Measurement and Modeling of Polychlorinated Biphenyl Bioaccumulation from Sediment for the Marine Polychaete *Neanthes arenaceodentata* and Response to Sorbent Amendment†

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Bioaccumulation rates of polychlorinated biphenyls (PCBs) for the marine polychaete *Neanthes arenaceodentata* were characterized, including PCB uptake rates from water and sediment, and the effect of sorbent amendment to the sediment on PCB bioavailability, organism growth, and lipid content. Physiological parameters were incorporated into a biodynamic model to predict contaminant uptake. The results indicate rapid PCB uptake from contaminated sediment and significant organism growth dilution during time-series exposure studies. PCB uptake from the aqueous phase accounted for less than 3% of the total uptake for this deposit-feeder. Proportional increase of gut residence time and assimilation efficiency as a consequence of the organism's growth was assessed by PCB uptake and a reactor theory model of gut architecture. Pulse-chase feeding and multilabeled stable isotope tracing techniques proved high sediment ingestion rates (i.e., 6−10 times of dry body weight per day) indicating that such deposit-feeders are promising biological indicators for sediment risk assessment. Activated carbon amendment reduced PCB uptake by 95% in laboratory experiments with no observed adverse growth effects on the marine polychaete. Biodynamic modeling explained the observed PCB body burdens for *N. arenaceodentata*, with and without sorbent amendment.

Introduction

Polychlorinated biphenyls (PCBs) are persistent and bioaccumulative contaminants. Despite being banned for production in the United States in 1979, PCBs are widely distributed and are among the most troublesome contaminants in sediments, accounting for the second-leading cause of fish consumption advisories (*1*). PCBs pose a risk to humans mainly by consumption of contaminated fish. Thus, it is a high priority to minimize contamination of food sources to higher aquatic organisms for mitigation of human health risks.

Reduced bioavailability of PCBs in sediments to invertebrates at the base of the food web can diminish PCB trophic transfer (*2*−*4*). Laboratory studies with contaminated field sediments showed that the addition of highly sorbent activated carbon (AC) reduces the availability of PCBs, PAHs, and DDT to water and uptake by organisms such as clams, amphipods, polychaetes, and mussels (*5*−*9*). The concept builds on prior studies that describe the role of black carbon to affect the transport, uptake, and biomagnification of hydrophobic organic contaminants in sediments (*10, 11*). Recent fieldwork at Hunters Point, California, demonstrated in situ management of PCBs in sediment for reducing the bioavailability and environmental exposure of PCBs by the addition of AC to the upper, biological-active sediment layer (*12, 13*). The AC repartitions the PCBs within the sediment, which reduces release to pore water and uptake by biota.

Previous laboratory studies with sediment and AC focused mainly on 28-day bioassays to assess the effect of sorbent amendment (*5, 6, 11*) rather than on time-series experiments to assess the organism's kinetic influx and efflux rates. The kinetics of contaminant fluxes can be predicted with species-specific physiological parameters incorporated in a biodynamic model, which then can predict tissue concentrations (*14*). Validated biodynamic models may serve as powerful tools to supplement physiochemical measurements and bioassays for environmental risk assessment and monitoring.

In this study, the marine polychaete *Neanthes arenaceodentata* was chosen as the test organism. Polychaetes represent 30−75% of benthic macro-invertebrates and serve as food for higher trophic organisms, e.g., snails, fish, birds, and crustaceans (*15*). Furthermore, deposit-feeding polychaetes ingest large amounts of sediment relative to their body weight. Thus, deposit-feeders may be among the most appropriate biological indicators to assess sediment quality and the effects of sorbent amendments on bioavailability and risk. In the present work, detailed assessments of PCB bioaccumulation (i.e., uptake and loss rates) with and without and response to AC amendment were undertaken. Species-specific physiological parameters were characterized and incorporated into a biodynamic model to describe for the first time PCB tissue concentrations for this marine polychaete.

Material and Methods

Biodynamic Model. The contaminant concentration in an organism's tissue can change over time, dC_{org}/dt in μg/g dry weight (dw) per day. The tissue concentrations result from the mass balance of uptake from sediment and water, and loss and growth dilution, and can be described by

$$\frac{dC_{org}}{dt} = \underbrace{IR \cdot AE_s \cdot C_s}_{\text{uptake from sediment}} + \underbrace{k_w \cdot C_w}_{\text{uptake from water}} - \underbrace{k_{e+g} \cdot C_{org}}_{\text{loss and growth}} \quad (1)$$

which can be solved in closed form (eq S1, Supporting Information) (*14, 16*).

Contaminant uptake from water is described by an aqueous uptake rate constant k_w (L/g dw per day) and the pore water contaminant concentration C_w (μg/L) as demonstrated by Sun et al. (*9*). Here, k_w can be determined from a relationship of contaminant tissue concentrations at different exposure times (on the order of hours) with constant aqueous concentration. The measurement of k_w is based on

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the assumption that elimination and growth dilution is not relevant during the short exposure to water without any food source. For hydrophobic compounds the maximum amount that will partition into the tissue from water, $C_{w,org}^{max}$ (μg/g dw), can be estimated by the organism's lipid content, f_{lipid}, and the contaminant's octanol−water partitioning coefficient, K_{ow}, as a conservative assumption of partitioning to lipids (*17*), where

$$C_{w,org}^{max} = f_{lipid} \cdot K_{ow} \cdot C_w \quad (2)$$

The loss of contaminant and growth dilution are described by a combined rate constant k_{e+g} (g/g dw per day) comprising

$$k_{e+g} = k_e + k_g \quad (3)$$

with k_e being the elimination rate constant and k_g being the growth rate constant (both in g/g dw per day). The value of k_{e+g} can be determined from depuration studies wherein previously exposed organisms loaded with the contaminant are transferred to a contaminant-free exposure test. The slope of tissue concentrations ($\ln C/C_0$) versus depuration time represents k_{e+g}.

The contaminant uptake from sediment is a function of the organism's ingestion rate IR (g/g dw per day), the contaminant's sediment concentration C_s (μg/g dw), and the organism's contaminant assimilation efficiency from ingested solids AE_s (-).

AE_s can be measured directly by targeted feeding studies when either feces collection is possible to analyze for non-assimilated contaminants or when radio-labeled compounds are tracked during feeding. Accurate feces collection is not always practical, e.g., when organisms excrete in the sub-surface of the sediment, and spiking sediment with radio-labeled compounds is not reflective of true desorption kinetics of aged sediment. Here, AE_s was estimated by solving eq 1 using observed contaminant concentrations (dC_{org}/dt) from bioassays under the condition that all other coefficients in the model are known (eq S2, Supporting Information). To quantify the assimilation efficiency from a sorbent (i.e., AC) added to the sediment, the value of AE_s can be expressed as

$$AE_s = F_{sed} \cdot AE_s^{sed} + (1 - F_{sed}) \cdot AE_s^{AC} \quad (4)$$

with F_{sed} being the fraction of PCBs that remains on the sediment after sorbent amendment, AE_s^{sed} being the assimilation efficiency from untreated sediment, and AE_s^{AC} being the assimilation efficiency from AC. F_{sed} can be estimated from the ratio of pore water concentrations in sediment and AC-amendment, as

$$F_{sed} = \frac{C_w^{AC}}{C_w^{no\ AC}} \quad (5)$$

with $C_w^{no\ AC}$ and C_w^{AC} (μg/L) being the pore water concentrations before and after AC-amendment, respectively, under the assumption of linear partitioning for very low aqueous concentrations, e.g., about 1 order of magnitude around 1 ng/L (*18, 19*). For the calculation of AE_s^{sed}, F_{sed} equals unity because no AC is added ($AE_s^{sed} = AE_s$). To quantify AE_s^{AC} eq 1 is solved for AE_s using the uptake data (dC_{org}/dt) obtained from bioassays with AC-amendment. Here, AE_s represents the assimilation efficiency from the combination of sediment and AC. Equation 4 is then solved for AE_s^{AC} with knowledge of AE_s^{sed} and F_{sed}.

In addition, an initial background tissue concentration (C_{org}^0, μg/g dw), may be present prior to sediment exposure, which will undergo the same concentration changes described by k_{e+g} (eq S1, Supporting Information).

In this study, specific time-series laboratory experiments were conducted to estimate the relevant physiological parameters that govern PCB uptake and loss in *N. arenaceodentata*. Then the biodynamic model was used to predict PCB accumulation and compared to observations from bioassays.

Sediment and Pore Water Characterization (C_s, C_w). PCB-contaminated sediment was collected from a control plot in South Basin at Hunters Point, California in spring 2007. The sediment was sieved (2.35 mm), homogenized, and stored at 4 °C. A portion of homogeneous sediment was amended with 3.4% activated carbon (TOG-NDS 50 × 200, Calgon Carbon, Catlettsburg, KY) and mixed on a roller for 28 days at 4 rpm in accordance with the procedure described by Zimmermann et al. (*20*). The carbon type and grain size were identical with the material used in a previous in situ study at Hunters Point (*13*). Congener-specific PCB analysis was performed using an Agilent model 6890 gas chromatograph with micro electron-capture detector (GC-μECD) following a modified EPA method as described by Ghosh et al. (*11*).

To measure equilibrium pore water concentrations (C_w), 30 g of wet sediment with 780 mL of 30‰ artificial marine water (AMW, RedSea) were placed into a 1-L jar with 0.78 g of sodium azide (Mallinckrodt Inc.) and kept on a roller at 4 rpm. Three replicates were prepared for both test sediments. After 30 days contact time, the supernatant was analyzed for PCBs after flocculation and centrifugation as described by Zimmerman et al. (*20*).

Test Organisms. Two-week old *N. arenaceodentata* were purchased from Dr. Donald Reish (California State University, Long Beach). The organisms were acclimatized in the laboratory in silica sand with overlying AMW of 31‰ for at least 2 days. The water temperature, salinity, total NH_3/NH_4, pH, and dissolved oxygen saturation were monitored and averaged (±SD) 22.5 ± 1.0 °C, 33 ± 2‰, 1 ± 0.5 ppm, 7.6 ± 0.3, and 87.5 ± 3.5%, respectively.

PCB Uptake from Sediment and Water (dC_{org}/dt). PCB bioaccumulation for *N. arenaceodentata* was observed using a modified protocol by Millward et al. (*5*). For the microcosms, 50 mL of sediment and 200 mL AMW of 31‰ were placed into a 300-mL beaker and gently aerated (16 beakers per test-sediment). After 1 day, the overlying water was exchanged and 12 juveniles were placed into each beaker. Twice a week, 12 mg of ground fish food powder (TetraMin, Tetra Holding Inc., Blacksburg, VA) was added to each beaker and the overlying seawater was exchanged prior to feeding. Every 7 days, for 4 consecutive weeks, organisms from 4 beakers (4 replicates) of each test-sediment were removed by gentle sieving. The individual organisms were kept in AMW until gut clearance was completed (12−36 h, visual inspection) and frozen at −20 °C before further analysis.

Tissue Analysis (k_g, C_{org}). Prior to PCB tissue analysis, individual organism wet weight (Sartorius Microbalance, CP2Pl) and length were recorded to monitor growth ($N >$ 300). Weight measurements outside the range of ±2.7 standard deviations were not considered for the growth rate (k_g) analysis. Composite samples of organisms from each replicate were analyzed for PCBs with a modified method based on Millward et al. (*5*) with the following exceptions. Briefly, the composite samples were frozen at −80 °C, lyophilized, and dry weights were recorded. The final extracts were concentrated to 40−100 μL before analysis with GC-μECD.

Lipid Content (f_{lipid}). Organism lipid content was measured using individuals that were removed from the composites of the microcosm studies described above. Three organisms per sampling time point were analyzed for lipid content using a spectrophotometric method described by van Handel (*21*). Absorbance was measured at 525 nm wavelength, 20−35 min after the vanillin-reagent was added

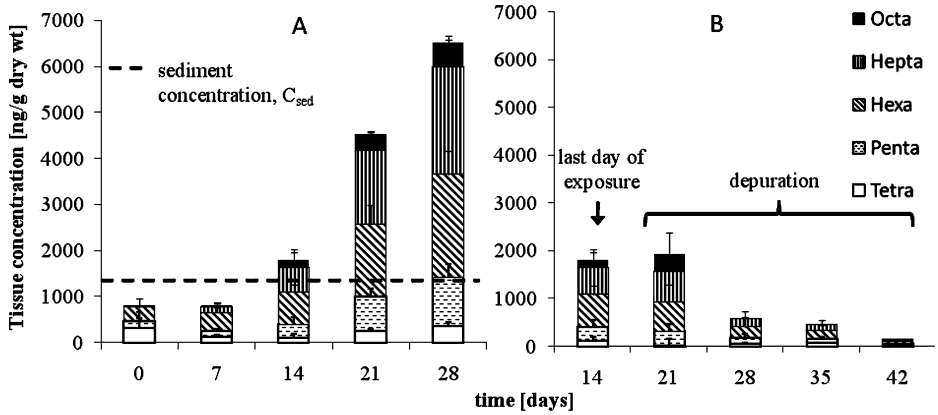

FIGURE 1. (A) Change in PCB tissue concentration of *N. arenaceodentata* for contaminants accumulated from Hunters Point site sediment. (B) Decrease in PCB tissue concentration during depuration after 14-day exposure to untreated sediment. Error bars represent one standard deviation, showing five homologue groups of prominent PCBs.

when the signal was constant and related to lipid concentration by a calibration derived from soybean oil (Sigma).

Combined Rate Constant for Loss and Growth (k_{e+g}). To determine the combined rate constant for loss and growth dilution, depuration experiments were conducted wherein organisms were first exposed to either untreated or AC-amended sediment for 14 and 28 days, respectively (12 beakers per test-sediment). To maximize the PCB tissue loading for a better observation of depuration, the exposure to AC-amendment was longer because less/slower PCB uptake was expected. The exposure occurred as described above for the sediment uptake studies. After exposure, all organisms were transferred to beakers containing presolvent-cleaned silica sand and overlying AMW to observe depuration. Water renewal and feeding was similar to that described above. Organisms from three beakers of each test-sediment were sampled every seven days for four consecutive weeks, frozen at −20 °C, and analyzed as described above.

Aqueous Uptake Rate Constant (k_w). *N. arenaceodentata* were exposed to aqueous PCBs in flow-through chambers at a flow rate of about 10 mL/min to assess the contaminant's partitioning from water into the tissue as described by Sun et al. (*9*). The flow-through system was designed to avoid depletion of the PCBs in the aqueous phase during exposure. The aqueous PCB solution was produced with a generator column as described by Ghosh et al. (*22*). Briefly, 2 g of glass wool was soaked in hexane with 8.38 mg of Aroclor 1242 (40.98% Aroclor 1232, 29.51% Aroclor 1248, 29.51% Aroclor 1262, UltraScientific) and the solvent was evaporated. A total of 20 L of AMW of 31‰ was first filtered through virgin glass wool and then passed through a column packed with the PCB-coated glass wool. The aqueous PCB solution from the generator column was diluted to 370 ng PCBs per liter. Seven-week old organisms were used to allow for depuration of initial PCB concentrations in juveniles and to have sufficient biomass available for analysis. Twelve test-organisms were placed into each of the four replicate flow-through chambers and exposed for 2−9 h. After exposure, the organisms were briefly rinsed with clean AMW, stored at −20 °C, and analyzed as described above. Control tests were conducted with PCB-free AMW.

Ingestion Rate (IR). A combination of pulse-chase feeding and multilabeled stable isotope techniques was used to determine the ingestion rate (IR, g/g dw per day) for *N. arenaceodentata*. Specifically, IR was determined by mass-balance calculations using the total amount of a specific tracer (i.e., ^{65}Cu, ^{106}Cd) retained in the polychaetes after depuration, the amount of tracer egested in the feces during depuration, the tracer concentration in the enriched food, the polychaete's dry weight, and the exposure duration as described by Croteau et al. (*23, 24*). For the pulse-chase feeding study the marine algae *Isochrysis*, a flagellate (University of Toronto Culture Collection) was exposed for 24 h to isotopically enriched ^{65}Cu and ^{106}Cd (details in Supporting Information). Some algae were used to determine the exposure concentrations and the remaining were offered as food to *N. arenaceodentata* ($n = 10$). After 5 h of feeding, polychaetes were removed, rinsed with AMW, and placed individually into 15-mL acid-washed vials filled with AMW for a 24-h depuration period. Unlabeled food was provided *ad libidum* during depuration. Feces from each organism were harvested by filtration onto a 1.2 μm filter and dried for 24 h at 50 °C. After depuration, polychaetes were placed individually on a piece of acid-washed Teflon sheeting, frozen, and then allowed to dry at 50 °C for 3 days. Dried tissue, feces, and algae were analyzed for the naturally occurring stable isotopes of Cu (^{63}Cu and ^{65}Cu), and Cd (^{106}Cd, ^{108}Cd, ^{110}Cd, ^{111}Cd, ^{112}Cd, ^{113}Cd, and ^{114}Cd) by inductively coupled plasma-mass spectrometry as described by Croteau et al. (*25*). The equations used to calculate the accumulated amount of tracers are presented in the Supporting Information. The algae represent 100% organic matter (OM) and the algae IR is equivalent to the OM IR. Total sediment IR was estimated by normalizing the algae IR by the fraction of OM of the sediment. The sediment OM content was calculated from measured total organic carbon (TOC) (Total Carbon Analyzer, Agvise Laboratories, Northwood, ND) using the chemical composition of OM as $C_5H_7O_2N$ (details in Supporting Information).

Results and Discussion

PCB Uptake from Sediment and Water (dC_{org}/dt). The tissue concentrations are presented as mass of total PCBs per mass of dry weight of tissue. Lipid contents are reported separately. Background PCB concentrations of 800 ± 550 ng/g and 480 ± 300 ng/g were observed in juveniles before exposure to sediments and AC-amendment, respectively (day 0, Figures 1A and 2A). A comparison of the homologue distribution of PCBs in the polychaete's tissue before and after sediment exposure revealed that lower-chlorinated PCB homologues are predominant at day 0, while an abundance of higher-chlorinated PCBs accumulate over time from sediment uptake. The preponderance of tetrachloro-PCBs in the background is lost during exposure (Figure S1).

The Hunters Point field sediment used in the microcosm studies has a PCB concentration of 1200 ± 300 ng/g dw. No net increase in tissue concentrations was detectable within the first 7 days of exposure. Then, PCB tissue concentration increased exponentially over 28 days of exposure to untreated sediment to 6500 ± 600 ng/g (Figure 1A). The PCB tissue concentrations exceeded the sediment concentrations after 14 days exposure. *N. arenaceodentata's* PCB uptake was still

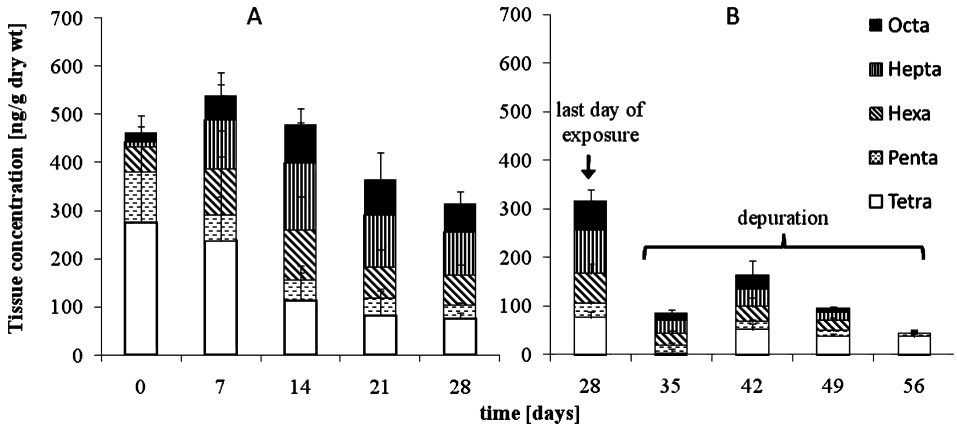

FIGURE 2. (A) Change in PCB tissue concentration of *N. arenaceodentata* exposed to AC-amended Hunters Point sediment. (B) Decrease in PCB tissue concentration during depuration after 28-day exposure to AC-amended sediment. Error bars represent one standard deviation, showing five homologue groups of prominent PCBs.

increasing throughout the 28-day bioassay indicating non-steady state.

Figure 2A shows the corresponding tissue concentrations resulting from exposure to AC-amended sediment. PCB tissue concentrations slightly decreased from the initial background concentration ($p < 0.05$). The PCB tissue concentrations after 28-day exposure to AC-amendment were 95% lower compared to those observed upon exposure to untreated sediment. Despite the absence of net increase in PCB tissue concentration through time (Figure 2A), the change of homologue distribution in the organism's tissue suggests exchange of background PCBs (tetra-homologue dominated) for sediment-associated PCBs (hexa- and hepta-homologues dominated). Thus, there was some residual bioavailability of higher chlorinated PCB congeners in the first 14 days of exposure but it was greatly reduced compared to data from the untreated sediments.

Combined Rate Constant for Loss and Growth (k_{e+g}). Figures 1B and 2B show PCB tissue concentrations for the depuration experiments after exposure to the test sediments. The value for k_{e+g} was obtained from the depuration test following exposure to untreated sediment because the higher PCB loading allowed for a more accurate estimate of the rate constant. The PCB tissue concentrations decreased by over 95% within 28 days of depuration compared to the load at day 14 and this represented 15% of the initial background concentrations found in juveniles (day 0, Figure 1A). The value for k_{e+g} was established from the slope of PCB tissue concentration (C/C_0) versus depuration time (Figure S2) as 0.126 g/g dw per day. Figure 2B shows that the tissue concentrations decreased to similar levels during depuration after exposure to either untreated or AC-amended sediment attaining less than 100 ng/g dw.

Growth Rate Constant (k_g). Individual organism wet weight and length were recorded at each sampling time during the microcosm studies as well as after 29 days in silica sand (control). Juveniles grew rapidly from 1.4 ± 0.7 mg ($N = 104$) to 15.3 ± 8.8 mg in sediment ($N = 64$, average weight from both test-sediments) and to 8.2 ± 6.8 mg in silica sand ($N = 10$) within 28 and 29 days, respectively (Figure S3). No significant difference between weights in AC-amendment (15.5 ± 5.2 mg, $N = 39$) versus untreated Hunters Point sediment (14.5 ± 12.4 mg, $N = 26$) was observed at day 28 ($p < 0.05$). The average value for k_g in sediment was determined to be 0.086 g/g·d (Figure S4). Millward et al. (*5*) reported that growth rates were reduced for these polychaetes by 30−50% in AC-amended sediment despite no change in digestive fluid surfactancy or function of digestive enzymes. Here, we followed Millward's methodology with the only difference being the sediment's origin which was further offshore at Hunters Point, away from the historic source, in finer-grained sediment that showed better survival in preliminary tests (data not shown). The uncertainty about the effect of AC on the organism's growth suggests the need for further studies, but may also depend strongly on sediment texture.

Similar variability was observed in all individual experiments, suggesting that the variability was independent of the medium (sand versus sediment) and contamination (untreated versus AC-amended). Pesch et al. found that male organisms are 6 times lighter compared to females and the male/female ratio is 5:1 (*26*). Although gender was not determined in our study, gender-specific differences may explain the observed range of weights.

The PCB elimination rate constant, k_e, was calculated as 0.04 g/g dw per day (eq 3), which is about 50% of the growth rate constant. It is concluded that growth dilution must be considered in biodynamic modeling to predict PCB concentrations in *N. arenaceodentata*.

Lipid Content (f_{lipid}). There was no significant temporal trend for lipid content of *N. arenaceodentata* (standardized by wet weight) during the sediment microcosm experiments (Figure S5). However, the lipid content of organisms grown in the AC-amendment was 0.4 ± 0.1% ($N = 9$) which was on average 3 times less compared to 1.2 ± 0.7% ($N = 14$) observed for organisms from untreated sediment ($p < 0.05$). Similar effects were observed earlier for oligochaetes (*27*). These effects cannot be explained with our study. Perhaps natural organic matter (NOM) in sediment becomes less available after AC addition. Control organisms maintained in silica sand that has no nutritional value itself showed similar low lipid contents of 0.6 ± 0.1% ($N = 6$) as did juveniles ($t = 0$) with 0.5 ± 0.3% ($N = 7$). The effects of AC-amendment on the lipid content should be evaluated in further studies. To account for the effect of body lipid on bioaccumulation (eq 2) in later modeling, average values of 1.2% and 0.4% for untreated and AC-amended sediment, respectively, were applied.

Aqueous Uptake Rate Constant (k_w). Continuous exposure to 370 ng/L of aqueous PCBs resulted in a linear increase of PCB tissue concentration at an observed uptake rate of 8 ng/g dw per hour (Figure S6). When normalized by the aqueous concentration, the aqueous uptake rate constant, k_w, was 0.5 L/g dw per day. The maximum PCB concentration for uptake from water, $C_{w,org}^{max}$, was estimated with the average lipid contents presented above, the respective pore water concentrations as obtained from equilibrium pore water characterization, C_w, in untreated (37 ± 11 ng/L) and AC-amended (0.2 ± 0.1 ng/L) sediment, and an average K_{ow} for PCBs of 10^6 (eq 2). The estimated value of $C_{w,org}^{max}$ was 444 ng/g and 0.8 ng/g, for untreated and AC-amended sediment, respectively, representing 6.8% and 0.2% of the total uptake

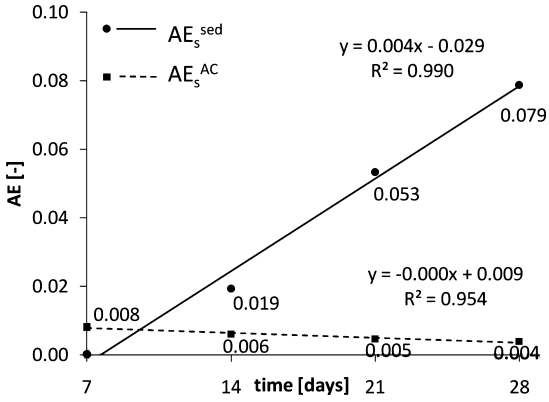

FIGURE 3. Assimilation efficiencies (AE) from sediment (AE_s^{sed}) and activated carbon (AE_s^{AC}) calculated for *N. arenaceodentata* with an average ingestion rate of 8.7 g/g dw per day.

measured in bioassays with sediment and AC-amendment for 28 day exposure. However, our model suggests that $C_{w,org}^{max}$ will not be attained within the polychaete's life cycle. The estimated uptake from the aqueous phase in untreated sediment and AC amendment after 28 days exposure (140 ng/g and 0.77 ng/g, respectively) represents less than 3% of the total uptake (Table S1).

Ingestion Rate (IR). The algae IR (±95% confidence interval) averaged 0.14 ± 0.08 g/g per day with organisms fed on a pure culture of marine algae. Upon normalization to account for the proportion of OM in Hunters Point sediment (0.7−1.1%) (*13*), the IR for total sediments was estimated to range between 10.6 and 6.8 g/g per day. Such rates will vary somewhat with the nature of the organic material, but Cammen (*28*) cited the dependence of IR on OM for polychaetes. He reported a similar sediment ingestion rate of approximately 5 g/g per day for the deposit feeder *Neanthes succinea* (*28*). Thus sediment ingestion rates of this general magnitude appear to be typical for deposit-feeding polychaetes in different kinds of sediments.

Assimilation Efficiencies (AE). The pore water concentration, C_w, showed a 99.5% reduction from 37 ± 11 ng/L in untreated Hunters Point sediment to 0.2 ± 0.1 ng/L in AC-amended sediment. Using eq 5, F_{sed} is estimated as 0.005 after amendment assuming that sediment particles and pore water are in quasi-equilibrium with the contaminant. Previous modeling approaches included ongoing mass transfer processes in biodynamic modeling to account for disequilibrium (*9*). As a result of our mixing regime to prepare the AC-amendment, 99.5% mass movement of PCBs to the AC was observed. Thus we neglect ongoing mass transfer and assume that C_w was essentially constant for each test-sediment in the studies presented.

The assimilation efficiency represents the degree of uptake after solubilization and adsorption of contaminants from sediment in the gut passage. Figure 3 shows the calculated assimilation efficiency of PCBs (average of all congeners) for untreated (AE_s^{sed}) and AC-amended sediment (AE_s^{AC}) over the exposure time of 28-days for the average IR of 8.7 g/g per day. A range of assimilation efficiencies was calculated considering the observed range of IR values (Figure S7). AE_s^{AC} was rather constant at 0.6 ± 0.1% which agrees with values observed previously (*6*).

AE_s^{sed}, on the other hand, increased linearly over time to about 8% at day 28. Extrapolation gives an estimated maximum AE_s^{sed} of 25% at day 70. Typically, the assimilation efficiency is a constant species-specific and sediment-specific parameter. For example, the nongrowing deposit-feeding oligochaete *Lumbriculus variegates* shows an AE of 20% for PCBs in sediment (*9*). A comparison of PCB uptake behavior from sediment for *Lumbriculus variegates* and *N. arenaceodentata* revealed that the nongrowing oligochaete's tissue concentration increases at a faster rate and converges earlier to the maximum concentration (Figure S8). Our results suggest that the AE_s^{sed} in *N. arenaceodentata* increases as a function of growth. The AE_s^{sed} at day 7 could not be quantified. The value for AE was either below detection or could have reflected delayed feeding of very young juveniles (*29*).

Gut Residence Time. The increase in AE_s^{sed} can be explained by the increase in gut residence time (GRT) as the animal grows. Longer GRTs translate to more complete sediment extraction. Penry and Jumars classified polychaetes by their gut architecture, and simple organisms with just one gut compartment can be modeled as a plug flow reactor (*30*). The simple gut construction allows for the fast growth and reproduction observed for *N. arenaceodentata*.

The GRT (days), is a function of the volume of the organism's gut, V_{gut} (mm^3), and the volumetric flow rate of ingested material, Q (mm^3/d) as given by

$$GRT = \frac{V_{gut}}{Q} \tag{7}$$

V_{gut} accounts for about 30% of the organism's total body volume, V_{org} (mm^3) (*31*) and can be approximated as a cylinder as given by

$$V_{gut} = \pi \cdot r_t^2 \cdot L_t \cdot 0.3 \tag{8}$$

with L_t (mm) being the organism's length, and r_t (mm) being the organism's radius. We found that L_t increased linearly at 0.35 mm/d from an initial average length of 5.4 mm (Figure S9). The increase of r_t was estimated from observations as 0.02 mm/d with a maximum of 3 mm at the age of 84 days. The mass flow Q is given by

$$Q = \frac{IR}{\delta} \cdot M_{org}(t) \tag{9}$$

with δ being the gut content's density (g/mm^3), and M_{org} being the organism's wet weight (g). While a constant relative IR (g/g·d) can be assumed (*31*), the absolute mass ingested increases proportionally to M_{org}. The value for δ was assumed to be equivalent to the density of ingested sediment measured gravimetrically as 0.002 g/mm^3.

We found that the GRT increased from half an hour for juveniles (age 14 days) to 3.4 h for organisms at the age of 6 weeks (day 28 in the bioassays presented above). The maximum GRT could be predicted as 10 h when the organism stops growing near the end of its life cycle at the approximate age of 70 days (Figure S10). The GRT increases during growth because the gut volume, V_{gut}, increases faster relative to the mass ingested, Q, which is a consequence of the cylindrical shape and organism's length increasing at a rate faster than its diameter (Figure S11).

Biodynamic Modeling. The biodynamic model was applied for *N. arenaceodentata* utilizing the physiological parameters empirically established in this study (Table S2). The calculation is similarly sensitive to the values chosen for ingestion rate, assimilation efficiency, organic carbon content, and sediment contamination levels because the uptake of PCBs by ingestion is dominant (Table S3). Empirical data were obtained for each parameter under the conditions of this study, and the model tracked bioaccumulation well. Figure 4 shows observed and predicted PCB tissue concentrations, considering the upper and lower bounds of the measured IR. In agreement with the reduced PCB concentrations in pore water, the model also captures the effect of reduced PCB bioavailability after AC-amendment.

Predictions beyond the time span of the experimental observations (Figure S12) must be evaluated with care. For

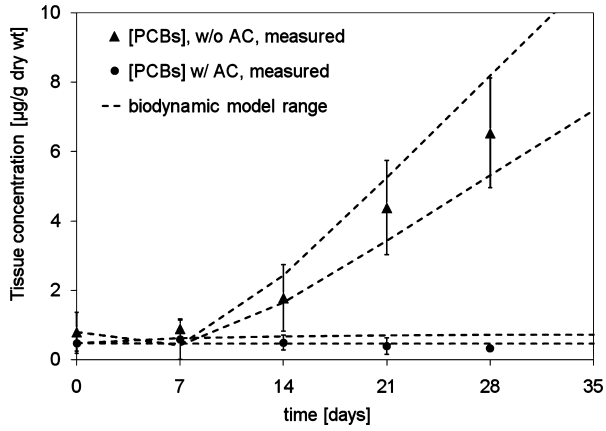

FIGURE 4. Measured values and modeled range of PCB tissue concentrations for organisms in sediment w/ and w/o AC-amendment considering the upper and lower bounds for sediment IR.

example, *N. arenaceodentata* undergo morphological changes near the end of their life cycle at the time of reproduction including changes in their feeding behavior.

Significance

The microcosm studies showed that AC-amendment can reduce the bioavailability of PCBs in sediment to *N. arenaceodentata* by up to 95% under laboratory conditions. The reduced PCB uptake in these polychaetes at the base of the food web (*15*) implies that AC-amendments can diminish trophic transfer from sediment to fish and hence decrease human health risk. Furthermore, a biodynamic model wherein diet was the primary source of bioaccumulation explained PCB accumulation in these polychaetes during the bioassays. Although changes in pore water concentration after AC-amendment of the sediment often correlate with reduced PCB bioaccumulation, the reduced availability of contaminants from ingestion of sediments appears to be the actual cause of lower tissue concentration. Direct uptake from ingested sediment appeared to account for more than 97% of the total PCB accumulation, partly because uptake from solution at environmental concentrations was very slow compared to uptake from food. Even though much effort is needed to validate the biodynamic model, as presented here, once the biodynamic parameters are quantified, the model is directly applicable to predicting tissue concentrations given some knowledge of the contamination levels and PCB availability from sediment (desorption kinetics, AE). Because it accounts for physiology and bioavailability, such modeling can help explain and supplement physiochemical measurements and bioassays to reduce uncertainties about sediment risk and in situ remediation.

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Supporting Information Available

Additional details on (1) established rate constants, (2) physiological parameters, and (3) summary table of model input parameters.This material is available free of charge via the Internet at http://pubs.acs.org.

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