

BIOLOGICAL UPTAKE OF POLYCHLORINATED BIPHENYLS BY *MACOMA BALTHICA* FROM SEDIMENT AMENDED WITH ACTIVATED CARBONPAMELA B. MCLEOD,[†] MARTINE J. VAN DEN HEUVEL-GREVE,[‡] SAMUEL N. LUOMA,[§] and RICHARD G. LUTHY*[†][†]Department of Civil and Environmental Engineering, Stanford University, Stanford, California 94305, USA[‡]National Institute for Coastal and Marine Management, RIKZ, NL-4330 Middelburg, The Netherlands[§]U.S. Geological Survey, Menlo Park, California 94025

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Abstract—This work characterizes the efficacy of activated carbon amendment in reducing polychlorinated biphenyl (PCB) bioavailability to clams (*Macoma balthica*) from field-contaminated sediment (Hunters Point Naval Shipyard, San Francisco Bay, CA, USA). Test methods were developed for the use of clams to investigate the effects of sediment amendment on biological uptake. Sediment was mixed with activated carbon for one month. Bioaccumulation tests (28 d) were employed to assess the relationships between carbon dose and carbon particle size on observed reductions in clam biological uptake of PCBs. Extraction and cleanup protocols were developed for the clam tissue. Efficacy of activated carbon treatment was found to increase with both increasing carbon dose and decreasing carbon particle size. Average reductions in bioaccumulation of 22, 64, and 84% relative to untreated Hunters Point sediment were observed for carbon amendments of 0.34, 1.7, and 3.4%, respectively. Average bioaccumulation reductions of 41, 73, and 89% were observed for amendments (dose = 1.7% dry wt) with carbon particles of 180 to 250, 75 to 180, and 25 to 75 μm , respectively, in diameter, indicating kinetic phenomena in these tests. Additionally, a biodynamic model quantifying clam PCB uptake from water and sediment as well as loss through elimination provided a good fit of experimental data. Model predictions suggest that the sediment ingestion route contributed 80 to 95% of the PCB burdens in the clams.

Keywords—Biodynamic modeling Polychlorinated biphenyls Activated carbon amendment Bioaccumulation Uptake routes

INTRODUCTION

Within the last two decades, the organic carbon sorption paradigm has shifted to consider carbon quality as well as quantity. Many researchers have observed strong sorption of hydrophobic contaminants to black carbon/soot carbon and other highly sorptive phases in sediment. These observations led to improved sorption models that include absorption to organic matter and adsorption to carbonaceous geosorbents [1,2].

The subsequent recognition that stronger sorption leads to lower contaminant bioavailability has prompted investigations into how these phenomena may be exploited in sediment remediation efforts. For example, West et al. [3] amended field-collected sediment with Ambersorb, a carbonaceous resin, and observed marked reductions in sediment pore-water concentrations and bioavailability to an oligochaete for eight target polycyclic aromatic hydrocarbons (PAHs). Subsequently, Lebo et al. [4] characterized the effectiveness of coarse and fine Ambersorb and coconut charcoal in reducing the bioavailability of a suite of hydrophobic contaminants, including PAHs, polychlorinated biphenyls (PCBs), and chlorinated pesticides, as measured by uptake into clusters of low-density polyethylene film.

Activated carbon amendment has been investigated and proposed for remediation of PCBs in South Basin at Hunters Point, San Francisco Bay, a Superfund site in northern California, USA. Zimmerman et al. [5] conducted a suite of physicochemical tests with contaminated sediment from Hunters

Point and showed that adding activated carbon reduced PCB concentrations in the aqueous phase, PCB uptake into semi-permeable membrane devices, and quiescent flux of PCBs into overlying water. In a companion biological study with Hunters Point sediment, Millward et al. [6] demonstrated that doses of activated carbon similar to those used by Zimmerman et al. [5] reduced PCB uptake by the marine amphipod *Leptocheirus plumulosus* and marine polychaete *Neanthes arenaceodentata*.

The present work investigates the effects of activated carbon amendment on a third biological end point: The brackish-water, deposit-feeding clam *Macoma balthica*. *Macoma balthica* was chosen specifically because it is native to San Francisco Bay, directly ingests sediment particles, and represents one of the uptake pathways to resident fish. An interim fish consumption advisory for San Francisco Bay ([7]; <http://www.oehha.ca.gov/fish/pdf/fishup99.pdf>) was issued in 1994, in part because of elevated PCB levels. This advisory remains in effect today. Thus, decreasing the amount of PCBs entering the benthic food chain in San Francisco Bay is a highly desired outcome, because this could ultimately result in lower PCB levels in resident fish.

MATERIALS AND METHODS

Sediment–sorbent contact and preparation

Sediment was contacted with activated carbon for one month according to the procedure described by Zimmerman et al. [5]. The activated carbon used in these experiments was TOG[®] 50×200 (Calgon Corporation, Pittsburgh, PA, USA). Properties of this carbon have been reported elsewhere [5].

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The carbon was boiled in water for at least 5 min to displace any gas in its pores. Approximately 4.9 kg wet weight of sediment were added to 4-L, glass roller tubes with 250 ml of 17 ppt seawater (Long Marine Station, Santa Cruz, CA, USA; prepared as described by McLeod et al. [8]) and the desired carbon dose. Tubes were rolled at 2 to 3 rpm for 30 d and then further shaken by hand once weekly.

Following the contact period, sediment was removed from the roller tubes and placed in glass jars (diameter, 23 cm). The jars were placed in separate, 38-L, glass aquaria in a 13°C temperature-controlled room. Approximately 1 L of 17 ppt seawater was added to the jars as overlying water. Sediment was allowed to settle for 5 d before clam addition, with the overlying water being replaced daily during this period. One day before clam addition, approximately 20 L of 17 ppt seawater were added to the aquaria. The resulting water level was approximately 2.5 cm above the top of the jars (6–7 cm above the sediment surface). The aquaria were aerated with glass pipettes attached to plastic tubing.

Bioaccumulation tests

Three bioaccumulation tests were performed. In bioaccumulation test I, we compared the ability of coke and activated carbon (3.4% dry wt) to reduce uptake by clams, with untreated Hunters Point sediment as a control. This also allowed us to investigate potential harmful effects of activated carbon treatment by comparing clam survival and PCB uptake in treated and untreated sediment from Hayward Nature Preserve, which is located southeast and across the bay from Hunters Point. Hayward sediment was chosen because it is texturally similar to Hunters Point sediment and contains low PCB levels. In bioaccumulation test II, we compared the efficacy of activated carbon treatment at three different doses: 3.4, 1.7, and 0.34% dry weight. Finally, in bioaccumulation test III, we investigated the efficacy of one dose (1.7% dry wt) applied in three different activated carbon particle size ranges: 25 to 75, 75 to 180, and 180 to 250 μm in diameter. Activated carbon was crushed using a hand grinder and then wet sieved to achieve the desired size fractions.

Sediment characterization

Sediment was collected from three sites in San Francisco Bay for use in these experiments: Hunters Point Naval Shipyard, Hayward Nature Preserve, and Palo Alto Baylands Nature Preserve. Sediment was stored, unaerated, at 4°C for up to one year before use. The PCB concentrations were measured for these sediments according to procedures described by Ghosh et al. [9]. The Hayward and Palo Alto sediments had PCB concentrations of 5.8 ± 0.6 and 14.7 ± 1.5 ppb, respectively (mean \pm standard deviation throughout). These levels reflect background PCB concentrations in San Francisco Bay [10]. The Hunters Point sediment used in bioaccumulation tests I, II, and III was collected during two different sampling events and contained 7.0 ± 2.3 , 6.5 ± 1.5 , and 3.0 ± 0.4 ppm, respectively, of total PCBs. The total organic carbon content of Hunters Point sediment, measured after the first sampling event, was 1.7% [5].

Clam exposure

Clams (*M. balthica*) were collected from the Palo Alto Baylands Nature Preserve as described previously by McLeod et al. [8]. *Macoma balthica* in the 18- to 27-mm shell length range were accepted. Clams were acclimated to laboratory

conditions and depurated in 17 ppt seawater in a 13°C room for 2 to 3 d, then randomly separated into groups. Twenty clams were measured for background PCB analyses. Dissection procedures are described below. Twenty live clams were placed on top of the sediment in each jar and allowed to burrow. After 24 h, any clams that did not burrow were removed and replaced. Also at that time, air to the aquaria was turned off, and *Phaeodactylum tricoratum* (25 ml) was added to each jar by gently pipetting or pouring over the sediment surface to ensure minimal sediment resuspension. Clams were allowed to feed for 1 h in quiescent conditions before aeration was restored. Clams were fed six or seven times weekly in this manner for the duration of the 28-d exposure period. Once weekly, at least 16 L of water were siphoned out of the tanks and replaced with fresh, 17 ppt seawater. Before water removal, pH and ammonia levels were recorded. On the 28th day of exposure, clams were retrieved by hand and rinsed with deionized water to remove sediment.

Postexposure burrowing and depuration

Sediment from the Palo Alto Baylands Nature Preserve was sieved to less than 1 mm. Sieved sediment was placed in small, plastic containers, and overlying 17 ppt seawater was added. Clams harvested from the exposure jars were placed on top of the sediment and allowed to burrow. Clams remained in the Palo Alto sediment to depurate for 2 d. Depuration was necessary to ensure that ingested, PCB-contaminated sediment particles would not confound tissue PCB analyses.

Dissection and tissue preparation

Clams were retrieved by hand from the depuration containers and rinsed with deionized water to remove sediment. Clams were dissected in groups of three or four individuals. Shells were discarded, and soft tissues were combined in 20-ml, glass vials. Vials were frozen at -80°C for at least 24 h. Frozen tissues were freeze-dried (VirTis Freezemobile 12ES; SP Industries, Gardiner, NY, USA), then crushed with a mortar and pestle immediately before PCB extraction.

Tissue extraction and cleanup

Extraction and cleanup procedures were adapted from published procedures [11,12]. Sodium sulfate was added to the freeze-dried, crushed tissues in 50-ml, glass beakers to form a free-flowing powder. Accumulated PCBs were extracted from 0.3 to 0.5 g of dried tissue with three sequential additions of 20 ml of dichloromethane and sonicating the slurry for 6 min (pulse: 15 s on, 15 s off). All solvents used were of pesticide grade or higher. Extracts were combined and concentrated to approximately 1 to 2 ml under a slow N_2 stream. Concentrated extracts were cleaned up first with a 1:1 ratio of sulfuric acid and water and then with 5% potassium permanganate to oxidize and remove biological interferences. When necessary, vials were centrifuged to enhance phase separation. Activated copper was added to the samples to scavenge free sulfur and allowed to sit overnight. The extracts were then passed through a column with 3% deactivated silica gel, 1% deactivated alumina, and sodium sulfate in a 50:50 ratio of dichloromethane and pentane to remove organic interferences. The concentrated eluate was solvent-exchanged to hexane before analysis. To test method recovery, a known quantity of PCB standard (a mixture of Aroclors 1232, 1248, and 1262) obtained from the U.S. Environmental Protection Agency (U.S. EPA) National Health and Environmental Effects Research

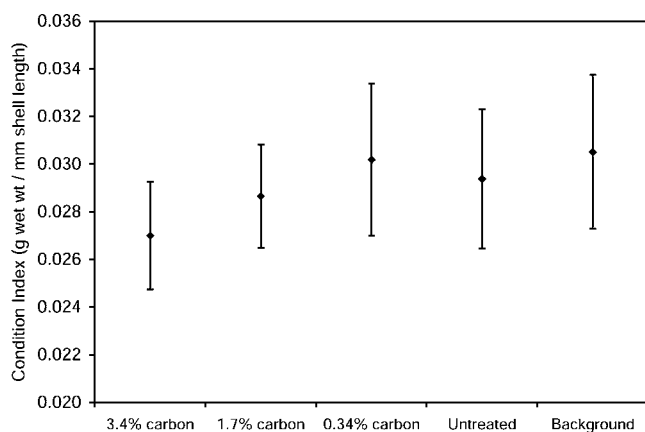


Fig. 1. Condition index calculated for clams in bioaccumulation test II. Error bars represent one standard deviation ($n = 5$ samples with 3–4 clams/sample).

Laboratory (Grosse IL, MI) [13] was added to extra crushed, freeze-dried, unexposed clam tissue before the first extraction step. Percentage recovery in six matrix spikes for total PCBs was $85 \pm 7\%$.

PCB analysis

Two internal standards (2,4,6-trichlorobiphenyl and 2,2',3,4,4',5,6,6'-octachlorobiphenyl) were added to all samples. Congener-specific PCB analysis was performed using an Agilent model 6890 gas chromatograph with electron-capture detector (Agilent, Santa Clara, CA, USA) according to a modification of U.S. EPA Method 8082 as described by Ghosh et al. [9]. Unless stated otherwise, all PCB concentrations reported herein represent total PCBs calculated as the sum of 91 congeners or coeluting congener groups. The PCB concentrations measured in unexposed clams were treated as background levels and subtracted from the results for exposed clams.

Calculations and statistical analyses

Calculations and statistical analyses were performed using Microsoft® Excel (Microsoft, Redmond, WA, USA). One-way analysis of variance (ANOVA) was used to analyze results. Differences were considered to be statistically significant at $p < 0.05$.

RESULTS AND DISCUSSION

Clam viability and condition

The survival rate for *M. balthica* in these experiments was 100%, indicating no acute toxicity to the organisms from the sediment or added sorbents. This finding is consistent with the findings by Millward et al. [6] of no lethality for *N. arenaceodentata* or *L. plumulosus* following activated carbon amendment to Hunters Point sediment [6]. Condition index, defined here as the organism wet weight divided by the average shell length, was calculated for each group of exposed clams and compared to the condition index for unexposed background clams. A representative plot of condition index is shown in Figure 1. In all cases, no statistically significant differences between clam groups were observed (one-way ANOVA: Bioaccumulation test I, $F = 0.74$, $p = 0.60$; bioaccumulation test II, $F = 1.08$, $p = 0.39$; bioaccumulation test III, $F = 1.20$, $p = 0.34$). In bioaccumulation tests I and II, clams exposed to sorbent-amended sediment exhibited lower average

condition indices than unexposed clams and clams exposed to untreated Hunters Point sediment. This could indicate that the clams in carbon-amended sediment had lower growth rates than those exposed to untreated sediment; however, this trend was reversed in bioaccumulation test III. Jonker et al. [14] found that amending sediment with anthracite and charcoal resulted in significantly lower lipid content in oligochaetes and concluded that black carbon amendments could have negative impacts on exposed biota. Our results are inconclusive but suggest limited adverse effects in our test systems.

PCB levels in unexposed clams

The PCB levels measured in unexposed clam tissues were 0.21 ± 0.16 , 0.36 ± 0.11 , and 0.15 ± 0.09 $\mu\text{g/g}$ dry weight for bioaccumulation tests I, II, and III, respectively. Homologue profiles in the clams were similar for the three tests. The hexa- and hepta-homologues constituted 65 to 70% of total PCBs, and the penta-homologue constituted an additional 15 to 20% of the body burden.

Bioaccumulation test I

As observed previously [5,6], adding identical proportions of activated carbon and coke to Hunters Point sediment resulted in very different PCB uptake (Fig. 2A). Clams exposed to coke-amended Hunters Point sediment (3.4% dry wt) accumulated 4% less PCBs than those in untreated sediment. As concluded by Zimmerman et al. [5], the relative ineffectiveness of coke may be attributed to its low specific surface area relative to activated carbon, its lack of connected pores, and the noncoplanar character of the vast majority of PCBs present in Hunters Point sediment. In contrast, 72% reduction in PCB uptake was observed in clams exposed to activated carbon-amended sediment. This result is similar to percentage reductions in PCB tissue burdens after one month of carbon-sediment contact for *L. plumulosus* (72%) and *N. arenaceodentata* (82%) [6].

Clams exposed to untreated Hayward Nature Preserve sediment accumulated 87 ± 68 ng/g dry weight of total PCBs. This concentration is already close to background levels (i.e., 100–200 ng/g dry wt), and activated carbon amendment resulted in an insignificant reduction (one-way ANOVA: $F = 0.03$, $p = 0.87$) in PCB uptake. No mortality was observed, and the condition indices of clams exposed to Hayward sediment were not statistically different from those exposed to Hunters Point sediment (one-way ANOVA: $F = 0.68$, $p = 0.43$).

Bioaccumulation test II

Dose-response relationship. The efficacy of activated carbon treatment was found to increase with increasing carbon dose. Figure 2B shows that body burdens of total PCBs in *M. balthica* decreased from 6.20 ± 1.75 $\mu\text{g/g}$ dry weight in clams exposed to untreated Hunters Point sediment to 0.99 ± 0.06 $\mu\text{g/g}$ dry weight in clams exposed to sediment treated with 3.4% carbon. Average reductions in bioaccumulation of 22, 64, and 84% relative to that with untreated Hunters Point sediment were observed for amendments of 0.34, 1.7, and 3.4%, respectively. This trend is consistent with the findings of Zimmerman et al. [15] that increasing the carbon dose to 3.4% resulted in aqueous equilibrium concentration reductions approaching 90%. It also agrees with the conceptual model developed by Werner et al. [16] to describe the effects of carbon particle dose on PCB availability in well-mixed systems.

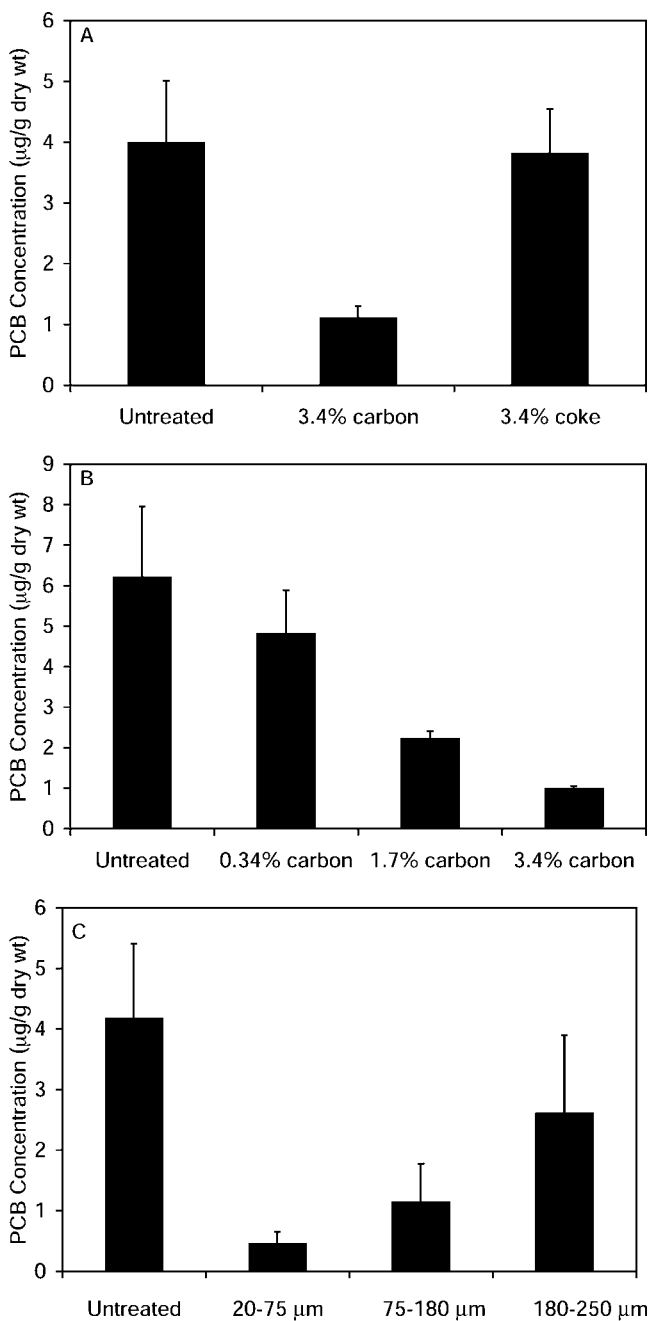


Fig. 2. Effects of added sorbents on total polychlorinated biphenyl (PCB) body burdens in (A) bioaccumulation test I, (B) bioaccumulation test II, and (C) bioaccumulation test III. Error bars represent one standard deviation ($n = 3-5$ samples with 3-4 clams/sample).

Figure 3 shows how clam tissue PCB concentrations vary by homologue. As observed in previous work [5,6,15] with both biological and physicochemical end points, activated carbon efficacy, as measured in short-term tests, is greater for the less hydrophobic congeners. Whereas activated carbon amendment results in lower body burden for all homologues, the effect is less pronounced for the higher-chlorinated PCBs. This phenomenon results in a shifting homologue profile in clam tissues toward higher-chlorinated, more hydrophobic congeners with increased carbon dose. Zimmerman et al. [5] observed that PCB desorption rates decreased with increasing chlorination and hydrophobicity and that the reduction of PCBs in the aqueous phase for more hydrophobic congeners in-

creased with carbon contact time. Based on these results, mass-transfer limitations also are likely to be affecting the biological uptake of PCBs by *M. balthica* in these tests. Longer carbon-sediment contact times and smaller carbon particle diameter would likely result in less of a shifted homologue profile relative to that of clams exposed to untreated sediment.

Bioaccumulation test III: Size response

An inverse relationship between carbon particle size and PCB uptake by clams was observed for the tested dose of 1.7% dry weight. As shown in Figure 2C, body burdens of total PCBs in *M. balthica* decreased from 4.18 ± 1.23 µg/g dry weight in clams exposed to untreated Hunters Point sediment to 0.46 ± 0.19 µg/g dry weight in clams exposed to sediment treated with carbon particles of 20 to 75 µm in diameter at a dose of 1.7%. Average reductions in body burdens of 89, 73, and 41% relative to those in untreated Hunters Point sediment were observed for carbon amendments in the size ranges of 20 to 75, 75 to 180, and 180 to 250 µm, respectively. Again, these trends are consistent with those observed by Zimmerman et al. [15] and predicted by Werner et al. [16] with respect to the effects of particle size on reduction in aqueous equilibrium PCB concentration.

We hypothesize that slower mass-transfer kinetics of the higher-chlorinated congeners results in the observed differences in tissue concentration reduction among homologues. In bioaccumulation test III, reduction in clam PCB uptake for a given homologue increased with decreasing particle size (Fig. 4), which supports this hypothesis.

Correlations with aqueous equilibrium results

Biological uptake of contaminants often is conceptualized as a two-phase process involving desorption from sediment into the aqueous phase or gut fluid, followed by uptake into the tissue. Accordingly, we investigated the correlation between observed clam PCB concentrations and pore-water concentrations measured in aqueous equilibrium tests. As shown in Figure 5, the trends observed for PCB uptake by clams in bioaccumulation tests II and III reflect similar trends in aqueous equilibrium as measured for Hunters Point sediment by Zimmerman et al. [15]. Our results are consistent with a growing body of evidence suggesting that pore-water contaminant concentrations predict organism uptake. For example, Kraaij et al. [17] found that the bioaccumulation of several PCBs, PAHs, chlorobenzenes, and DDE by *Tubificidae* (oligochaetes) could be described as bioconcentration from pore water. Lu et al. [18] observed a good correlation between predicted and measured biota-sediment accumulation factors for several PAHs in the oligochaete *Ilyodrilus templetoni* using measured pore-water concentrations. Millward et al. [6] also successfully related PCB uptake from Hunters Point sediment to *N. arenaceodentata* and *L. plumulosus* using pore-water concentrations and bioconcentration factors.

Although measuring pore-water contaminant concentrations may help to predict bioaccumulation, it should be emphasized that the correlation between the two is not necessarily causative. For example, Lu et al. [18] found that pore-water concentrations of benzo[a]pyrene predicted its bioaccumulation in *I. templetoni* even though literature data strongly suggest that sediment ingestion is the major uptake route for this compound. Similarly, an inspection of our data from bioaccumulation test II presented in Figure 6 reveals that the PCB homologue profile in clam tissue more closely resembles the

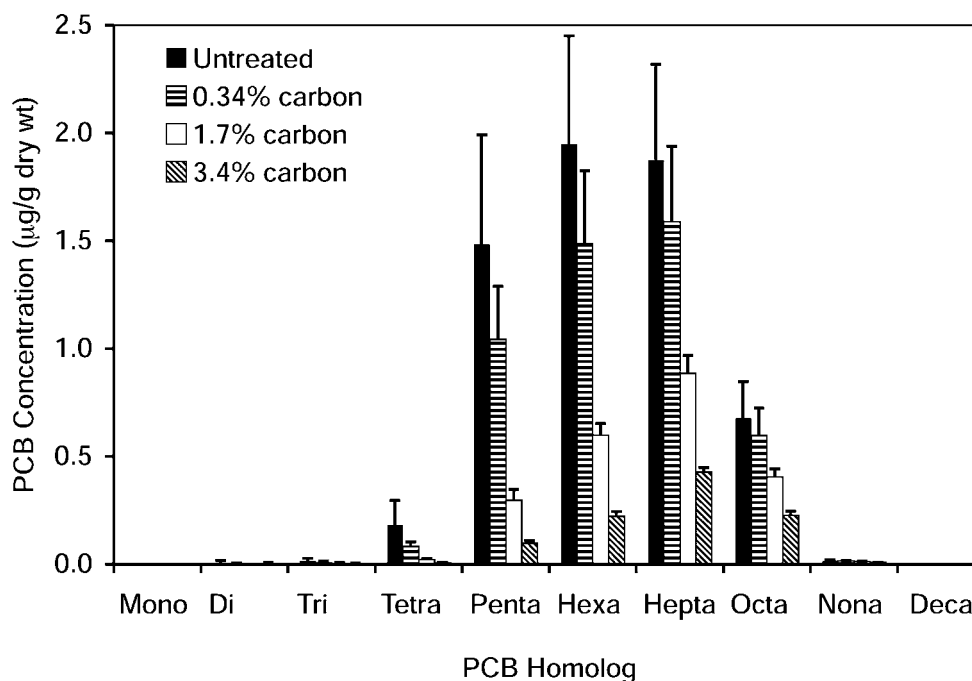


Fig. 3. Clam tissue polychlorinated biphenyl (PCB) homologue concentrations for clams exposed to Hunters Point (San Francisco Bay, CA, USA) sediment amended with varying doses of activated carbon. Error bars represent one standard deviation ($n = 3-5$ samples with 3-4 clams/sample).

sediment signature than the pore-water distribution. To discern the relative importance of uptake from sediment and water, we employed a biodynamic model to describe the PCB accumulation by *M. balthica* in our tests.

Biodynamic modeling

If *M. balthica* is considered to be a single compartment for PCB uptake, the following equation describes the PCB accumulation by the clam over time:

$$\frac{dC_{\text{clam}}}{dt} = \text{FR} \cdot \text{AE}_{\text{aq}} \cdot C_{\text{aq}} + \text{IR} \cdot \text{AE}_{\text{sed}} \cdot C_{\text{sed}} - k_c \cdot C_{\text{clam}} \quad (1)$$

where C_{clam} is the PCB concentration in clam tissue ($\mu\text{g/g}$ dry wt), t is time (d), FR is the water filtration rate (L water/g dry

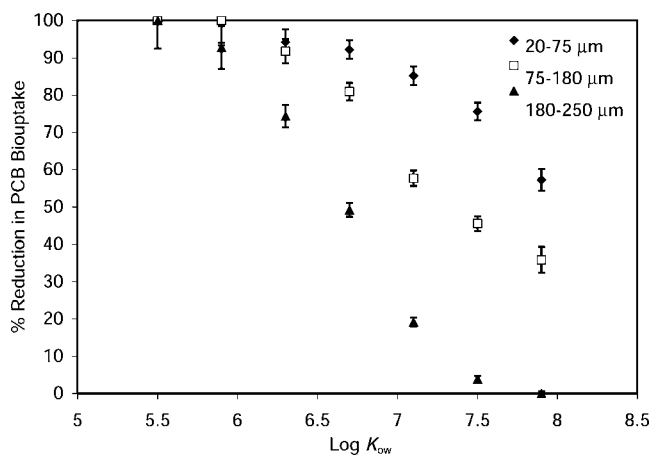


Fig. 4. Effect of carbon particle size on polychlorinated biphenyl (PCB) biological uptake reduction for tri- through nona-chlorinated homologues. Error bars represent one standard deviation. Representative octanol/water partitioning coefficients (K_{ow}) are from Millward et al. [6].

wt/d), AE_{aq} is the PCB absorption efficiency from water, C_{aq} is the aqueous PCB concentration ($\mu\text{g/L}$), 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 ($\mu\text{g/g}$ dry wt), and k_c is the proportional rate constant of loss (1/d). Growth is assumed to be negligible within the time frame of these experiments and is not included in Equation 1. Additionally, we assume that the aqueous PCB concentration remains constant over the course of the 28-d exposure.

Models of this general form have been successfully used to describe laboratory accumulation of different metals by various species of aquatic invertebrates via water and food uptake routes (see, e.g., [19-21]). Recently, Luoma and Rainbow [22] advocated biodynamics as a unifying concept in environmental and laboratory metal bioaccumulation [22]. Similar formulations have been incorporated into PCB food web models (see, e.g., [23-25]) and have been used to discern assimilation efficiency of PCBs to mussels from water and algal food uptake routes [26].

Parameter values used in this modeling exercise are summarized in Table 1. Filtration rate (FR) and ingestion rate (IR) were obtained from Luoma et al. [21]. Absorption efficiency from water (AE_{w}) was estimated from values measured by Bjork and Gilek [26] for aqueous uptake of PCB 153 by *Mytilus edulis*. Aqueous PCB concentrations (C_{aq}) were measured by Zimmerman et al. [5,15] in aqueous equilibrium tests. The proportional rate constant of loss (k_c) was estimated from those obtained by Boese et al. [27] for higher-chlorinated PCBs in *Macoma nasuta*. Sediment PCB concentrations were measured in the laboratory. Values for AE_{sed} under different carbon amendment scenarios were calculated as follows: Percentage reduction in aqueous equilibrium PCB concentration was considered to be a proxy for the proportional mass of PCBs transferred from native sediment to added carbon particles. A modified AE_{sed} was then calculated as a weighted average of the

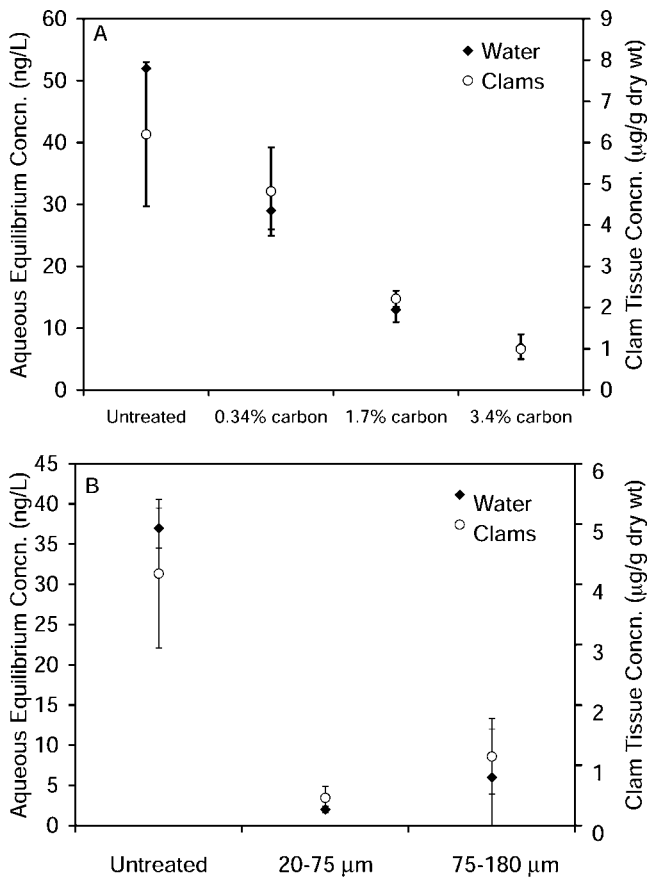


Fig. 5. Correlation between aqueous equilibrium and clam tissue polychlorinated biphenyl (PCB) concentrations with (A) varying carbon dose and (B) varying carbon particle size. Error bars represent one standard deviation. Aqueous equilibrium data are from Zimmerman et al. [15].

nonamended AE_{sed} (20%) and the AE for PCB 52 on activated carbon (1.44%) as measured by McLeod et al. [8]. For example, if the observed reduction in aqueous equilibrium PCB concentration were 86.5%, then the calculated AE_{sed} used in the model would be 3.9% [i.e., $(1 - 0.865)(0.2) + (0.865)(0.0144)$].

Integrating Equation 1 yields

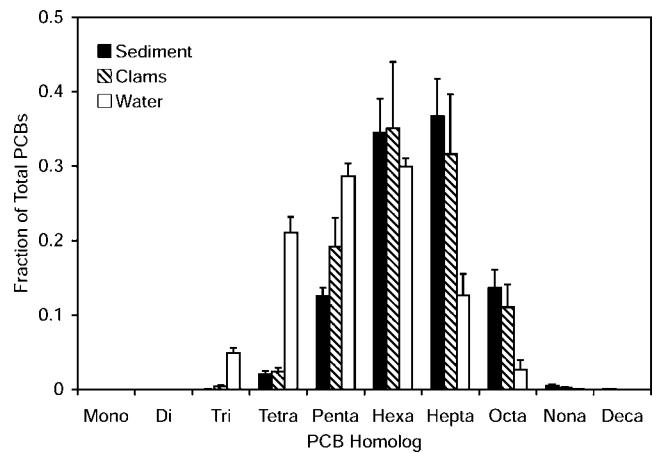


Fig. 6. Polychlorinated biphenyl (PCB) homologue distributions for Hunters Point (San Francisco Bay, CA, USA) sediment in untreated sediment, exposed clams in bioaccumulation test II, and pore water (aqueous equilibrium). Error bars represent one standard deviation. Aqueous equilibrium data are from Zimmerman et al. [15].

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

which was solved for $t = 28$ d using the parameters reported in Table 1 to generate model predictions for the various clam exposures in bioaccumulation tests I, II, and III. In all cases, model predictions were within a factor of two of the observed PCB concentrations in the clams. Figure 7 depicts model predictions versus observed results, with the linear regression shown as a solid line. The slope of the regression is 0.96 ($r^2 = 0.8175$), indicating an almost 1:1 correlation between predicted and observed data.

Based on modeling results, the sediment ingestion route contributes 80 to 95% of the PCB body burdens of the clams. Thus, even though pore-water PCB concentrations correlate with biological uptake, the clams in our tests accumulated PCBs predominantly via sediment ingestion. We suggest that bioaccumulation of PCBs in these clams reflects the pore-water concentration because site-specific sorption characteristics, which ultimately control PCB availability, are integrated into measurements of pore-water concentration. This is especially useful when we consider activated carbon-amended systems.

Table 1. Values of biodynamic model parameters used to describe polychlorinated biphenyl (PCB) accumulation in *Macoma balthica*

Parameter	Symbol	Unit	Value ^a
Filtration rate	FR	L water/g dry wt/d	2.0 ^b
Aqueous absorption efficiency	AE_{aq}	%	50.0 ^c
Aqueous concentration	C_{aq}	μg/L	0.037 ^d (I) 0.052 ^d (II) 0.0375 ^d (III)
Ingestion rate	IR	g sediment/g dry wt/d	0.25 ^b
Sediment absorption efficiency	AE_{sed}	%	20.0 ^c
Sediment concentration	C_{sed}	μg/g	7.0 (I) 6.5 (II) 3.0 (III)
Rate constant of loss	k_c	1/d	0.05 ^f

^a I = bioaccumulation test I; II = bioaccumulation test II; III = bioaccumulation test III.

^b Luoma et al. [21].

^c Estimated from Bjork and Gilek [26].

^d Zimmerman et al. [5,15].

^e Calculated using experimental results for PCB 52.

^f Estimated from Boese et al. [27].

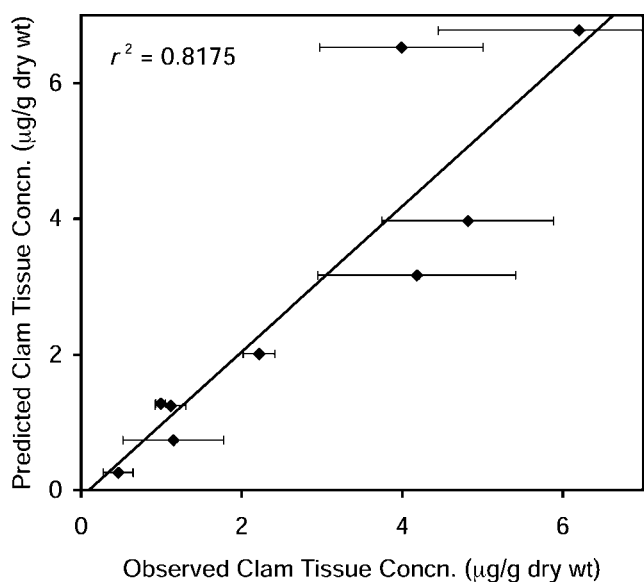


Fig. 7. Predicted clam tissue polychlorinated biphenyl concentrations using the biodynamic model versus experimental observations. Error bars represent one standard deviation ($n = 3-5$). Solid line represents the linear regression between predicted and observed concentrations.

As described in our model formulation, reductions in aqueous equilibrium or pore-water concentrations provide an indirect indication of the proportional mass transfer of PCBs from native sediment to amended particles. In turn, the absorption efficiency of PCBs to *M. balthica* from these added activated carbon particles is much lower than that for native Hunters Point sediment.

Implications

The present results demonstrate that adding activated carbon to sediment from Hunters Point can reduce PCB uptake in *M. balthica* by almost one order of magnitude. Furthermore, the biodynamic modeling exercise strongly suggests that this reduction is accomplished through the mass transfer of PCBs from native sediment particles to the activated carbon. Additional work is needed to characterize the reductions in bioavailability achieved by activated carbon amendment under field conditions. This includes tests to assess the impact of nonideal mixing conditions on treatment efficacy. If the biodynamic model is informed by aqueous equilibrium PCB reductions and modified to account for reduced mass transfer, it may serve as an invaluable tool for engineers and marine biologists to predict the impact of activated carbon amendment on the uptake of PCBs by benthic organisms.

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