5,2′,4′,5′-hexachlorobiphenyl (HCB). The kinetics data suggest that uptake occurs largely via the sediment interstitial water and is kinetically controlled by desorption from sediment particles and dissolved organic matter. Assimilation from ingested material may be significant for the more strongly sorbed compounds such as benzo[*a*]pyrene and HCB. The desorption rate of contaminants from the sediment matrix appears to determine whether the major sediment contaminant source is interstitial water or ingested particles. The log of the contaminant uptake clearance is inversely proportional to the log octanol–water partition coefficient for PAHs. Bioavailability of sediment-sorbed contaminants declined as the contact time between the sediment and contaminant increased. Chemical extractability remained high even though bioavailability was reduced. A conceptual model to describe accumulation of organic contaminants from sediments is described.

Introduction

Many aquatic systems are burdened with a large inventory of sediment-associated pollutants. As legislative controls on contaminant release from point sources have improved, the major sources of contaminant loads have shifted to secondary sources such as nonpoint runoff, atmospheric input, groundwater leachate, and reintroduction of sediment-associated pollutants. In some cases, these secondary sources are now the only apparent source of contamination.

The movement of sediment-associated contaminants into the benthic component of the food chain is not well-defined (*1*). However, Great Lakes field studies suggest that the amphipod, *Pontoporeia hoyi*, the most abundant invertebrate (on a mass basis) in the Great Lakes (*2*), obtains a substantial portion of its organic contaminant load from sediments (*3*). The bioaccumulation factor (BAF) for sediment accumulation (defined as "concentration in the organism divided by the concentration in the sediment") ranges from 1.2 to ~10 for polycyclic aromatic hydrocarbons (PAHs) (*3, 4*).

Previous laboratory research suggests that the accumulation of chlorinated compounds from sediments is slow, often requiring months to achieve apparent steady state (*5–11*). The chlorinated hydrocarbon accumulation from sediments was greatest for compounds with a log octanol–water partition coefficient (K_{ow}) of ~6 and generally declines with compounds of both higher and lower log K_{ow}'s (*9, 10*). Sediment accumulation of PAH has been less well studied compared to the chlorinated compounds. Accumulation of naphthalenes and methylnaphthalenes from sediments does not appear to occur (*12*), but higher molecular weight PAHs are accumulated by marine invertebrates with some organism concentrations an order of magnitude greater than the sediment concentrations (*13, 14*).

In this study, the uptake kinetics of selected PAHs and 2,4,5,2′,4′,5′-hexachlorobiphenyl (HCB) from sediments were measured for *P. hoyi*. Four questions were investigated to examine potential factors that may affect bioavailability: (1) Do changes in the chemical properties of the contaminants alter the accumulation from the sediments? (2) Does the contact time between the contaminant and the sediment affect the contaminant bioavailability? (3) Do contaminant concentrations measured in sediments reflect bioavailable concentrations? (4) Can the source of bioavailable sediment-associated contaminants, sediment particles or interstitial water, be identified?

Materials and Methods

Organisms. The *P. hoyi* were collected from surficial sediment at a water depth of 23–27 m in Lake Michigan approximately 3 miles southwest of Grand Haven, MI, between spring and fall during the field seasons of 1981–1986. The amphipods were screened from the sediment, transported to the laboratory in cool lake water, and housed in 3–4 cm of Lake Michigan sediment and 10 cm of lake water at 4 °C (*15*). (Note: Lake Michigan water was used throughout the studies.)

Sediments. The sediments for bioassay were collected from 45 m depth by PONAR grab, placed in coolers, transported to the laboratory, and stored at 4 °C until use. The sediments were wet sieved (1-mm screen size) with lake water to remove macroinvertebrates and any other large materials; a portion of the sediments was further sieved at 72 μm. Both of the resulting size fractions were dried at 60 °C and weighed. The size distribution of the <72-μm fraction was determined by Coulter Counter techniques (*16*). The organic carbon content of the sediments was determined by the method of Menzel and Vaccaro (*17*).

Compounds. The chemicals used were ^{14}C-labeled anthracene (Anth, 3.3 mCi mmol^{-1}), phenanthrene (Phe; 14 mCi mmol^{-1}), 2,4,5,2′,4′,5′-hexachlorobiphenyl (HCB; 14.06 mCi mmol^{-1}), benzo[*a*]pyrene (BaP; 29.6 mCi mmol^{-1}), and benz[*a*]anthracene (BAA; 49 mCi mmol^{-1}) and ^{3}H-labeled benzo[*a*]pyrene (23.8 Ci mmol^{-1}) and pyrene (PY; 34 Ci mmol^{-1}). All compounds were checked for radiopurity prior to use by a combination of thin-layer chromatography (TLC) and liquid scintillation counting (LSC) (*18*) and were >98% pure. All preparative and analytical procedures were performed under gold fluorescent lights (λ > 500 nm) to avoid PAH photodegradation.

Analyses. The amphipods were analyzed for radioactivity by direct extraction of the contaminant by the scintillation cocktail and LSC (*19, 20*). The *P. hoyi* lipid content was measured by a microgravimetric procedure (*21*).

Sediment samples were taken at each sample time to determine the dry-to-wet weight ratios and contaminant concentration. The dry-to-wet weight ratio was determined by weighing a wet sediment sample and drying the sample at 60 °C to constant weight. Aliquots of sediment were prepared for contaminant analysis by determining the wet weight, desiccating the aliquot with anhydrous sodium sulfate, and storing the sample under ethyl acetate

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Table I. Native and Dosed Concentrations and Recoveries for Contaminants in the Exposure Sediments

compd	concn, ng g^{-1} native[a]	concn, ng g^{-1} dosed	recovery abs[b]	recovery rel[c]
phenanthrene	59.4	41–332	75 ± 7	98 ± 21
anthracene	26.9	125–144	74 ± 11	71 ± 16
fluoranthene	233	NS[d]		
pyrene	120	0.32–0.33	63 ± 9	96 ± 2
benz[a]anthracene	ND[d]	48.4	ND	100 ± 8
chrysene	52.3	NS		
benzo[e]pyrene	34.7	NS		
benzo[a]pyrene	43.1	24–55[e] 0.18–0.37[f]	72 ± 11	90 ± 11
hexachlorobiphenyl	ND	16.7	ND	86 ± 8

[a] Eadie et al. (4). [b] Percent recovery based on amount dosed to the sediment. [c] Percent recovery based on analysis of the sediment at time zero. [d] NS, not studied; ND, not determined. [e] ^{14}C-Labeled BaP. [f] ^{3}H-Labeled BaP.

in a freezer prior to analysis. The desiccated sediments were Soxhlet extracted in ethyl acetate/cyclohexane (50:50, V/V) for 12–18 h. Recovery based on the amount of contaminant dosed to the sediments was generally ~70% (Table I). Recoveries over the course of the experiments relative to the concentration determined at the beginning of the experiment were nearly quantitative (Table I).

Extract radioactivity was determined by LSC of extract subsamples. The limit of detection for LSC was considered to be twice background (31 ± 6 and 15 ± 5 cpm for ^{14}C and ^{3}H, respectively). Extract volumes were then reduced by a combination of rotary flash and nitrogen stream evaporation. Samples were analyzed for degradation by the combination of TLC and LSC.

Preparation of Exposure Media. An aqueous slurry was prepared from the sieved sediments, 1 kg of wet sediment to 2 L of lake water. The sediment slurry was then dosed with the radiolabeled contaminant in either acetone or methanol carrier (<250 μL), mixed vigorously by mechanical stirring at room temperature for 8–18 h, and allowed to settle 18–24 h at 4 °C. The overlying water was decanted, fresh lake water was added to make an easily dispensable slurry, and the sediments were dispensed to replicate test chambers with approximately equal weights of wet sediment in each chamber. Samples for contaminant concentration and sediment dry-to-wet weight ratio determinations were taken at the beginning, middle, and end of the sediment distribution. After the sediments were distributed to all chambers, overlying lake water was added gently, to minimize sediment disturbance. Sediments were allowed to settle for an additional 24 h before the organisms were added.

Experimental Designs: Static and Flow-Through. Two types of experiments were performed: static and flow-through. Static experiments involved exposures with no overlying water exchange and a ratio of approximately 300 mg of organism weight to 2 L of overlying water; flow-through experiments involved exposures with a constant exchange (with approximately 12 exchanges per day) of overlying water. For static experiments, small Petri dishes (6–7 dishes per aquarium) with approximately 10 g (wet weight) of sediment were placed in aquariums with 2–3 L of water. After settling 24 h at 4 °C, the *P. hoyi* were added (approximately 50 organisms per aquarium). One Petri dish was removed from each of three replicate aquariums at each sampling time. The sampling days were 1, 2, 4, 7, 15, and 30 with actual sampling times used in the kinetic analyses. Sampling times varied somewhat from experiment to experiment to accommodate the slower uptake of compounds with high log K_{ow}. Prior to removing

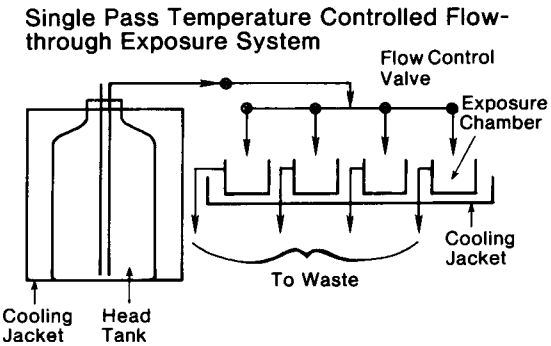

Figure 1. Configuration for flow-through experiments.

a sediment sample, a sample of overlying water was taken for measurement of radioactivity.

In initial experiments, an additional sample of overlying water was filtered, the dissolved organic carbon (DOC-) bound contaminant was separated by the reverse-phase separation technique (22), and particle- and DOC-bound contaminant was assayed by LSC. After the overlying water was sampled, a Petri dish containing the sediment and organisms was gently removed and the overlying water decanted, retaining the floc on top of the sediment. Organisms were removed from the sediments with forceps and placed in water to remove attached sediment debris. The organisms were blotted dry, weighed, and placed in scintillation cocktail for radioanalysis (19). The sediment subsamples were prepared for analysis as described above.

In one set of static experiments with Phe, the number of Petri dishes was tripled. Exposed animals were removed at 2-week intervals and fresh (previously unexposed) animals added to the sediments for a total of three 2-week exposures. The sampling schedule was 1, 2, 4, 7, and 15 days for each successive exposure period. Additionally, a separate subsample of dosed sediment was held at 4 °C, and animals were exposed to the aged sediments on the same schedule as fresh animals were added successively to the above sediments.

In another set of dual-labeled experiments with Phe and PY, the dosed sediment was split into two equal fractions and one set aside for 10 days at 4 °C. Two experiments were run; one immediately after the initial dosing (as described above), the other after an additional 10 days of aging.

For two replicate flow-through experiments, sediments dosed with both [^{3}H]BaP and [^{14}C]Phe were placed in 200-mL flow-through chambers (Figure 1). Four chambers were accommodated by each of two head tanks. After the sediments had settled in the chambers overnight, a flow of approximately 100 mL h^{-1} of uncontaminated unfiltered lake water was initiated (turnover time, 2 h), and the flow was maintained for the entire course of the experiments. Twenty-four hours later, 20 organisms were added to each of seven chambers. An eighth chamber was used as a control to permit examination of desorption loss of contaminants in the absence of organisms. Chambers were sampled at each time point for organism and sediment data as described for the static experiments. (Equipment restrictions restricted collections to single samples per time point.) [^{14}C]HCB uptake clearance was also determined under flow-through conditions.

Data Analysis. The accumulation data were fit to a two-compartment model that allowed the concentration of the containment to decline as a result of distribution between a bioavailable pool and an biologically unavailable pool (eq 1 and 2).

$$dC_a/dt = K_s C_s^0 e^{-\lambda t} - K_d C_a \quad (1)$$

with the integrated form

$$C_a = [K_s C_s^0(e^{-\lambda t} - e^{-K_d t})]/[K_d - \lambda] \quad (2)$$

where C_a is the concentration of the compound in the organism (ng g^{-1} of wet weight organism), C_s^0 is the initial contaminant concentration in sediment (ng g^{-1} of dry sediment), K_s is the uptake clearance of the compound from the sediment (g of dry sediment g^{-1} of organism h^{-1}), Kd is the elimination rate constant (h^{-1}), λ is the rate constant for the chemical to become biologically unavailable (h^{-1}), and t is time (h). K_s incorporates information about the bioavailable fraction of chemical from both ingested particles and the interstitial water and the rate of uptake. This conditional constant is the mass-normalized relationship between the contaminant's rate of uptake and concentration in the sediment. The $e^{-\lambda t}$ term describes the rate of contaminant movement to a biologically unavailable pool. This process is conceived to be analogous to the reversible/slowly reversible partitioning for changes in chemical extractability of contaminants from sediments (*23*, *24*). However, the process does not necessarily represent the identically same rate or fraction that exhibits changes in chemical extractability.

The data were fit to the integrated form of the model (eq 2) or to simplifications of the model based on the contaminant's chemical and pharmacological behavior. For Anth, Phe, and PY the data were fit nonlinearly with NLIN (*25*) to eq 2. The average K_d value determined previously (*26*) was supplied so that a finite solution to the nonlinear fit would result. This fit yields a least-squares estimate for K_s and λ.

The data for BaP, BAA, and HCB were described by simplifications of the general model. For BAA, the $e^{-\lambda t}$ term in the model approaches a value of 1 because λ becomes negligible. The model can then be simplified to a two-compartment model with a constant sediment contaminant concentration (eq 3). The nonlinear fit of the data yields estimates for K_s and K_d.

$$C_a = [K_s C_s(1 - e^{-K_d t})]/K_d \quad (3)$$

For HCB and BaP, the data suggest that in addition to the $e^{-\lambda t}$ approaching 1 because of a negligible λ value and the constant contaminant concentration in the sediment, there was no appreciable elimination. Thus, a further simplification in the model to a one-compartment linear model (eq 4) was possible, and the data fit by linear regression (*25*) to yield an estimate of K_s.

$$C_a = K_s C_s t \quad (4)$$

Results

Sediment Characterization. The dry sediments contained 1.3 ± 0.5% organic carbon, consistent with previously reported data from this area (*27*). The <72-μm sediment fraction was 21.5% of the sediment dry weight. The particle distribution of this fine material centered around 10 μm diameter. Sediments from this station had been analyzed previously for PAHs and the individual PAH ranged from 40 to ~200 ng g^{-1} of dry weight (Table I) (*4*). No degradation of the dosed chemicals was observed relative to the samples taken at the beginning of each experiment.

Radioactivity in the overlying water samples was low—not greater than twice background. The small amount of radioactivity in the water was primarily associated with small particles or dissolved organic matter.

Organisms. *P. hoyi* collected from 23–27 m had background concentrations for specific PAH congeners ranging from <100 to 2000 ng g^{-1} (*4*). These background concentrations are about half that for *P. hoyi* collected from 45 m (*4*), the site where the sediments used for these studies were collected. Accumulation of radiolabeled PAH by *P. hoyi* was assumed to be independent of the background body burden. The "health" of the organisms was followed by measuring the lipid content of *P. hoyi* over the course of some later studies. Although a slight decline in mean lipid content (percent lipid = 31.1 − 0.009*t*) occurred, there was no statistical difference between sample means at time zero and 844 h. The animals were presumed to be healthy for the duration of the study; in any event no overt mortality occurred.

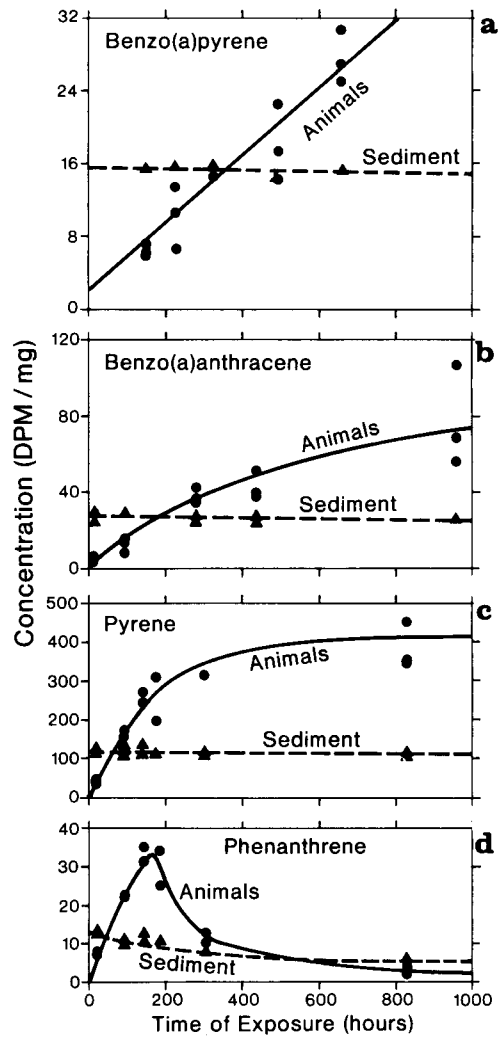

Figure 2. Example of a typical *P. hoyi* accumulation curve for (a) benzo[*a*]pyrene (Note: the curve shape would be the same for hexachlorobiphenyl except that the concentrations and the slope would be different), (b) benz[*a*]anthracene, (c) pyrene, and (d) phenanthrene.

Hexachlorobiphenyl and Benzo[*a*]pyrene. The model assumption of constant sediment contaminant concentration was verified by measuring sediment concentrations over the course of the experiment (Figure 2a). The assumption of negligible elimination was based on the linearity of the plot of C_a with time (Figure 2a). The K_s for BaP was relatively constant for experiments performed on animals collected during different field seasons from 1981 to 1985 (0.0029 ± 0.001, n = 7).

The potential for accumulation of BaP from overlying water was assessed three times by measuring uptake under flowing water conditions. The K_s under flow-through conditions was 0.0025 ± 0.0005 (n = 3)—not significantly different from that determined under static conditions, 0.0032 ± 0.0013 (n = 4). The K_s for BaP (0.0023 ± 0.001)

Table II. Reduction in Chemical and Biological Availability in Lake Michigan Sediment

compd	half-life, h	
	chem avail.[a]	bioavail
pyrene	547	298
anthracene	600[b]	77
phenanthrene	1196	151
	825[b]	

[a] Estimated from K_p, Karickhoff and Morris (*24*). [b] Measured.

was determined twice as a single compound spike and was also determined in dual-labeled experiments using [^{3}H]-BaP in the presence of [^{14}C]Anth (0.0025 ± 0.0009, n = 2), Phe (0.0034 ± 0.0012, n = 3), and HCB [0.0021 ± 0.001 (standard error from the slope of the regression line for the determination of the clearance), n = 1]. There was no significant difference between the K_s values in the presence of other compounds or spiked singly.

The [^{14}C]HCB K_s, measured in a dual-labeled experiment with [^{3}H]BaP, was greater than twice that for BaP (0.0057 ± 0.0033 vs 0.0021 ± 0.001, respectively).

Benz[*a*]anthracene. The BAA K_s (0.005 ± 0.001) was also determined only once (eq 3). The assumption of constant sediment contaminant concentration was verified by measurement (Figure 2b). By using the simplification that λ was negligible, an estimate of K_d (0.0014 ± 0.0006 h^{-1}) was obtained that was not significantly different from previously observed values (*26*). When the BAA data were fit to the general model [using the previously determined K_d value (*26*)], the λ value was very small and negative, verifying the validity of the use of the simplified model to determine K_s.

Pyrene. Fitting PY data (Figure 2c) to the two-compartment model (eq 3), resulted in K_d values 4–7 times larger than any previously reported values (*26*). Therefore, PY was fit to the general model (eq 2) and the K_s were 0.019 ± 0.001. Exposure to 10-day-aged sediment resulted in a K_s of 0.015 ± 0.001, a value that was significantly lower than for amphipods exposed to nonaged PY-dosed sediments. The measured PY sediment concentration did not change with time over the course of the experiments or during the 10-day aging (0.32 ± 0.02 and 0.33 ± 0.01 ng g^{-1} for nonaged and aged sediments, respectively). Although measured sediment PY concentrations remained constant over the experimental time course, this pattern did not provide sufficient justification to employ a simplification of the general model; the $e^{-\lambda t}$ expression describes the loss from a bioavailable pool rather than from a chemically extractable pool. The λ value for the nonaged sediment was 0.0030 ± 0.0003 h^{-1}, while the value for the aged sediment was 0.0019 ± 0.0004 h^{-1}. The half-time for this process was 231 h in the nonaged sediment and 365 h in the aged sediment (Table II). If the apparent reduction in bioavailable concentration were as rapid in sediment not mixed by organisms as in sediments with organisms present, the 10-day storage should have reduced the bioavailable pool by 50%. However, the final concentrations in the organisms were similar (0.94 and 1.2 ng g^{-1}), although the animals in the nonaged sediment came to the apparent steady-state concentration twice as fast as did those in the aged sediment.

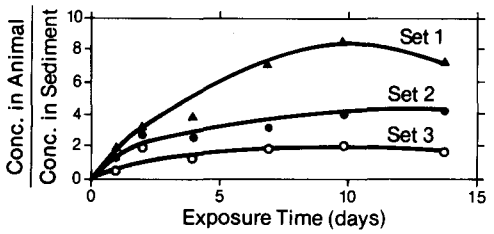

Figure 3. Phenanthrene accumulation curves for amphipods exposed to the same sediment sequentially. Each set represents a 2-week accumulation of phenanthrene by fresh (previously unexposed amphipods.

Phenanthrene. The decline in the measured sediment Phe concentrations dictated the use of the general model to describe Phe accumulation (Figure 2d). The average K_s for Phe was 0.041 ± 0.023 (n = 6). The λ value for Phe was 0.0055 ± 0.003 and the resulting bioavailable half-time approximately 126 h (Table II).

Aging sediments for 10 days reduced the Phe K_s from 0.038 ± 0.009 to 0.028 ± 0.002, while λ remained the same at 0.010 ± 0.002 h^{-1}. The *P. hoyi* exposed to 10-day-aged sediment attained only ~50% of the Phe concentration compared to those exposed to the freshly prepared (72 h) sediment. The uptake clearances for Phe, like BaP, are not thought to be affected by the presence or absence of other compounds. When Phe was run singly, the average K_s was 0.063 ± 0.029 (n = 3), while when measured in dual-labeled experiments, K_s with [^{3}H]BaP was 0.033 ± 0.017 (n = 3) and with [^{3}H]PY was 0.038 ± 0.009 (error is standard error from the regression line from determining the uptake clearance, n = 1). The high mean value when Phe was run alone apparently results primarily from a measurement made in early spring (1986) when *P. hoyi* is known to feed at the greatest extent (*28*). The K_s determined under flow-through conditions (0.023 ± 0.003, n = 2) was significantly different from that achieved under static conditions (0.050 ± 0.023, n = 4). Again, the difference was presumably due to the high value for the early spring experiment.

Serial exposures of fresh organisms to a Phe-dosed sediment in three 2-week sets examined the potential reduction of the biologically available pool that resulted from removal of an ingestable sediment fraction. These results were compared with exposure to a second amount of sediment dosed at the same time and held for the same lengths of time to which no organisms had been added

Table III. Comparison of Uptake Clearances and λ Values for a Series of Phenanthrene Exposures

sample	set A		set B	
	K_s[a]	λ[a]	K_s	λ
new sediment	0.080 ± 0.006	0.0036 ± 0.0004	0.080 ± 0.009	0.0033 ± 0.0006
	Second 2 Weeks			
same sediment, new *P. hoyi*	0.053 ± 0.007	0.006 ± 0.001	0.035 ± 0.007	0.004 ± 0.002
new sediment, new *P. hoyi*	0.075 ± 0.011	0.007 ± 0.002	0.075 ± 0.011	0.007 ± 0.002
	Third 2 Weeks			
same sediment, new *P. hoyi*	0.036 ± 0.01	0.008 ± 0.003	0.030 ± 0.009	0.008 ± 0.003
new sediment, new *P. hoyi*	0.058 ± 0.006	0.006 ± 0.001	0.047 ± 0.023	0.006 ± 0.003

[a] Units: K_s, g of dry sediment g^{-1} of organism h^{-1}; λ, h^{-1}.

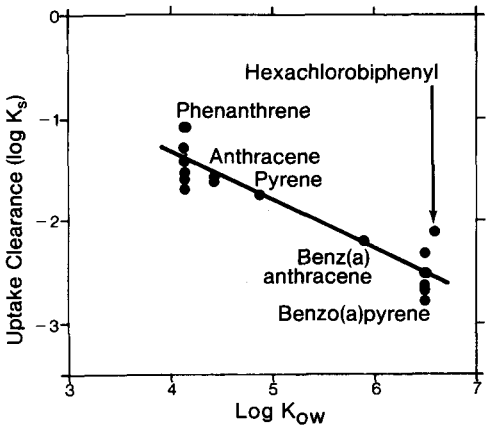

Figure 4. Linear relationship of log K_s to log K_{ow}.

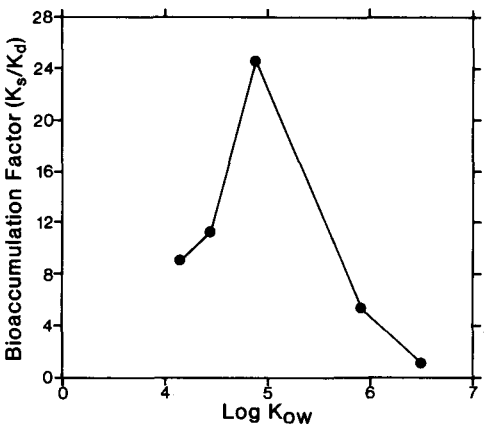

Figure 5. Plot of calculated bioaccumulation factors against log K_{ow} showing a peak at log K_{ow} of 5.

(Table III, Figure 3). The K_s values for aged sediment declined over the course of the 6-week study by ~34% (Table III). Correspondingly, the λ value increased by a factor of ~1.7, indicating that the bioavailable fraction declines more rapidly in aged sediment. In the sediment exposed to three successive sets of *P. hoyi*, K_s declined ~60%, while the λ value increased by a factor of ~2.3 (Table III). Thus, the presence of the animals increased the rate of reduction of bioavailable Phe, implying a removal of ingestable material.

The reduction in Phe bioavailability was compared to the measured reduction in chemical availability, determined as amount extractable (Table II). The rate constant for reduction of amount of extractable Phe with time averaged 0.0005 ± 0.0005 h^{-1} (n = 16), while the rate constant for reduction in bioavailability (λ) averaged 0.0057 ± 0.0029 h^{-1} (n = 16). The respective half-lives were 1386 h for chemical extractability and 121.6 h for bioavailability.

Anthracene. the Anth K_s (0.024 ± 0.002, n = 1, error is the standard error from the least-squares fit) was also determined from the general model (eq 3). The accumulation was measured in the presence of BaP. The λ value was 0.009 ± 0.002 h^{-1}, with a corresponding half-life of 77 h (Table II).

Relationships with log K_{ow}. The logs of the K_s values, in this sediment type, were found to be inversely proportional to the corresponding log K_{ow} values [log K_s = 0.589 (±0.21) − 0.479 (±0.039) log K_{ow}, r^2 = 0.90, n = 19] (Figure 4). Estimated bioaccumulation factors (BAF) were calculated from the ratio of K_s/K_d by using previously determined average K_d values (*26*). These calculated BAF values are effectively ratios of the concentration of contaminant in the organism on a wet weight basis divided by the concentration of contaminant in the sediment on a dry weight basis. The calculated BAF may be converted to a dry weight organism basis by dividing the calculated BAF by the dry-to-wet weight ratio for *P. hoyi*, 0.269 (*26*). BAF is functionally equivalent to a bioconcentration factor from water except that in this case the sediment, rather than the water, is the source term. The calculated BAFs exhibited a maximum value for PY with BAF of ~25. The calculated BAFs were lower for PAH of both higher and lower log K_{ow} (Figure 5).

Discussion

The accumulation of compounds by *P. hoyi* from a single sediment is complex and depends on the characteristics of the compound, the amount of aging, and the organism's toxicokinetics. When these complex interactions are sorted out, the physicochemical properties of the compound govern the accumulation of PAHs within a single sediment type. From the relationships with log K_{ow}, the K_s values of compounds with log K_{ow} greater than 7 will be extremely small. The relationship between log K_s and log K_{ow} suggests that the desorption rate of the compound from the sediment is probably important for governing the accumulation by the organism.

The concentrations of background PAH in the sediment were low and similar to the concentrations of the radiolabeled contaminants that had been added (Table I). It was assumed that the radiolabeled chemicals would track their respective native bioavailable chemical. In all clearance calculations, the concentration in the sediment was taken as the concentration of the tracer. The ability of the radiolabel to track the bioavailable pool is supported, in part, by the BaP uptake clearances that were the same whether BaP was added at nearly equivalent concentrations to the native BaP (as a ^{14}C-labeled compound) or in trace amounts (as a ^{3}H-labeled compound) (Table I). An alternative explanation would be the absence of any interaction between the native material and the radiotracer that would result in equivalent clearances for the radiotracer regardless of dosed-sediment concentration. This latter situation seems unlikely since *P. hoyi* in the natural environment have contaminant concentrations proportional to the sediment concentrations they inhabit (*3*, *4*), indicating that some of the natural material is bioavailable.

The assumption that no competition results from the other contaminants in the natural material on the accumulation kinetics of the radiotracer is supported by the apparent absence of interference between compounds when they are added as dual-labeled pairs. This observation is supported especially well by the relatively constant uptake of BaP—whether added as a single compound or as a ^{3}H-labeled material with other ^{14}C-labeled compounds present. This suggests that *trace* contaminants have independent toxicokinetics and implies that the fate of a mixture can be predicted from data derived for single compounds, as long as all the contaminants are in *trace* quantities.

In spite of the low concentrations of contaminant in the overlying water in the static systems, the influence of this potential source on the uptake clearance could have been significant—if the compounds were bioavailable—because the reported uptake clearance from water (*26*) is approximately 5 orders of magnitude greater than the clearances measured for sediments. From the studies under flow-through conditions, where the overlying water was flushed continuously, the uptake clearances were similar for both BaP and Phe compared to static measurements. Thus, the accumulation of sediment-associated contaminant probably resulted from ingestion of labeled particles and/or

exposure to interstitial water.

The complexity of accumulation for sediment-sorbed contaminants is exemplified by the greater uptake clearance for HCB over that of BaP, even though the HCB has the greater log K_{ow} [6.7 for HCB (*29*) vs 6.5 for BaP (*30*)]. The suggestion that such differences in the clearance result from differential desorption rates is supported by differential desorption kinetics in gas-stripping experiments where HCB was much more readily desorbed from humic material compared to BaP (B. J. Eadie, personal communication, Great Lakes Environmental Research Laboratory, NOAA, Ann Arbor, MI).

The peak in the calculated BAFs for PAH is thought to occur because (1) chemicals with a lower log K_{ow} are more readily eliminated and (2) compounds with a higher log K_{ow} are taken up more slowly because they are more strongly sorbed to the sediments. In some cases, uptake has also been reduced because of slower transport of large molecules across membranes (*31*). Membrane transport reduction was not important for the PAH under study because *P. hoyi* uptake clearance from water is directly proportional to log K_{ow} for the PAH (*26*). A similar maximum, at a log K_{ow} of 6, has been reported for oligochaetes exposed to chlorinated hydrocarbons sorbed to lake sediments for both laboratory-dosed and natural sediments (*9, 10*). The same explanation was suggested for the peak in chlorinated hydrocarbon BAFs for oligochaetes (*9, 10*) as stated for the PAHs. The differences in the BAF maximums between PAHs and the chlorinated hydrocarbons with oligochaetes may be due, in part, to the differences in the sediment sorption characteristics suggested by the HCB and BaP data, differences in the exposure scenario of the organisms as the oligochaetes were exposed to sediments that were aged longer, and/or differences in feeding characteristics of the two organisms.

In recent studies of polychlorinated biphenyl congener accumulation by chironamids, the bioaccumulation, defined as "concentration in the organism divided by the concentration in the overlying water", was maximum at a log K_{ow} of about 5.4–5.8—the range of the trichlorobiphenyls (*32*). This work also emphasized the importance of sediment desorption for the accumulation of contaminants by chironamids. As with oligochaetes, comparisons with *P. hoyi* must take into account many differences between exposure scenarios and compound characteristics. However, even within one sediment type, the BAF for sediment-associated compounds is apparently not well described by a simple relationship with log K_{ow}.

The source of contaminant from sediments (Interstitial water vs ingested particles) can be estimated by examining the relationship between feeding rate and the uptake clearance. The gut turnover rate for *P. hoyi* was estimated as 1.46 days^{-1} (0.061 h^{-1}) and the gut volume as 1.62×10^{-4} cm^3 (M. A. Quigley, personal communication, Great Lakes Environmental Research Laboratory, Ann Arbor, MI 48105). If the sediment density is 1.5 g cm^3 and the average mass of *P. hoyi* is 6.0 mg (*26*), the feeding rate would be 0.0025 g of fine-grained sediment g^{-1} of organism h^{-1}. Because the animals feed only on the fine-grained material, which generally contains the bulk of the contaminant, to compare the total sediment mass based K_s values to feeding clearance, the above through-put needs to be corrected for the fraction of fine-grained material in the sediment. The through-put corrected to a total mass sediment basis (K_i) would be 0.012 g of sediment g^{-1} of organism h^{-1}, based on the 21.5% fine grain material by weight. K_i has the same units as the uptake clearances; with both constants based on total sediment mass, the two values can be compared. The clearance due to ingestion can be expressed as follows:

$$K_f = K_i E \tag{5}$$

where K_f is the clearance due to ingestion (g of dry sediment g^{-1} of organism h^{-1}), K_i is defined above, and E is the assimilation efficiency. K_s was greater than K_i for three of the compounds (Table IV). Where K_s is larger than K_i, it is unlikely that ingestion is the sole source of accumulated contaminant, because even with an assimilation efficiency of 100%, K_f would be smaller than K_s. Assimilation efficiencies are probably less than 100%. The assimilation efficiency for sediment-sorbed HCB by oligochaetes was reported to be ~24% (*33*). If this assimilation efficiency is applied to all the compounds investigated, comparison of K_f with K_s indicates that all BaP could come from ingested sediment while a second source, presumably interstitial water, would have to contribute 40–90% of the accumulation for the other compounds (Table IV). Thus, interstitial water is likely an important source for accumulation of most of the sediment-associated chemicals but ingestion can play an important role.

Table IV. Uptake of Contaminants for Ingested Particles Based on a Sediment Through-Put of 0.012 g of Sediment g^{-1} s^{-1}

compd	clearance[a]	% accum by ingestn assim effic	
		100%	24%[b]
benzo[*a*]pyrene	0.0029	100	100
hexachlorobiphenyl	0.0057	100	50
benz[*a*]anthracene	0.005	100	58
pyrene	0.015	80	19
anthracene	0.024	50	12
phenanthrene	0.041	29	7

[a] Unit: g of dry sediment g^{-1} h^{-1}. [b] Assimilation efficiency measured for hexachlorobiphenyl by oligochelates [Klump et al. (*33*)].

The effect of aging of chemicals on sediments was previously reported as "changes in the chemical extractability" (*23, 24*). My observed changes in chemical extractability are generally in good agreement with estimates predicted from the equation presented by Karickhoff and Morris (*24*). Reductions in chemical extractability are slower with increasing log K_{ow}. Thus, for a chemical whose log K_{ow} is similar to that of BaP, the establishment of steady state between all the internal sediment pools may require more than a year.

This decline in chemical availability can be compared to the decline in apparent bioavailability. In several cases, the bioavailability declined as much as an order of magnitude faster than the chemical availability. This aging effect on bioavailability may have been responsible, in part, for the larger variability in Phe clearances, compared to other PAH, due to the failure to recognize the significance and magnitude of the λ value on the preparation of the sediments for exposure. Variable preparation times may promote variability in accumulation. Since at least 3 days is required to prepare such sediments, lengthening the preparation time by even 1 day should reduce bioavailability for contaminants with characteristics similar to Phe. For BaP, HCB, and BAA, no change in biological or chemical availability was observed.

This changing bioavailability is apparently accelerated when organisms are present as exemplified by the sequential exposure experiments. The uptake clearances and the λ values changed more rapidly when organisms were present than from aging alone. These changes may be due,

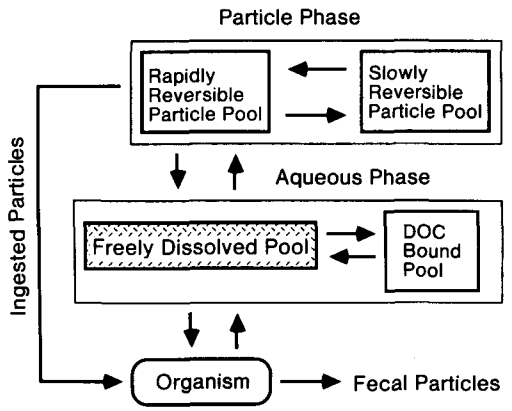

Figure 6. Conceptual model for accumulation of sediment-associated contaminants.

in part, to sediment mixing by *P. hoyi*. In addition, reduction of the amount of ingestable-size particles (through removal and packaging as large fecal pellets) would reduce particle ingestion as a source for the subsequent organisms. The reduction in K_s and increase in λ support the notion that ingestion is important for the accumulation of sediment-associated contaminants—even for Phe. Thus, grain size and composition should be important for contaminant accumulation from sediments. Further work is required to sort out the mechanisms for the accumulation from sediments and verify the conceptual model described below.

Sediment-associated contaminants can be conceptualized as accumulation from two sources: interstitial water and ingested particles (Figure 6). The accumulation is balanced by elimination both as aqueous material and—when feeding is occurring—as fecal pellets. In *P. hoyi*, there is little or no biotransformation capability (*15, 19*), so the elimination is presumed to be parent chemical. The freely dissolved pool (Figure 6) presumably contains the biologically available chemical in the aqueous phase. Chemicals move in the direction of thermodynamic gradients, creating steady-state distributions between the particle and aqueous pools, between the readily reversible and slowly exchangable particle pools (*23, 24*), and between the freely dissolved pool and the dissolved organic matter in the interstitial water (*18, 20, 22*). The freely dissolved pool is assumed to be of limited size; thus, its contaminant concentration must be maintained through desorption from the particles and DOC and through diffusion from adjoining interstitial water as compound is accumulated by the organisms. The rapidly reversible chemical fraction of the total particle pool presumably contributes the bioavailable material taken up by *P. hoyi* during particle ingestion. The bioavailabiltiy of material associated with DOC has been shown to be reduced (*18, 20*) and the slowly reversible particle pool is assumed to be biologically unavailable. Therefore, if the freely dissolved pool size is limited, the flux into the organism will be controlled by desorption rates from the particles and DOC and by ingestion rates.

The conceptual model provides a *qualitative* explanation of the observed results assuming that the freely dissolved pool is of limited size. The limited pool size assumption is defensible, in part, by the slow uptake clearance, compared to the clearance from water, and by the reduction in accumulation with increased log K_{ow}. Uptake clearances for PAHs from water are in the range from 100 to 200 mL g^{-1} h^{-1} (*26*). If the interstitial water is in instantaneous equilibrium with the particles, K_s values should be much larger and should increase with increasing log K_{ow}, as with uptake from water (*26*). Rapid depletion of the freely dissolved pool will result in a thermodynamic gradient and the contaminant will move from the storage pools on particles and DOC to the freely dissolved pool. Freely dissolved material from adjoining areas will also diffuse with the thermodynamic gradient.

Apparently, the overall uptake clearance depends on (1) the rate of contaminant transfer to the interstitial water freely dissolved pool, (2) the uptake clearance from water, which is large compared to sediment clearances, (3) the rate of ingestion of particles, and (4) the associated assimilation efficiency.

This apparent dependence on desorption rates to explain the different uptake clearances is supported by the relative clearance of BaP and HCB and is based on our understanding of the desorption from humic materials (described above). The balance between the importance of ingested compound and accumulation from interstitial water is also supported from the conceptual model and from the dependence on the desorption process to regulate uptake. When the desorption rate from particles and humics is rapid compared to the ingestion rate, uptake from interstitial water should prevail—as with Phe; when the desorption rate is slow compared to the ingestion rate then ingestion should become more competitive—as for BaP. The conceptual model also accounts for the effect of aging through the removal of material to a particle pool with very slow equilibrium kinetics, as suggested by the λ value, reducing the bioavailability for the total particle pool.

Summary

The conceptual model permits a qualitative description of some very complex data and can be used as a basis for experiment design. The rate of contaminant accumulation from a single sediment is inversely proportional to the log K_{ow}. However, compounds with higher water solubility (lower log K_{ow}) become biologically unavailable more rapidly. The relationship between the bioavailable and the chemically available materials requires further examination. The amounts of contaminants that are bioavailable and chemically available are subsets of the total contaminant in the sediment and are not necessarily the same subsets. Further, the age of sediments ingested by different benthic organisms may be quite different; for instance, oligochaetes ingest sediment several centimeters below the surface while *P. hoyi* feed at the surface. Thus, the amount of bioavailable compound may well be different for the different organisms, even with equal chemically extractable concentrations. Further studies are required to define the role of differences in sediment composition and grain size on the accumulation from sediment.

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Registry No. BaP, 50-32-8; HCB, 26601-64-9; BAA, 56-55-3; Py, 129-00-0; Anth, 120-12-7; Phe, 85-01-8; fluoranthene, 206-44-0; chrysene, 218-01-9; benzo[*e*]pyrene, 192-97-2.

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