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Biodynamic Modeling of PCB Uptake by *Macoma balthica* and *Corbicula fluminea* from Sediment Amended with Activated Carbon

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Activated carbon amendment was assessed in the laboratory as a remediation strategy for freshwater sediment contaminated with polychlorinated biphenyls (PCBs) from the Grasse River (near Massena, NY). Three end points were evaluated: aqueous equilibrium PCB concentration, uptake into semipermeable membrane devices (SPMDs), and 28-day bioaccumulation in the clam *Corbicula fluminea*. PCB uptake by water, SPMDs, and clams followed similar trends, with reductions increasing as a function of carbon dose. Average percent reductions in clam tissue PCBs were 67, 86, and 95% for activated carbon doses of 0.7, 1.3, and 2.5% dry wt, respectively. A biodynamic model that incorporates sediment geochemistry and dietary and aqueous uptake routes was found to agree well with observed uptake by *C. fluminea* in our laboratory test systems. Results from this study were compared to 28-day bioaccumulation experiments involving PCB-contaminated sediment from Hunters Point Naval Shipyard (San Francisco Bay, CA) and the clam *Macoma balthica*. Due to differences in feeding strategy, *M. balthica* deposit-feeds whereas *C. fluminea* filter-feeds, the relative importance of the aqueous uptake route is predicted to be much higher for *C. fluminea* than for *M. balthica*. Whereas *M. balthica* takes up approximately 90% of its body burden through sediment ingestion, *C. fluminea* only accumulates approximately 45% via this route. In both cases, results strongly suggest that it is the mass transfer of PCBs from native sediment to added carbon particles, not merely reductions in aqueous PCB concentrations, that effectively reduces PCB bioavailability and uptake by sediment-dwelling organisms.

Introduction

In recent years, concern over the limited effectiveness of dredging has led to interest in the development of nonconventional, in situ contaminant remediation strategies (*1*). For example, contaminant sequestration via activated carbon amendment has been proposed as an alternative or add-on to dredging at sites contaminated with polychlorinated biphenyls (PCBs). In prior work, the addition of activated carbon to PCB-contaminated sediment from Hunters Point Naval Shipyard (San Francisco Bay, CA) was shown to significantly reduce aqueous equilibrium PCB concentration, uptake into semipermeable membrane devices (SPMDs), quiescent flux, and bioaccumulation by three different benthic organisms (the amphipod *Leptocheirus plumulosus*, polychaete *Neanthes arenacaeodentata*, and clam *Macoma balthica*) in laboratory tests under well-mixed carbon-sediment conditions (*2*–*5*). A pilot field deployment is currently underway (*6*). Werner et al. (*7*) found that similar, small doses of activated carbon effectively sequestered PCBs in sediment from Lake Hartwell, SC, as measured by aqueous equilibrium PCB concentrations in the laboratory.

While the efficacy of activated carbon amendment continues to be documented, less is known regarding the mechanisms by which this remediation strategy reduces body burdens in benthic organisms. Biodynamic modeling may provide scientists and engineers with a useful tool to better understand PCB uptake dynamics and therefore better inform risk assessment and treatment decisions at contaminated sites. Standard assessments rely on 28- or 56-day bioaccumulation tests, biota−sediment accumulation factors (BSAFs), and equilibrium partitioning models. Bioaccumulation tests provide empirical data, whereas BSAFs and equilibrium partitioning models allow gross risk calculations based on measured sediment PCB concentrations. Unlike these traditional methods, biodynamic modeling affords an understanding of the relative importance of uptake routes and depuration governing organism accumulation of contaminants.

This research is focused on evaluating and modeling the biodynamics of PCB uptake by clams in field-contaminated sediment. As a case study, we investigate the potential application of activated carbon amendment in PCB-contaminated Grasse River sediment through laboratory tests measuring reduction in aqueous equilibrium PCB concentration, uptake into SPMDs, and bioaccumulation by a freshwater clam, *Corbicula fluminea*. We then compare the bioaccumulation test results for Hunters Point (*5*) and Grasse River sediment, and use a biodynamic model to explore the geochemical and biological factors that impact PCB uptake by *M. balthica* and *C. fluminea* from the two PCB-contaminated field sediments. Our goals are to (1) establish biodynamic modeling as a tool to understand PCB biouptake from contaminated sediments, (2) explore the influences of sediment- and species-specific properties on PCB bioavailability, and (3) gain insight into the mechanisms by which activated carbon amendment reduces PCB bioavailability to these clams.

Materials and Methods

Sediment Characterization. The Grasse River (near Massena, NY) has elevated levels of PCBs that were derived mainly from the Alcoa Massena plant. Stakeholders are interested in new, innovative remediation techniques including activated carbon amendment (*8*). Surficial sediment from the lower Grasse River was obtained from Alcoa. Sediment was composited and homogenized by mixing with a shovel, and stored at 4 °C prior to use. PCB content was measured following procedures described by Ghosh et al. (*9*). The Grasse River sediment used in these tests contained 6.49 ± 0.16 ppm total PCBs (dry weight basis). Sediment total organic carbon (TOC) was measured by Huffman Laboratories (Golden, CO) by combustion of acidified samples as 5.1%.

Physicochemical Tests. Aqueous equilibrium PCB concentrations and PCB uptake into semipermeable membrane

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devices (SPMDs) for Grasse River sediment were measured following procedures in Zimmerman et al. (*2*). Sediment−carbon contact was for one month with TOG 50 × 200 carbon (Calgon Corporation, Pittsburgh, PA). Results of physicochemical tests with Hunters Point sediment are reported elsewhere (*2, 3*). Briefly, aqueous equilibrium PCB concentrations were obtained via liquid–liquid extraction with hexane following the one month sediment-carbon contact and additional two week equilibration with overlying water. To obtain PCB concentrations in SPMDs, the SPMDs were dialyzed with hexane, following procedures in Zimmerman et al. (*3*).

Bioaccumulation Experiment Setup. Sediment−sorbent contact and bioaccumulation tests were performed following previously described procedures (*5*). Approximately 1.0 kg wet sediment was added to 1 L amber glass bottles with 100 mL of deionized water and the desired carbon dose. The activated carbon doses investigated in this study were 0.7, 1.3, and 2.5% (dry wt). Bottles were rolled at 2–3 rpm for 30 d, and further shaken by hand once weekly for 30–60 s during these 30 d.

Since *C. fluminea*, unlike *M. balthica*, reside near the sediment−water interface and prefer rocky/sandy environments, a thinner layer of sediment was used. To achieve overlying water conditions similar to those in our bioaccumulation tests with Hunters Point sediment and *M. balthica* (*5*) and provide *C. fluminea* with a rocky substrate, aquarium gravel (Wonder Rock, Novalek Inc., Hayward, CA) was added to 23 cm diameter glass jars to a depth of approximately 10 cm. Synthetic freshwater was added to fill the pore spaces. Following the 30-d sediment−sorbent contact period, contacted sediment was placed atop the aquarium gravel. The depth of the resulting sediment layer was approximately 2.5 cm. The jars were placed in separate 38 L glass aquaria in a 13 °C temperature-controlled room. Approximately 1 L of synthetic freshwater was added to the jars as overlying water. Sediment was allowed to settle for 2–3 days prior to clam addition, with the overlying water replaced daily. Several hours before clam addition, approximately 20 L of synthetic freshwater was added to the aquaria. The aquaria were aerated with glass pipets attached to plastic tubing.

28-Day Clam Exposure. Clams (*Corbicula fluminea*) were collected by hand from the Guadalupe River, San Jose, CA. *C. fluminea* were transported to the laboratory in Guadalupe River water, then transferred to prechilled synthetic freshwater and acclimated to laboratory conditions in a 13 °C room for 2–3 d. Twenty *C. fluminea* were measured for background PCB analyses. Twenty live *C. fluminea* were placed atop the sediment in each jar and exposed for 28 days. Clams were fed 5–7 times weekly with 25 mL of *Cryptomonas ozolini* (Marine Sciences Research Center, SUNY Stony Brook, NY). Once weekly, at least 16 L of water was replaced with fresh synthetic freshwater. Due to the hydrophobicity of PCBs, this water replacement is not expected to have a dilution effect on PCBs in the system. On the 28th day of exposure, clams were retrieved by hand, and rinsed with deionized water to remove sediment particles. The groups of exposed *C. fluminea* were each placed in approximately 500 mL of synthetic freshwater to depurate for 2–3 d. Calculations suggest the clams could lose 10–15% of their PCB burden during this period. Water was continuously aerated and replaced daily. At the end of the depuration period, clams were blotted dry with paper towels and frozen in Ziploc bags at −20 °C.

Dissection and Tissue Preparation. Partially thawed *C. fluminea* were dissected in groups of three to four. Shells were discarded and soft tissues combined in 20 mL glass vials. Vials were frozen at −80 °C. Frozen tissues were Freeze-dried (VirTis Freezemobile 12ES, Gardiner, NY), then crushed with mortar and pestle immediately prior to PCB extraction. Tissue extraction and cleanup were performed following procedures reported in McLeod et al. (*5*). Briefly, sonication with dichloromethane was used to extract PCBs. Extracts were cleaned up using sulfuric acid and potassium permanganate, then passed through a column with 3% deactivated silica gel, 1% deactivated alumina, and sodium sulfate in 50:50 dichloromethane:pentane. The concentrated eluate was solvent-exchanged to hexane prior to analysis.

PCB Analyses. Analytical procedures are described in Ghosh et al. (*9*). Briefly, congener-specific PCB analyses were performed using an Agilent model 6890 gas chromatograph with electron-capture detector, following a modified EPA method 8082. A calibration curve prepared with standards from the Lake Michigan mass balance study (*10*) was used for peak identification. Two internal standards (2,4,6-trichlorobiphenyl and 2,2′,3,4,4′,5,6,6′-octachlorobiphenyl) were used for quantitation. PCB concentrations measured in unexposed clams were treated as background levels and subtracted from exposed clam results. Recoveries from spiked clam tissue averaged 80–95% across homologues. All results are reported as total PCBs unless otherwise stated.

Results and Discussion

Physicochemical Tests. Total PCB concentrations in porewater, SPMDs, and clams versus carbon dose in Grasse River sediment are shown in Figure 1. The general trend of decreasing concentration with carbon dose observed in physicochemical tests with Grasse River sediment are similar to those reported for Hunters Point (*2, 3*) and Lake Hartwell (*7*). As shown in Figure 1A−B, a highly pronounced dose–effect is observed for Grasse River amended with activated carbon. The aqueous equilibrium PCB concentration for untreated Grasse River sediment was 1.03 ± 0.08 μg/L. Average percent reductions in aqueous equilibrium PCB concentration were 82, 94, and 97% for carbon doses of 0.7, 1.3, and 2.5 dry wt, respectively. PCB uptake into SPMDs from the untreated Grasse River sediment was 476 ± 61 μg/g. Average percent reductions in SPMD uptake were 54, 83, and 92% for carbon doses of 0.7, 1.3, and 2.5% dry wt, respectively. Consistent with results from previous studies (*2, 3, 7*), treatment efficacy was higher for lower-chlorinated congeners. SPMD data are provided as another line of evidence for treatment efficacy, and were not used in subsequent modeling efforts.

Bioaccumulation Test. As shown in Figure 1C, the trend of decreasing PCB concentration in clam tissues was similar to what was observed in the companion physicochemical tests. The PCB concentration measured in unexposed *C. fluminea* was 0.127 ± 0.033 μg/g dry wt, which was treated as background and subtracted from exposed clam data. Background-corrected PCB levels in clams exposed to untreated Grasse River were 1.07 ± 0.25 μg/g. Average percent reductions in clam tissue PCBs were 67, 86, and 95% for carbon doses of 0.7, 1.3, and 2.5% dry wt, respectively. Consistent with tests using *M. balthica* and Hunters Point sediment, reductions in bioavailability increased with increasing carbon dose (*5*). Results are presented on a dry weight basis to be consistent with biodynamic modeling parameters.

Reductions in bioavailability are negatively correlated with PCB homologue hydrophobicity, as seen in Figure 2 and observed in previous physicochemical and biological tests with Hunters Point and Lake Hartwell sediment (*2–5, 7*). Similar patterns were seen for aqueous equilibrium and uptake into SPMDs in this study (data not shown). All our results to date strongly suggest that the lower-chlorinated PCBs exhibit faster mass transfer kinetics to the added carbon particles. Desorption tests performed by Zimmerman et al. (*2*) and Werner et al. (*7*) provide evidence for the time-dependent interaction between desorption resistance and activated carbon uptake of the more hydrophobic congeners.

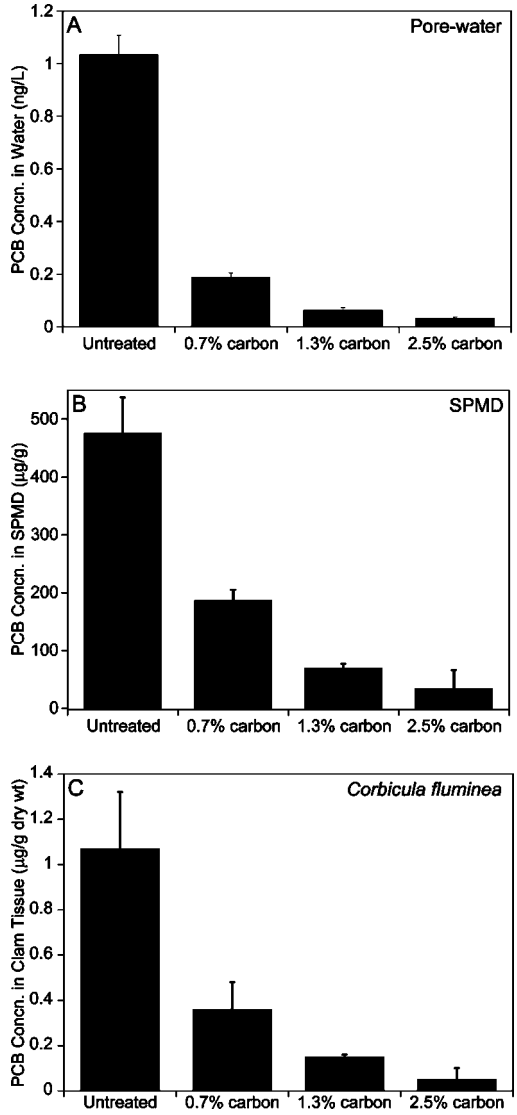

FIGURE 1. PCB concentrations in pore-water (A), SPMDs (B), and clams (C) in untreated and amended Grasse River sediment. Error bars represent one standard deviation (n = 3–5).

Inspection of our congener-specific data shows similar trends as well. Supporting Information (SI) Figure 1 depicts congener-specific PCB concentrations in sediment and clams (untreated and 2.5% carbon dose) for the 17 congeners with average sediment concentrations exceeding 100 ppb. SI Figure 2 is a similar plot for the six dioxin-like congeners or coeluting groups containing a dioxin-like congener measured in these studies.

PCBs in Grasse River sediment are dominated by the di- through tetra-chlorinated biphenyls, whereas Hunters Point PCBs consist predominantly of hexa-and hepta-chlorinated biphenyls. Figure 3 depicts this difference in homologue profile between Hunters Point and Grasse River sediment. As previously stated, the mass transfer of lower-chlorinated PCBs to added carbon particles is thought to be faster than that of higher-chlorinated congeners. Based on this sediment characteristic alone, it would seem a priori that PCB sequestration via activated carbon addition in Grasse River sediment is highly attractive. Our biological and physico-chemical tests confirm this.

Twelve out of 80 clams died during the exposure period. The highest mortality rate (25%) was observed in the treatment with the highest carbon dose. The untreated and 1.3% carbon dose showed 15% mortality; mortality was lowest

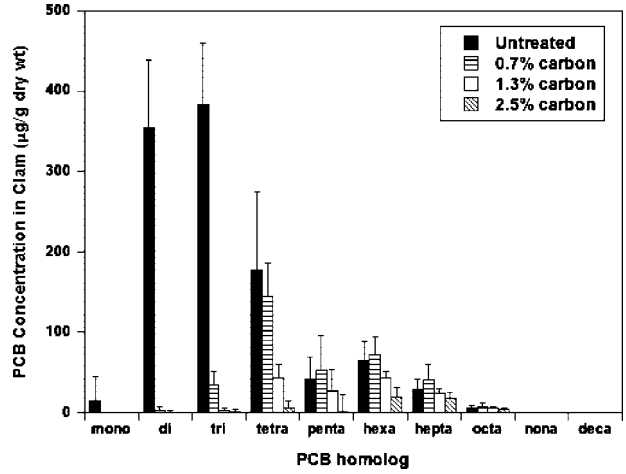

FIGURE 2. PCB homologue distribution in *C. fluminea* exposed to untreated and carbon-amended Grasse River sediment. Error bars represent one standard deviation (n = 3–5 samples with 3–4 clams per sample).

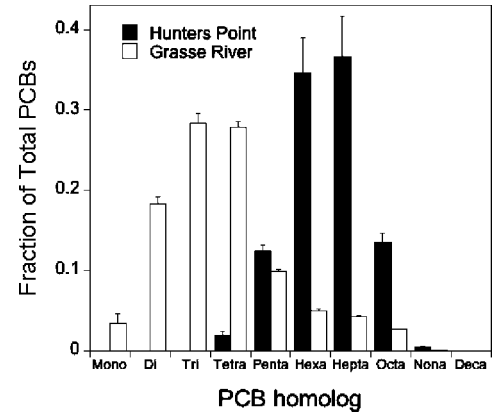

FIGURE 3. Homologue profiles of Hunters Point and Grasse River sediment. Error bars represent normalized standard deviation (n = 3).

(5%) for the 0.7% carbon treatment. Unlike in experiments with Hunters Point and *M. balthica* (*5*), there was a statistically significant difference (One-way ANOVA, $F = 3.1$, $p = 0.043$) in condition index, defined as wet wt divided by shell length, for *C. fluminea* exposed to treated versus untreated Grasse River sediment. As shown in Figure 4, the lowest condition index was observed in clams exposed to sediment treated with 2.5% carbon. However, it should be noted that the condition index of unexposed (background) *C. fluminea* was lower than those exposed to untreated Grasse River sediment. Other studies have conflicting conclusions from laboratory tests regarding the effects of carbon amendment on organism health. Jonker et al. (*11*) observed reduced lipid content in oligochaetes exposed to soot-amended sediment. Millward et al. (*4*) noted reduced growth rate in *N. arenaceodentata* but not in *L. plumulosus*, no reproductive effects for *L. plumulosus* (not tested for *N. arenaceodentata*), and no effects on lipid content in either organism when exposed to Hunters Point sediment amended with activated carbon. Taken together, all of these results suggest more study is warranted on the biological effects of activated carbon on benthic organisms.

Biodynamic Modeling. Although total sediment PCB concentrations are similar between Hunters Point and Grasse River sediment, body burdens of PCBs varied greatly between clams exposed to sediment from the two sites. *M. balthica* accumulated 4−6 times the amount of PCBs accumulated by *C. fluminea*. We hypothesize that this difference is due to

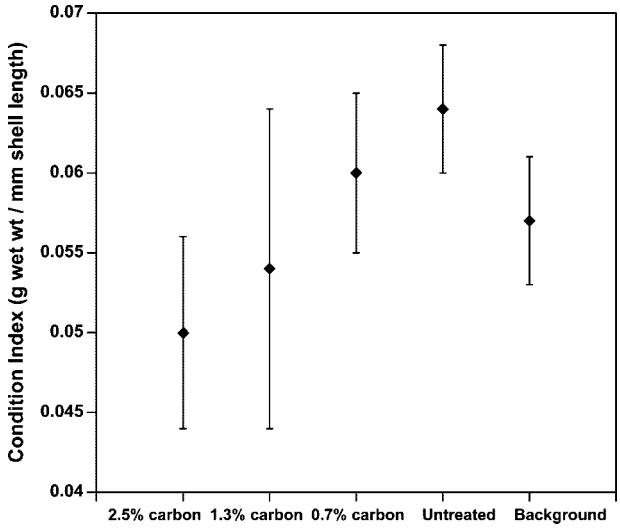

FIGURE 4. Condition index for *C. fluminea* in Grasse River bioaccumulation tests. Error bars represent one standard deviation (n = 3–5 samples with 3–4 clams per sample).

(1) geochemical differences in the two sediments and (2) different feeding strategies of the two clams. To investigate this hypothesis, we used a biodynamic model described in McLeod et al. (*5*) to interpret the bioaccumulation results in our test systems. This model incorporates sediment geochemistry and biological traits, and allows us to discern the relative importance of dietary and uptake routes of PCBs to the clams.

PCB accumulation in the clams was described using the following model formulation:

$$\frac{dC_{clam}}{dt} = FR \times AE_{aq} \times C_{aq} + IR \times AE_{sed} \times C_{sed} - k_e \times C_{clam} \quad (1)$$

where C_{clam} is the PCB concentration in clam tissue (μg/g dry wt), FR is the water filtration rate (L water/g dry wt/d), AE_{aq} is the PCB absorption efficiency from water, C_{aq} is the aqueous PCB concentration (μg/L), IR is the sediment particle ingestion rate (g sediment/g dry wt/d), AE_{sed} is the PCB absorption efficiency from sediment, C_{sed} is the sediment PCB concentration (μg/g dry wt), and k_e is the proportional rate constant of PCB loss (d^{-1}). Growth is assumed to be negligible (0.0029/d based on clam weight results) over the timecourse of these experiments, and is not included in eq 1.

Integrating eq 1 yields

$$C_{clam,t} = \frac{FR \times AE_{aq} \times C_{aq} + IR \times AE_{sed} \times C_{sed}}{k_e}(1 - e^{-k_e t}) \quad (2)$$

which was solved for 28 d using the parameters reported in Table 1 to predict PCB concentrations in *M. balthica* and *C. fluminea*. The choice of parameter values for *M. balthica* is discussed elsewhere (*5*). Here we will discuss the parameter values chosen for *C. fluminea* and comment on the differences between the two clam species. In this exercise, we focus on understanding total PCBs because reliable congener-specific values for modeling parameters are not available.

The filtration rate (FR) for *C. fluminea* was estimated from data in Foe and Knight (*12*) and a temperature regression (*13*). The filtration rate of *C. fluminea* is approximately 20 times higher than that of *M. balthica*. This difference is due to the different feeding strategies of the two organisms. Whereas *M. balthica* is a facultative deposit-feeder, *C. fluminea* predominantly filter-feeds and is equipped to process large throughputs of water at a high rate.

The aqueous absorption efficiency (AE_{aq}) for *C. fluminea* was estimated from absorption efficiencies reported by Bjork and Gilek (*14*) for PCBs in the mussel *Mytilus edulis*. Our choices were motivated by the homologue distributions in Grasse River and Hunters Point sediment. Bjork and Gilek (*14*) report aqueous absorption efficiencies for a tri and tetra-chlorinated biphenyl in the range of 0.1–0.4. A median value of 0.2 was chosen to use in our modeling efforts with Grasse River and *C. fluminea*. This value is lower than that of 0.5 used for *M. balthica* in our systems, which was chosen based on the observed AE_{aq} range of 0.3–0.6 for a hexa-chlorinated biphenyl (*14*).

For modeling efforts with *M. balthica* and Hunters Point sediment, we used aqueous equilibrium PCB concentrations for C_{aq}. Aqueous equilibrium PCB concentration is indicative of pore-water concentration, and *M. balthica* is exposed to large volumes of pore water during surface deposit-feeding (*15, 16*). In contrast, *C. fluminea* is exposed mainly to overlying surface water as it filter-feeds. Therefore, for use in the model, we estimated the overlying surface water PCB concentration in our experimental aquaria. PCBs are introduced to the surface water via flux from sediment and efflux from clams, and removed via aqueous uptake into the clams. Because of the high filtration rate of *C. fluminea*, the clams were turning over the water in our aquaria six or seven times per day. Overlying water PCB concentration was estimated to be 0.0035 μg/L based on flux calculations presented in the Supporting Information and data in ref *17*. Based on these low aqueous PCB concentrations and high filtration rates, we did not consider uptake from algae as a separate route.

The particle ingestion rate (IR) used for *C. fluminea* was derived from a determined phytoplankton clearance rate for *C. fluminea* at 17 °C (*18*). The particle ingestion rate for *C. fluminea* is 1 order of magnitude lower than that for *M. balthica* (*19*), which is related to the organisms' feeding strategies. Since *M. balthica* regularly ingest sediment particles that have a high nonnutritious component, they must ingest particles at a higher rate to obtain sufficient food. We suspect that the *C. fluminea* in our test systems ingested sediment primarily through pedal feeding since the quiescent conditions in our aquaria resulted in imperceptible sediment resuspension. Pedal feeding is a form of deposit feeding in which clams collect sediment particles using cilia on their foot, and has been observed for adult *C. fluminea* (*20, 21*). Nichols et al. (*20*) found that algae ingested through siphon and nonsiphon areas were transferred and processed equally inside the clams they studied. Therefore, physiological parameters such as AE_{sed} and k_e should not be affected by actual particle ingestion route (i.e., pedal feeding versus particle entrainment during filtration).

The absorption efficiency from sediment (AE_{sed}) was calculated as for *M. balthica* in (*5*). Briefly, a value of 0.2 was taken for untreated Grasse River sediment. This value was calculated for the absorption efficiency of PCB-52 from untreated Hunters Point sediment in *M. balthica*. A similar calculation could not be performed for *C. fluminea* because sediment ingestion is not the primary route of PCB uptake for these filter-feeding organisms. Therefore, the absorption efficiency was set to the same value (0.2) as a first approximation in the absence of other appropriate data. Since PCB absorption efficiency in clams will be different for native sediment particles versus activated carbon, a modified AE_{sed} was calculated for amended sediment. To assess the fractions of PCBs on activated carbon particles or native sediment, we consider the reductions in aqueous equilibrium as indicative of the proportional mass of PCBs transferred from native sediment to added activated carbon particles. A modified AE_{sed} was then calculated as a weighted average of the nonamended AE_{sed} and the AE for PCB-52 on activated carbon measured by McLeod et al. (1.44% (*22*)).

TABLE 1. Values of Biodynamic Model Parameters Used to Describe PCB Accumulation in *Macoma* and *Corbicula*

parameter	symbol	unit	value *Macoma*	value *Corbicula*
filtration rate	FR	L water/g dry/d	2[a]	45[g]
aqueous absorption efficiency[b]	AE_{aq}	%	50	20
aqueous concentration	C_{aq}	μg/L	0.037[c] (I) 0.052[c] (II) 0.0375[c] (III)	0.0035
ingestion rate	IR	g sediment/ g dry/d	0.25[a]	0.03[h]
sediment absorption efficiency[d]	AE_{sed}	%	20	20
sediment concentration	C_{sed}	μg/g	7.0[e] (I) 6.5[e] (II) 3.0 (III)	6.5
rate constant of loss[f]	k_e	d^{-1}	0.05	0.04

[a] From ref *19*. [b] Estimated from ref *25*. [c] Aqueous equilibrium concentrations reported in *refs 2, and 3*. [d] Calculated using experimental results for PCB-52 (*5*). [e] J. R. Zimmerman, unpublished results. [f] Estimated from ref *23*. [g] Estimated from *refs 12, 13*. [h] From ref *18*.

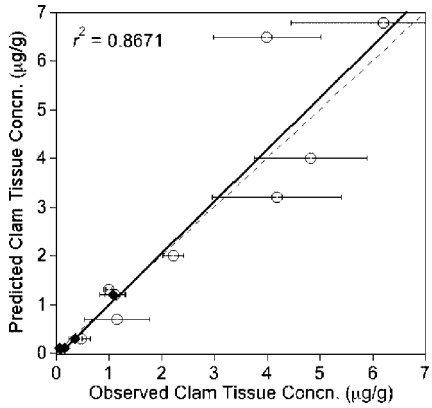

FIGURE 5. Clam PCB concentrations predicted by eq 2 vs those observed in 28-day bioaccumulation experiments. Closed symbols represent *Corbicula* and Grasse River sediment; open symbols represent *Macoma* and Hunters Point sediment (*5*). Error bars represent one standard deviation.

The proportional rate constant of loss of PCBs from the clams (k_e) was estimated from those obtained by Boese et al. (*23*) for lower-chlorinated PCBs in the bent-nose clam, *Macoma nasuta*. The rate chosen for *C. fluminea*, 0.04 d^{-1}, is only slightly lower than that used for *M. balthica* in our modeling efforts (0.05 d^{-1}), which was based on higher-chlorinated PCBs from the same study (*23*). It is likely that k_e is similar among the clam species, as Reinfelder et al. (*24*) observed that efflux rates were relatively constant for a suite of trace metals among several different bivalves.

Considering the data sets for *M. balthica* and *C. fluminea* in our test systems together, Figure 5 depicts the almost 1:1 correlation between modeled and observed total PCB concentrations in clam tissues. The linear trendline has a slope of 1.06 ($r^2 = 0.87$). Plotted separately (SI Figure 3), the *C. fluminea* data linear trendline has a slope of 1.12 ($r^2 = 0.98$). This result suggests that the model is successfully capturing the major processes affecting bioaccumulation in our experiments.

The model can also be used to investigate the relative importance of dietary and aqueous uptake routes for PCB accumulation by the two species. As shown in Figure 6, the relative contributions of these two uptake routes to PCB body burden differ markedly between *M. balthica* and *C. fluminea* in our test systems with untreated sediment. For *C. fluminea*, aqueous uptake is almost equally important to dietary uptake. However, *M. balthica* appear to take up approximately 90% of their PCB body burden through sediment ingestion. Similar patterns are seen when modeling uptake from treated sediment (not shown). These findings strongly suggest that PCB reductions in the aqueous phase alone are not sufficient to effectively reduce PCB uptake by sediment-dwelling organisms.

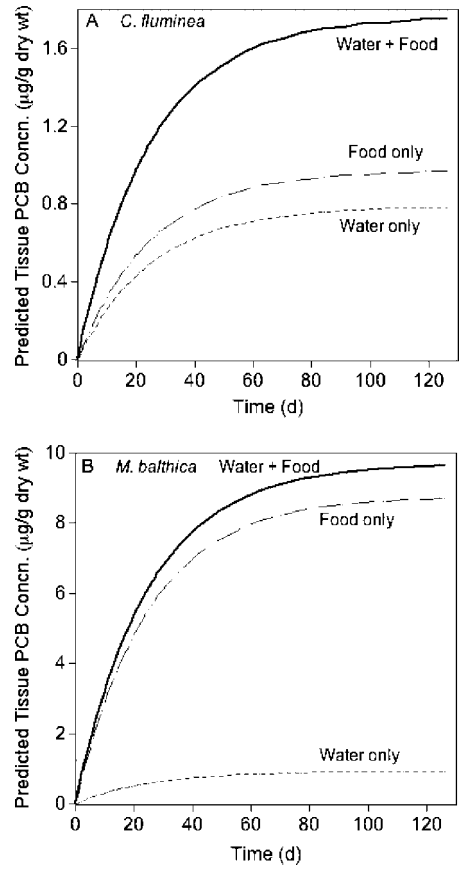

FIGURE 6. Relative contributions of PCB uptake via food and water for *Corbicula* in untreated Grasse River sediment (A) and *Macoma* in untreated Hunters Point sediment (B), as predicted by eq 2.

Additionally, these findings have implications for the choice of monitoring species for sediment quality assessment. As demonstrated in Figure 6, deposit-feeders such as *M. balthica* may be more reflective of the local sediment environment than filter feeders such as *C. fluminea*. Especially in a flow-through riverine system, organisms like *Corbicula* will integrate more regional sediment and water quality through their filtering of water that originated upstream of the test site. Therefore, if the goal of a monitoring study is to assess local sediment conditions in open systems, we strongly recommend using sediment-ingesting benthic organisms.

Sensitivity Analysis. To test the sensitivity of the biodynamic model to variability in input parameters, estimated 28-d clam bioaccumulation in untreated Hunters Point and Grasse River sediment was calculated for reasonable ranges of filtration rate (FR), AE_{aq}, ingestion rate (IR), AE_{sed}, and rate constant of loss (k_e) (Table 2). Biologically relevant ranges

TABLE 2. Model Sensitivity to Biodynamic Parameters Used to Describe PCB accumulation in *Macoma* and *Corbicula*

	Macoma balthica, Hunters Point				*Corbicula fluminea*, Grasse River			
	parameter range		$C_{clam,28}$ (μg/g)		parameter range		$C_{clam,28}$ (μg/g)	
parameter	low	high	w/low	w/high	low	high	w/low	w/high
FR (L/g/d)	1.0[a]	2.5[a]	5.7	6.3	10[b]	100[c]	0.8	1.7
AE_{aq}	0.3[d]	0.6[d]	5.8	6.2	0.1[d]	0.4[d]	0.9	1.7
IR (g/g/d)	0.1[a]	1.0[a]	2.9	21.9	0.024[e]	0.033[e]	1.0	1.2
AE_{sed}	0.1[f]	0.5[f]	3.4	14.0	0.1[f]	0.5[f]	0.8	2.1
k_e (d^{-1})	0.02[g]	0.09[g]	8.6	4.1	0.02[g]	0.09[g]	1.4	0.7

[a] From ref *19*. [b] Estimated from ref *26*. [c] Estimated from ref *12*. [d] Range reported in ref *14* for *Mytilus edulis*. [e] 95% confidence intervals reported in (*18*). [f] Approximate range measured in ref *22* for PCB-52 in *Macoma balthica*. [g] Approximate range measured in ref *23* for PCBs in *Macoma nasuta*.

for input parameters were estimated from the literature. When testing the sensitivity of a given parameter, all other parameters were held constant at the values reported in Table 1. For comparison, the predicted 28-d clam body burdens for *M. balthica* in Hunters Point (Test II in ref (*5*)) and *C. fluminea* in Grasse River using Table 1 parameter values were 6.1 μg/g dry and 1.2 μg/g dry, respectively.

Given the existing distribution of PCBs between the aqueous and sediment compartments, parameters affecting uptake from ingested sediment, IR and AE_{sed}, are the most sensitive over the input ranges tested. This suggests that for hydrophobic contaminants such as PCBs, reliable measurements of ingestion rate and AE_{sed} are essential for bioaccumulation modeling efforts.

It is also instructive to construct hypothetical scenarios to inform our understanding of model sensitivity. For example, if *M. balthica* exposed to untreated Hunters Point sediment stopped ingesting sediment, their uptake rate from the aqueous phase (FR $\times$ AE_{aq}) would need to increase by a factor of 7.5 for the clams to achieve a body burden of 6.1 μg/g dry wt after 28 d. This would be virtually impossible within biologically relevant constraints. In contrast, it might be biologically plausible for *C. fluminea* to stop ingesting sediment and achieve body burdens similar to those measured in our experiments. *C. fluminea* exposed to untreated Grasse River sediment could stop sediment ingestion and still achieve PCB clam concentrations of 1.2 μg/g dry wt with a 2-fold increase in uptake rate from the aqueous phase. Such an increase is possible within documented ranges of FR and AE_{aq} for this species.

Implications. This work demonstrates that activated carbon amendment can reduce the bioavailability of PCBs from Grasse River sediment to the freshwater clam *Corbicula fluminea* in short-term laboratory tests. A companion study (*5*) shows similar results for Hunters Point sediment and the brackish-water clam *Macoma balthica*. Considered together, these studies support the potential for activated carbon amendment as a sediment remediation strategy in both freshwater and marine systems. As described in Zimmerman et al. (*2*), further work addressing the application of activated carbon in the field and site-specific consideration are required. Such studies are already underway (*6, 8*).

The biodynamic model presented herein offers promise as a predictive tool for engineers and practitioners. As long as species-specific input parameters can be obtained or measured, sediment-specific parameters may be estimated and adjusted to describe potential bioavailability at a prospective treatment site. Measures of aqueous equilibrium PCB concentrations can be used to estimate the proportional mass transfer of PCBs from native sediment particles to the added carbon. Use of sediment-ingesting benthic organisms in model calculations will provide the best indicator of local bioavailability. More research on modeling parameters is necessary to achieve comprehensive, congener-specific predictive capability.

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Supporting Information Available

Additional details relating to congener-specific PCB concentrations in sediment and clams, concentrations of dioxin-like congeners in sediment and clams, predicted and observed PCB concentrations in *C. fluminea* alone, and discussion of flux calculations to determine aqueous PCB concentration in overlying water. This material is available via the Internet at http://pubs.acs.org.

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