Published in final edited form as:

Sci Total Environ. 2012 April 15; 423: 168–175. doi:10.1016/j.scitotenv.2012.01.042.

Effect of reactive core mat application on bioavailability of hydrophobic organic compounds

Dogus Meric^{a,*}, Sara M. Barbuto^{a,1}, Akram N. Alshawabkeh^{a,1}, James P. Shine^{b,2}, and Thomas C. Sheahan^{a,1}

^a Department of Civil and Environmental Engineering, Northeastern University, 400 Snell Engineering Center 360 Huntington Avenue, Boston, MA 02115, United States

^b Department of Environmental Health, Harvard School of Public Health, 401 Park Drive Landmark Center 404-H West, Boston, MA 02215, United States

Abstract

Sediment remediation techniques to limit the bioavailability of contaminants are of special interest due to related acute or chronic toxicities associated with sediment contaminants. Bioavailability in aquatic sediments can be particularly problematic due to their accessibility to food chain biota, and interactions with surface and ground water. The effect of a reactive core mat (RCM) containing organoclay on the bioavailability of hydrophobic organic compounds (HOCs) (i.e., PCBs and naphthalene) was studied using oligochaete worms (*Lumbriculus variegatus*). Sediment sampled from the Neponset River (Milton, MA) with 10 ppm background PCB contamination was used in the experimental study. The objective of this study is to investigate the difference in HOC concentration of worms exposed to: a) a grab sample of contaminated sediment (10.4% total organic carbon); and b) an initially clean mixture of sand and organic matter (the so-called biouptake layer), placed on top of the RCM-capped sediment during consolidation coupled solute transport experiments. In addition to the experimental data, the U.S. Army Corps of Engineers (USACE) biota-sediment accumulation factor (BSAF) database was validated and used to model biouptake of contaminants for certain cases. Results indicate that RCM capping reduced the average bioavailability of both PCBs and naphthalene by a factor of about 50. In fact, worms exposed to the RCM-protected biouptake layer show virtually the same HOC concentrations as those measured in the control worm samples.

Keywords

PCBs; Naphthalene; Bioavailability; Reactive core mat; Sediment; Remediation

1. Introduction

Contaminated sediments have become one of the most challenging national and global environmental problems. Hydrophobic organic compounds (HOCs) are the major

contaminants of concern at Super-fund sites, with polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) dominating the ecological exposure risk at more than 20% of contaminated sediment sites (U.S. EPA, 2011). Aquatic sediments in particular pose further challenges to remediation and reducing bioavailability — when compared to terrestrial sediments, they can contain higher organic content for increased adsorption, are more accessible to the food chain and potential human consumption, and have a greater likelihood of interacting with both surface and ground water, both of which can lead to biological exposure pathways.

Traditional practices for the remediation of contaminated aquatic sediments include: dredging and ex-situ treatment, in-situ passive capping, and controlled natural attenuation (Meric et al., 2011a). Dredging is the most widely used method for EPA remediation projects involving aquatic sediments since permanent removal of the contaminated sediment and ex-situ treatment/disposal is often thought to be the most effective means to reduce risks and provide greater control of contamination; thus, it seems inherently more preferable (Knox et al., 2008; Reible et al., 2003). However, the method poses the potential for sediment resuspension and release of the contaminants following dredging, potentially increasing the compound's bioavailability. Also, dredging's high cost often limits its use to relatively small areas or target hot spot zones. In passive capping applications, the contaminated sediment layer is covered with a clean soil layer to minimize the bioavailability of contaminants to the overlying benthic and pelagic biota. However, the thickness of the clean soil required is typically significant, a new benthic zone must be developed post-capping, and several studies have shown that submarine discharge can enhance breakthrough and decrease the cap's efficacy (Alshawabkeh et al., 2005; Barth et al., 2003; Meric et al., 2014; Meric et al., 2011c). Since the main focus of remediation efforts has shifted to methods that can result in a higher degree of prevention/limitation of bioavailability and reduction in toxicity of contaminants, new remediation technologies are needed.

The reactive core mat (RCM), typically 1.25 cm thick, consists of a core reactive material such as organoclay with filtering layers on top and bottom. It is placed on the sediment, and then overlain by approximately 7.5–10 cm of soil or other armoring layer for stability and protection. RCM caps are similar to passive caps in the way they isolate the contaminated sediments from the overlying water column with a physical barrier. However, RCM caps use their reactive layer to sequester or degrade the contaminants, thus retarding and/or mitigating contaminant breakthrough (Yin et al., 2009), and potentially decreasing the bioavailability (Sun and Ghosh, 2008; Knox et al., 2007). A contaminant barrier that includes an RCM cap is much thinner compared to traditional passive caps, and can be applicable for hot spots in up-welling areas that can pose significant risk to efficacy and integrity of passive caps (Meric et al., 2011c).

This paper presents an experimental study on the efficacy of RCM capping to isolate PCB and naphthalene contaminated sediment from a model biouptake layer, using worm samples in column solute transport experiments (Table 1), and makes use of biota sediment accumulation factor (BSAF) modeling (U.S. ACE, 2011) to evaluate the biouptake of PCBs and naphthalene by oligochaete worms (*Lumbriculus variegatus*) before and after RCM

capping. The results are intended to test the hypothesis that the RCM can be effective in significantly reducing the bio-availability of HOCs from aquatic sediments to overlying biota.

2. Materials and methods

2.1. Sediment

The baseline sediment used was sampled from the Neponset River (Milton, Massachusetts, USA), upstream of the Tilestone and Hollingsworth Dam, which is a Massachusetts Department of Environmental Protection (MA DEP) cleanup site within the Neponset River restoration project. The site was chosen in coordination with US EPA Region 1. Sampling was performed at mid-channel of the Neponset River using an Ekman sediment sampler (Wildco® Corp.). Collected sediment was transferred into clean, non-translucent 5 gallon HDPE buckets that were sealed, transported to the laboratory, and stored in a 10 °C temperature room to reduce microbial activity. The samples were stored until settling of the solids had taken place. Based on sediment chemical analysis, the sampled sediment from this location (obtained over the course of two sampling trips) has trace levels of background PAH contamination and 10,619 ng/g total PCB concentration with a similar congener profile to Aroclor 1248.

After the settling period for the sampled sediment, the overlying water was decanted by siphoning. Large organic debris and stones were removed from the sediment by hand. Using one sample from each bucket, tests were conducted on the remaining sediment to determine gravimetric water content, organic matter content (ASTM D2974, 2007), specific gravity of solids (ASTM D854, 2010), and hydraulic conductivity (ASTM D2434, 2006) of the sediment. On average, the test sediment had a gravimetric water content of 248%, 23% total organic matter (based on loss on ignition at 550 °C), a specific gravity of solids, $G_s=2.3$, and an initial hydraulic conductivity of 4×10^{-5} m/s.

2.2. Sediment spiking

Because the sediment sampled had enough background PCB contamination for testing but only trace levels of PAH contamination, the sediment was spiked with naphthalene. Naphthalene (Acros Organics 99%, #180902500) was chosen as the PAH model due to its 1 to 2 orders of magnitude higher solubility in water (12.5 to 34 mg/L) compared to other PAH compounds (Neff, 1979), resulting high mobility in aqueous solutions, and the availability of background biouptake data on *L. variegatus* (Brunson et al., 1998), the intended up-take organism model for the present research. A nominal concentration of 250 mg/kg dry sediment was targeted, which provided sufficient resulting concentrations above background values for measurement and modeling of reactive transport through the sediment and RCM.

Sediment samples were kept in their field-wet condition with natural hydration both before and during spiking to prevent biogeochemical alterations due to drying processes (Van Gestel et al., 1996). Spiking was performed in 1 L amber glass jars to prevent photochemical reactions. A high solvent volume technique (Northcott and Jones, 2000) with solvent-to-

solid ratio greater than 1:20 (volume of solvent:weight of compound) was adopted. Analytical grade acetone was used as the solvent with 1:8 solvent-to-naphthalene ratio. Given the large amount of sediment being spiked, this method was expected to provide better compound distribution by solvent permeation into the sediment (Reid et al., 1998). The acetone allows for easy mixing of hydrophobic compounds in saturated soil/sediment samples, although care must be taken since excess acetone can alter the sediment's native organic contaminants (Northcott and Jones, 2000), induce toxic effects on microbial communities (Reid et al., 1998) and promote denitrification in the sediments (Fuller et al., 1997). The desired quantity of naphthalene (typically around 160 mg) and 20 ml of analytical grade acetone solvent (Fisher Scientific, A 928-4, Pittsburgh, PA) were first mixed separately, and the resulting solution (containing 160 mg naphthalene) was added to each sample jar containing 640 g dry mass of sediment.

The jars were then capped tightly and mixed by rotation to allow homogenous distribution of the spiked chemical compound and to ensure proper sorption-based equilibrium between solid particles of the sediment and the pore fluid. While no standard mixing time is specified for spiking procedures, Reid et al. (1998) have suggested a mixing time of 2 weeks (14 days), which was adopted for the present study. At the end of spiking, the sediment–naphthalene mixture was immediately used in the experiment with no significant post-mixing storage duration.

2.3. Contaminant transport column: device and testing procedures

The Integrated Contaminated Sediment Testing Apparatus Column (ICSTAC; Fig. 1) device is a coupled, large-strain consolidation and contaminant transport device that physically models the aquatic sediment “stack” or column, including the contaminated sediment, the RCM, overlying clean sand layer with organic matter (biouptake layer or zone) and water column. Column tests were demarcated NEP-XX to indicate that Neponset River sediments were used, with XX indicating the test number. Five experiments with PCB-contaminated sediment and 12 experiments with naphthalene-spiked sediment were performed with the column device. Neponset River sediment in this device tends to consolidate very rapidly and with significant associated deformations (vertical strains up to 40% are typically measured) due to the additional surcharge applied by a loading piston (representing the surcharge on the RCM; Fig. 1), which creates consolidation-induced advective flux of the pore fluid to the overlying biologically active benthic zone and water column (Meric et al., 2010).

For the tests reported, the biouptake layer consisted of a medium coarse sand mixed with 3% (by mass) Omega One® “trout chow” organic matter to promote retention of any contaminants that may break through the RCM, and thereby promote contaminant exposures during the bioaccumulation tests using the sand–organic mixture (as opposed to non-reactive sand layer only). It was assumed that this would provide greater similitude to the typically high organic content of most aquatic sediments. It is emphasized that the organic matter was introduced to provide a reactive component into the biouptake layer. It is not intended to mimic in situ organic matter; rather, it is intended to capture any breakthrough contaminant for more robust bioavailability testing. A 7.6 cm (3 in.) thick layer of this sand-trout chow mixture was placed on top of the loading plate and the remainder of the column filled with

deionized water. The water column can be pressurized to mimic any water depth up to 25 m (82 ft). Sampling ports in each fluid line allow chemical samples to be taken during the test from both the sediment layer and from the overlying water column. The loading piston that initiates the consolidation-induced advective gradient is actuated by deadweight loads. The development and proof-testing of this device is presented elsewhere (Yu et al., 2009; Meric et al., 2010).

Once the set-up procedures were completed, backpressuring of the system began, with the goal of saturating the column and pore fluid system (this is a typical procedure in many geotechnical laboratory tests on sediments assumed to be saturated in the field). The backpressure was increased in 50 kPa increments, with each increment left on for about 4 to 6 h until the desired, final backpressure of 200 kPa was reached. Consolidation was initiated approximately 24 h later. Consolidation was applied with three stress increments of 10, 25 and 55 kPa, with each increment applied for 24 h. To quantify the contaminant transport in the testing column, water samples (at least 5 mL volume for each) were taken from top and bottom sampling ports at the following elapsed times during each loading increment: $t=0^-$ (just before loading), 15 min, 30 min, 1 h, 3 h, 6 h, 9 h, 12 h and 24 h. Collected water samples were placed in 20 ml glass vials and refrigerated at 4 °C until analysis. During all increments, movement of the loading piston (corresponding to sediment layer deformation) was measured using a displacement transducer. Discussion of the water sample analysis is presented elsewhere (Meric et al., 2014).

At the end of the test, the overlying water was drained into a sampling bottle, the biouptake layer (sand–trout chow mixture) collected in a wide-necked sampling bottle, and the RCM and the contaminated sediment each placed in individual, air-tight, zip-locked plastic bags, frozen and stored until subsequent biouptake testing.

2.4. Bioaccumulation test procedures

To prepare for the biouptake experiments, 100 mL of the post-column test sand–trout chow mixture or sediment was placed into a 1 L glass beaker; this beaker served as the exposure test chamber. To this, 900 mL of standard, synthetic freshwater was added, and the beaker was then aerated for 14 days with twice weekly water changes (Ingersoll et al., 1998). This incubation period was intended to remove ammonia that could be toxic to the worms.

Exposure tests were conducted in accordance with the U.S. EPA 600/ R-93/183 method (U.S. EPA, 1993) for Bedded Sediment Bioaccumulation Tests. To begin the test, 1 to 5 g (wet weight) of worms (procured from Aquatic Research Organisms, Inc.) was added to each beaker. Aeration was continued in each beaker throughout the exposure test by hoses at a rate of 50 cm³/min. A consistent light cycle of 16 h light and 8 h dark was provided with an automatic lamp with an illuminance range of 100–1000 lux. Beakers were placed in a circulating water bath to maintain an ambient temperature of 20°±1 °C and were loosely capped to prevent significant evaporation from the test chamber. The test chamber's overlying freshwater was renewed throughout the test by changing half the water every 3 days. New freshwater was added by pouring it slowly down the beaker sides to avoid disturbing the worms that had since self-buried in the sand. The worms were not fed during the exposure period.

At the end of the 28-day exposure test period, worms were removed, rinsed clean with water, and weighed. The worms did not undergo a gut elimination in clean sand prior to chemical analysis since the EPA standard indicates that this is an optional process as long as: i) the organisms used do not selectively ingest high levels of organic particles; ii) the organisms used do not have a large gut capacity; iii) the exposure period is of sufficient length such that tissue residues are high enough; and iv) bioaccumulating compounds are being measured. Since the gut contents constitute 15–20% of a worm's dry weight, placement of the worms into clean sand could cause significant dilution of bioaccumulated contaminants (Ingersoll et al., 1998). Worms were maintained at 4 °C until extracted for lipid and chemical analysis. Sands, sediments, and other materials were kept frozen until analysis.

For the experiments with PCBs, several associated bioaccumulation test controls were performed: worms that were placed in sand that had not been used in column testing (“clean sand”), and those that were tested directly upon receipt from the vendor. Overlying sand from the column tests on naphthalene-spiked sediment was also used in bioaccumulation tests. In addition to these tests, three naphthalene-spiked sediments from column tests were used in bioaccumulation tests.

2.5. Chemical analysis

Upon completion of the exposure period, worm, sand and sediment samples were analyzed for either PCBs or naphthalene content using the methods described in Vorhees et al. (1999) for PCBs and Vinturella et al. (2004) for naphthalene. Briefly, the sediment/sand or homogenized worm tissue (mixed with sodium sulfate) was spiked with appropriate surrogate standards and extracted via vortexing and sonication with three sequential additions of 1:1 acetone/hexane. The samples were then reduced using a Kuderna-Danish apparatus and evaporated to 1 ml under a gentle stream of high purity nitrogen. The extracts were further cleaned up by elution through silica cartridges, followed by the addition of an internal standard. The final extract volume was approximately 500 µl. For the worm extractions, a sub-sample of the initial extraction was placed in a pre-weighed aluminum weighing dish for gravimetric determination of lipid content. Further details are given in Vorhees et al. (1999) and Vinturella et al. (2004).

Samples for naphthalene were analyzed on an Agilent Gas Chromatograph with mass selective detector in selected ion mode. The PCB samples were measured on an Agilent Gas Chromatograph equipped with a ⁶³Ni electron capture detector. For the PCBs, a 30 m, 0.25 mm i.d., 0.25 µm film thickness DB-5 capillary column (J&W Scientific, Folsom, CA) was used to separate the PCB congeners. For naphthalene, a 30 m, 0.18 mm i.d., 0.18 µm film thickness DB-KLB column was utilized to quantify naphthalene. Quantification was based on external standards containing surrogates, the internal standard, and the analytes of interest. For PCBs, 65 target PCB congeners were measured. Several peaks were quantified as individual congeners but may contain a small contribution from coeluting congeners (i.e., IUPAC 138, 153, and 170). Method detection limits were calculated for each analyte by multiplying the procedural blank standard deviation value for each analyte by 3.

2.6. BSAF modeling

The biota-sediment accumulation factor (BSAF) is an empirically derived quantity (Eq. 1) relating the concentration of a specific compound in a given medium with specific organic carbon content and the concentration of that compound in a specific organism with specific lipid content.

$$BSAF = \frac{(Organism\ Wet\ Conc.) / (Lipid\ Content)}{(Dry\ Sediment\ Conc.) / (Organic\ Carbon\ Content)} \quad (1)$$

BSAF modeling was performed in the present study to predict the response of the uptake organism, *L. variegatus*, to direct exposure to PCB contaminated sediment, since experimental data was not available for that specific case. BSAF calculations were also made for all the other cases with PCBs and naphthalene-contaminated sediment tests to assess the validity of the experimental conditions. The U.S. Army Corps of Engineers BSAF database (U.S. ACE, 2011) was used for the BSAF model. BSAF modeling for the oligochaete worms exposed to PCB contaminated samples was performed with total-homolog based BSAF model values (relating total PCB concentration of each homolog group; Ankley et al., 1992; Kukkonen et al., 2004). There are distinct laboratory and field condition BSAF values for naphthalene exposed *L. variegatus* in the database. Naphthalene concentrations measured in oligochaete worms exposed to naphthalene contaminated samples were used to backcalculate the laboratory condition BSAF values reported in the database for validation (Brunson et al., 1998). Compound concentration predictions were made by using the known fat content of worms used in each NEP test, and the dry concentration of the medium (i.e., sediment or sand–trout chow mixture) with known organic carbon content. The error ranges of predictions were defined by using the standard deviation of the listed BSAF values (Brunson et al., 1998; Ankley et al., 1992; Kukkonen et al., 2004).

3. Results

3.1. Sediment and sand characterization

Regarding the geotechnical response of the tested sediment to the surcharge load applied by the column piston (Fig. 1), PCB contaminated tests NEP-4 and -5 had vertical strains of 38.7 and 30.8% respectively after all stress increments had been applied. These strains correspond to 7.74 and 6.08 cm deformation over an initial sediment height of 20 cm. These sediment deformations correspond to 5.52 and 4.33 cm vertical pore fluid transport, respectively, computed using the sediment porosity. Similarly for the Naphthalene spiked sediment tests, NEP-15 and -16, 32.4 and 22.7% vertical strains were measured, respectively, corresponding to 4.62 and 3.24 cm vertical transport of pore fluid to the overlying biouptake layer and water column.

Pore fluid concentrations for NEP-15 and -16 monitored throughout the test were in the range of 2.24 ± 0.51 mg/L naphthalene, which is 63 times larger than the measured breakthrough concentration in the overlying water layer (0.036 ± 0.02 mg/L). The control test with no overlying RCM layer had pore fluid concentrations of 1.68 ± 1.02 mg/L, compared to

the overlying water concentrations of 0.52 ± 0.34 mg/L. It is believed that this is due primarily to dilution of the pore fluid within the initially clean overlying layer (Meric et al., 2014). Advection-based consolidation was completed in all tests for all stress increments within the testing duration, indicating that no further consolidation-induced advective flux was left to occur after the completion of the test.

For the PCB analysis, the concentrations for 54 congeners were evaluated for all samples, with congeners PCB-30 and PCB-204 used as the surrogates to evaluate the recovery of the extraction method. Samples of Neponset River sediment and column test biouptake layer respectively yielded 88-116% and 76-87% surrogate recovery, which are within the acceptable recovery range of 60–130% (Sun and Ghosh, 2008). Post-column test material from two tests, NEP-4 and -5, and clean sand were evaluated for background PCB concentrations.

The PCB congener profile of Neponset River sediment (Fig. 2) is composed mostly of PCBs with lower chlorination levels, which is consistent with the findings of studies on reductive dechlorination over time due to microbial activity (Pakdeesusuk et al., 2003; US EPA, 2008; Sokol et al., 1994; Abramowicz, 1995). The sand–trout chow mixture obtained from tests NEP-4 and -5 contained 4 orders of magnitude lower PCB concentrations (0.388 to 0.475 ng/g) compared to that of Neponset river sediment specimens (10,619 ng/g) covered with the RCM material during the tests, and a two-fold increase in PCB concentration over that obtained from clean control samples (0.204 ng/g), which is lower than the mean background soil total PCB concentration of 5.41 ng/g reported by Meijer et al. (2003) for 200 sites worldwide. Percentage changes in homolog group concentrations of biouptake zone material (sand–trout chow mixture) obtained from NEP-4 and -5 tests relative to clean control sample homolog group concentrations (Fig. 3) show significant increases in almost all homolog group concentrations, particularly for octa-CBs (655–874%). PCB homolog compositions of the sand–trout chow mix from NEP-4 and -5 (Fig. 4) showed bell-shaped profiles skewed to lower chlorinated biphenyl (CB) homolog groups, with the peaks at the hexa-CB homolog group, while the homolog profile of the control sample is uniform at the center between tri- to hepta-CBs with significantly less at the lowest and highest chlorination level homologs.

For the naphthalene spiked tests (NEP-15 and -16), the post-column test spiked sediment and sand–trout chow mix were analyzed. No clean control samples were analyzed due to the volatility of the naphthalene, and were assumed to be at trace levels. Due to the anticipated high naphthalene concentrations in the spiked sediment, these samples were diluted for analysis; post-column test naphthalene concentration was found to be 38,666 and 42,206 ng/g. Naphthalene concentrations in the sand-trout chow mixture collected from NEP-15 and -16 are 4 orders of magnitude lower (1.253 to 4.445 ng/g) than the measured concentration of the spiked sediment.

3.2. Oligochaete worm biouptake results

For tests NEP-4 and -5 (PCBs tests), clean worms and worms exposed to the biouptake zone sand–trout chow mix overlying the RCM layer were analyzed experimentally for the selected 54 PCB congeners. PCB congeners PCB-30 and PCB-204 were used as surrogates to measure recovery, which was 85 to 93% after blank correction. Worms used in the

experiments had 2.1 to 4.8% fat content, consistent with existing data (Brunson et al., 1998; Ankley et al., 1992; Kukkonen et al., 2004; Nebeker et al., 1989; Kukkonen and Landrum, 1994; Fisk et al., 1998; Pickard et al., 2001, 2005; Croce et al., 2005). Since PCB content analysis of the worms exposed directly to PCB-contaminated sediment was not performed, the U.S. ACE BSAF model was used. To check the applicability and level of error of the BSAF model, it was used in a back-analysis of known results from sand-trout chow biouptake experiments.

Worms exposed to sand and trout chow mix collected from NEP-4 and -5 tests showed more than two times the total PCB concentration compared to the control worms (5.515 and 5.729 ng/g, respectively, versus 2.443 ng/g). Percent change in homolog group concentrations (Fig. 5) indicates decreases in di-CB (71 to 80%) and deca-PCB (40 to 48%) concentrations, no significant change in tri-CB concentration, and increases in all other homolog groups' concentrations, ranging from 96 to 1414%. The highest increase after bioaccumulation is observed for hepta- and octa-CB homologs (540 to 1414%). PCB homolog fractions in the worms (Fig. 6) obtained from NEP-4 and -5 have a bell-shaped distribution as compared to the control samples, which are primarily comprised of tri- to hexa-CB homologs.

The BSAF model was used for validation purposes to predict the PCB concentration of worms exposed to sand and trout chow mix and directly exposed to sediment. Comparison of experimental biouptake data and BSAF model prediction of worms exposed to sand and trout chow mix from NEP-4 and -5 yields fair to good prediction of total PCB concentration, with the BSAF model versus experimental results as follows: 4.805 ng/g versus 5.515 ng/g, and 5.469 ng/g versus 5.729 ng/g, for NEP-4 and -5, respectively. The BSAF model also provided a reasonable prediction for the homolog group profile of the worms exposed to sand and trout chow mix (Fig. 7). When the BSAF model is applied to the sediment, the predicted PCB concentration in *L. variegatus* directly exposed to sediment was 1644 ng/g (Fig. 8).

PAH 1-fluoronaphthalene was used to measure the efficacy of the extraction process for NEP-15 and -16 associated biouptake tests, and resulted in recovery rates of 88 to 92%, respectively. Worms exposed to the sand and trout chow mixture overlying the RCM from NEP-15 and -16 tests yielded 11.92 ng/g and 67.57 ng/g naphthalene concentrations, respectively, while those worms exposed directly to sediment had naphthalene concentrations of 1292 ng/g and 2289 ng/g, respectively. BSAF values are also used to predict the worm concentrations exposed to sand and trout chow from NEP-15 and -16 to compare with the experimental data. Calculated worm naphthalene concentrations based on BSAF values reported (Brunson et al., 1998) (15.64 and 58.21 ng/g, respectively) matches well with the experimental data reported in this study.

4. Discussion of results

Results from laboratory exposure of *L. variegatus* to PCB and naphthalene contaminated sediment have been presented from samples collected at the end of the contaminant transport column tests. For experiments with PCB contaminated sediment, concentrations observed in the sand-trout chow mix at the end of column tests are 4 orders of magnitude lower than the

Neponset River sediment and twice as high as the control sample. Similarly, analysis of samples from naphthalene spiked sediment column tests yields concentrations more than 4 orders of magnitude lower in sand and trout chow mixture compared to the sediment concentration. Considering the degree of vertical deformation, associated pore fluid flux, overlying water concentrations compared to the given pore fluid concentrations in tests with RCM layer (as opposed to the no overlying barrier tests), and the degree of reduction in worm biouptake in tests with RCM (as opposed to direct exposure of *L. variegatus* to the contaminated sediments) it can be concluded that the RCM technology provides effective contaminant isolation of pore fluid HOC contamination and a reduction in bioavailability of HOCs.

Percent change in PCB homolog group concentrations in the sand and trout chow mixture from NEP-4 and NEP-5 tests showed significant increases specifically for octa-PCBs (Fig. 3). This may be related to relatively lower homolog fraction of octa-PCB measured in the control sample (Fig. 4) rather than an indication of selective/preferential sorption. Also observed was a decrease in some of the lower-chlorinated homolog groups, consistent with the relatively higher mobility of these homolog group congeners.

For the naphthalene tests, analysis of the post-column experiment sediment from NEP-15 and NEP-16 showed significantly lower naphthalene concentrations than the spiking concentration (38,666 to 42,206 ng/g versus 250,000 ng/g). This may be due to the combined effects of the efficiency of the spiking process (Murdoch et al., 1997), desorption and dissolution in pore fluid and/or overlying water (Meric et al., 2011a; Meric et al., 2014), sorption by the RCM, and volatilization losses during sample handling and analysis.

Worms exposed to sand-trout chow mixture collected from NEP-4 and NEP-5 tests showed total PCB concentrations that were twice as high as the control samples, with hepta- and octa-PCBs showing the highest percent increase (Fig. 5). Similar to the previous discussion on the percent change in homolog group concentration in the sand and trout chow mix, this change may be due primarily to low concentrations of these homolog groups in the control sample (Fig. 6). The BSAF model was validated for the experimental work by comparing the model with the worm data from those exposed to the biouptake layer in NEP-4 and NEP-5. The BSAF model predicted reasonable worm tPCB concentrations, and for the PCB homolog profile of worms exposed to sand-trout chow, errors varied from 1.25 to 58.8% for tri- to octa-PCB homologs. Errors observed for the di- and deca-PCB homolog groups are relatively large (168 to 301%) due to significantly lower experimental baseline concentrations observed for these homolog groups.

Thus, the BSAF model appears to be a reasonable method for predicting PCB concentrations of worms exposed directly to the sediment. Predicted concentration for the worms exposed to sediment is 3 orders of magnitude higher than control worm samples and almost 300 fold higher than the worms exposed to sand-trout chow located on top of the contaminated sediment capped with RCM. Similarly, worms exposed to sand-trout chow above the RCM cap for the naphthalene contaminated tests have significantly lower concentrations compared to the worms directly exposed to the sediment collected from the column device at the end of NEP-15 and NEP-16 tests.

5. Conclusion

The efficiency of using an RCM for reduction of contaminant bio-availability has been investigated for aquatic sediment containing natural levels of PCB and spiking-induced concentrations of naphthalene (the most soluble PAH compound). In the benchscale tests performed, contaminated sediment was covered with the RCM, which was then overlain with clean sand and organic trout chow mix in a consolidation-coupled contaminant transport column device. Following the tests, the sand–trout chow mixture was analyzed for either PCB or naphthalene and then used for biouptake tests with oligochaete worms (*L. variegatus*) and compared to worms directly exposed to contaminated sediment. The BSAF model was validated with experimental data and used to predict the PCB concentration of worms exposed directly to sediment, while measured data was available for worms exposed to naphthalene-spiked sediment.

The sand–trout chow mixture from the column device and control samples indicates limited breakthrough during the column test via consolidation-induced advective and dispersive flux through the RCM. This is consistent with the pore fluid and overlying water concentrations sampled and analyzed during column tests (Meric et al., 2011a). It has been observed that worms exposed directly to contaminated sediment had significantly higher contaminant concentrations as compared to worms exposed to the overlying sand and trout chow mixture, where biota regeneration may be expected to occur in situ (Yu et al., 2009; Meric et al., 2010). These findings indicate a significant decrease in bioavailability of the persistent HOCs in aquatic sediments to the biota due to the placement of an RCM, which may potentially decrease the exposure of contaminants of concern to humans through the food web. Further field testing should investigate the performance of the RCM in field conditions both for isolation, remediation and bioavailability reduction.

Acknowledgments

The work described in this paper is supported by the National Institute of Environmental Health Sciences under grant numbers R01ES16205 and ES00002. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the NIEHS. The authors also acknowledge the efforts of Derek J. Yu and Brian Franklin, undergraduates at Northeastern University, who assisted with the experimental work, and both Brian LaBreque and Scott Forsberg in the organic chemical analytical laboratory at the Harvard School of Public Health, who performed the PCB chemical analyses.

References

- Abramowicz DA. Aerobic and anaerobic PCB biodegradation in the environment. *Environ Health Persp.* 1995; 103:97–9.
- Alshawabkeh AN, Rahbar N, Sheahan TC. A model for contaminant mass flux in capped sediment under consolidation. *J Contam Hydrol.* 2005; 78:147–65. [PubMed: 16005541]
- Ankley GT, Cook PM, Carlson AR, Call DJ, Swenson JA, Corcora HF. Bioaccumulation of PCBs from sediments by oligochaetes and fishes: comparison of laboratory and field studies. *Can J Fish Aquat Sci.* 1992; 49:2080–5.
- ASTM D2434. Standard test method for permeability of granular soils (constant head). ASTM International; West Conshohocken, PA: 2006. www.astm.org. doi: 10.1520/D2434-68R06
- ASTM D2974. Standard test methods for moisture, ash, and organic matter of peat and other organic soils. ASTM International; West Conshohocken, PA: 2007. www.astm.org. doi:10.1520/D2974-07A

- ASTM D854. Standard test methods for specific gravity of soil solids by water pycnometer. ASTM International; West Conshohocken, PA: 2010. www.astm.org. doi: 10.1520/D0854-10
- Barth EF, Reible DD, Bullard A. Evaluation of the physical stability, groundwater seepage control, and faunal changes associated with an AquaBlok® sediment cap. *Remediation*. 2003; 18:63–70.
- Brunson EL, Canfield TJ, Dwyer FJ, Ingersoll CG, Kemble NE. Assessing the bioaccumulation of contaminants from sediments of the upper mississippi river using the field-collected oligochaetes and laboratory-exposed *Lumbriculus variegatus*. *Arch Environ Con Tox*. 1998; 35:191–201.
- Croce V, De Angelis S, Patrolecco L, Polesello S, Valsecchi S. Uptake and accumulation of sediment-associated 4-nonylphenol in a benthic invertebrate (*Lumbriculus variegatus*, freshwater oligochaete). *Environ Toxicol Chem*. 2005; 24:1165–71. [PubMed: 16110996]
- Fisk AT, Wiens SC, Webster GRB, Bergman A, Muir DCG. Accumulation and depuration of sediment sorbed C12- and C16-polychlorinated alkanes by oligochaetes (*Lumbriculus variegatus*). *Environ Toxicol Chem*. 1998; 17:2019–26.
- Fuller ME, Skow KM, Lau S, Ferris H. Trichloroethylene (TCE) and toluene effects the structure and function of the soil community. *Soil Biol Chem*. 1997; 29:75–89.
- Ingersoll CG, Brunson EL, Dwyer FJ. Methods for assessing bioaccumulation of sediment-associated contaminants with freshwater invertebrates. *Proceedings of National Sediment Bioaccumulation Conference*. 1998:125–9.
- Knox AS, Reible DD, Paller MH, Petrisor IG. Innovative in-situ remediation of contaminated sediments for simultaneous control of contamination and erosion. *Savannah River National Laboratory Annual Report 2007, SERDP ER-1501*. 2007:102.
- Knox AS, Paller MH, Reible DD, Ma X, Petrisor IG. Sequestering agents for active caps-remediation of metals and organics. *Soil Sediment Cont*. 2008; 17:516–32.
- Kukkonen JVK, Landrum PF. Toxicokinetics and toxicity of sediment-associated pyrene to *Lumbriculus variegatus* (oligochaete). *Environ Toxicol Chem*. 1994; 13:1457–68.
- Kukkonen JVK, Landrum PF, Mitra S, Gossiaux DC, Gunnarsson J, Weston D. The role of desorption for describing the bioavailability of select polycyclic aromatic hydrocarbon and polychlorinated biphenyl congeners for seven laboratory-spiked sediments. *Environ Toxicol Chem*. 2004; 23:1842–51. [PubMed: 15352471]
- Meijer SN, Ockenden WA, Sweetman A, Breivik K, Grimalt JO, Jones KC. Global distribution and budget of PCBs and HCB in background surface soils: implications for sources and environmental processes. *Environ Sci Technol*. 2003; 37:667–72. [PubMed: 12636263]
- Meric D, Sheahan TC, Alshawabkeh AN, Shine JP. A consolidation and contaminant transport device for assessing reactive mat effectiveness for subaqueous sediment remediation. *Geotech Test J*. 2010; 33:423–33.
- Meric, D.; Rad, MN.; Barbuto, S.; Sheahan, TC.; Alshawabkeh, AN.; Shine, JP. Testing the efficiency of a reactive core mat to remediate subaqueous, contaminated sediments.. *ASCE Proceedings of Geofrontiers 2011 Conference*; Dallas, TX. 2011a. doi: 10.1061/41165(397)92
- Meric, D.; Sheahan, TC.; Alshawabkeh, TC.; Rahbar, N. Numerical modeling of coupled contaminant transport through reactive core mats.. [DVD-ROM] *Proceedings of Battelle 6th International Conference on Remediation of Contaminated Sediments*; New Orleans, LA. 2011c.
- Meric D, Barbuto S, Sheahan TC, Shine JP, Alshawabkeh AN. Bench scale test to assess the efficacy of a reactive core mat to remediate PAH-spiked aquatic sediments. *Soil Sediment Cont*. 2014; 23:18–36. DOI: 10.1080/15320383.2013.772093.
- Murdoch MH, Chapman PM, Norman DM, Quintino VM. Spiking sediment with organ-ochlorines for toxicity testing. *Environ Toxicol Chem*. 1997; 16:1504–9.
- Nebeker AV, Griffis WL, Wise CM, Hopkins E, Barbitta JA. Survival, reproduction and bioconcentration in invertebrates and fish exposed to hexachlorobenzene. *Environ Toxicol Chem*. 1989; 8:601–11.
- Neff, JM. Polycyclic aromatic hydrocarbons in the aquatic environment: sources, fates and biological effects. *Applied Science Publishers Ltd*; Essex, UK: 1979.
- Northcott GL, Jones KC. Spiking hydrophobic organic compounds into soil and sediment: a review and critique of adopted procedures. *Environ Toxicol Chem*. 2000; 19:2418–30.

- Pakdeesusuk U, Freedman DL, Lee CM, Coates JT. Reductive dechlorination of polychlorinated biphenyls in sediment from the twelve mile creek arm of Lake Hartwell, South Carolina, USA. *Environ Toxicol Chem.* 2003; 22:1214–20. [PubMed: 12785576]
- Pickard SW, Yaksich SM, Irvine KN, McFarland VA. Bioaccumulation potential of sediment-associated polychlorinated biphenyls (PCBs) in Ashtabula Harbor, Ohio. *J Great Lakes Res.* 2001; 27:44–59.
- Pickard SW, Clarke JU, Lotufo GR. Bioaccumulation and bioavailability of Mirex from Lake Ontario sediments. *B Environ Contam Tox.* 2005; 74:1084–91.
- Reible DD, Hayes D, Lue-Hing C, Patterson J, Bhowmik N, Johnson M, et al. Comparison of the long-term risks of removal and in situ management of contaminated sediments in the Fox River. *Soil Sediment Cont.* 2003; 12:325–44.
- Reid BJ, Northcott GL, Jones KC, Semple KT. Evaluation of spiking procedure for the introduction of poorly water soluble contaminants into soil. *Environ Sci Technol.* 1998; 32:3224–7.
- Sokol RC, Kwon O, Bethoney CM, Rhee G. Reductive dechlorination of polychlorinated biphenyls in St. Lawrence river sediments and variations in dechlorination characteristics. *Environ Sci Technol.* 1994; 28:2054–64. [PubMed: 22191744]
- Sun X, Ghosh U. The effect of activated carbon on partitioning, desorption, and biouptake of native polychlorinated biphenyls in four freshwater sediments. *Environ Toxicol Chem.* 2008; 27:2287–95. [PubMed: 18517308]
- [2011 June] U.S. Army Corps of Engineers, ERDC, EL, BSAF Database. c2011. Available from: <http://el.erd.usace.army.mil/bsafnew>
- U.S. Environmental Protection Agency. Bedded sediment bioaccumulation tests. 1993:231. EPA/600/R-93/183.
- U.S. Environmental Protection Agency. Determination of Rates and Extent of Dechlorination in PCB-Contaminated Sediments During Monitored Natural Recovery. 2008:7. EPA/600/S-08/012 Sediment Issue.
- U.S. Environmental Protection Agency. [2011 June] CERCLIS Database: Superfund Site Information. c2011. Available from: <http://cfpub.epa.gov/supercpad/cursites/srchsites.cfm>
- Van Gestel M, Merckx R, Vlassak K. Spatial distribution of microbial biomass in micro-aggregates of a silty-loam soil and the relation with the resistance microorganisms to soil drying. *Soil Biol Chem.* 1996; 28:503–10.
- Vinturella AE, Burgess RM, Coull BA, Thompson KM, Shine JP. Use of passive samplers to mimic uptake of polycyclic aromatic hydrocarbons by benthic polychaetes. *Environ Sci Technol.* 2004; 38:1154–60. [PubMed: 14998031]
- Vorhees DJ, Cullen AC, Altshul LM. Polychlorinated biphenyls in house dust and yard soil near a superfund site. *Environ Sci Technol.* 1999; 33:2151–6.
- Yin, K.; Viana, PZ.; Rockne, KJ. Verification of active cap contaminant breakthrough simulations via laboratory column studies.. [DVD-ROM] Proceedings of Battelle 5th International Conference on Remediation of Contaminated Sediments; Jacksonville, FL. 2009;
- Yu, D.; Meric, D.; Sheahan, TC.; Alshawabkeh, AN.; Shine, JP. A new sediment testing column to assess reactive mat effectiveness for isolation and remediation.. [DVD-ROM] Proceedings of 5th Intl. Conf. on Remediation of Contaminated Sediments; Jacksonville, FL. 2009;

Fig. 1.
Schematic of the ICSTAC testing device.

Fig. 2.
PCB congener profile of the Neponset River (Milton, MA) sediment.

Fig. 3.
Percent change of homolog group concentrations of sand-trout chow mixture during ICSTAC tests.

Fig. 4.

PCB homolog fraction profiles of sand–trout chow mixtures sampled after ICSTAC test and control sample; a) NEP-4 test, b) NEP-5 test, and c) control sample.

Fig. 5.
Percent change of PCB homolog groups of sand-trout chow exposed worms (*Lumbriculus variegatus*) during the bioaccumulation tests.

Fig. 6. PCB homolog fraction profiles of worms (*Lumbriculus variegatus*) after bioaccumulation test and control sample; a) NEP-4 test, b) NEP-5 test, and c) control sample.

Fig. 7. Comparison of experimental data and BSAF model prediction of PCB biouptake of worms (*Lumbriculus variegatus*); a) exposed to NEP-4 sand and trout chow mix, and b) exposed to NEP-5 sand and trout chow mix.

Fig. 8. BSAF model prediction for PCB biouptake of worm (*Lumbriculus variegatus*) with direct exposure to Neponset River sediment (no RCM capping).

Table 1

Solute transport experiments summary.

Test name	Contaminant used	Contamination type
ICSTAC-NEP-4	PCBs	Sampled
ICSTAC-NEP-5	PCBs	Sampled
ICSTAC-NEP-15	Naphthalene	Spiked
ICSTAC-NEP-16	Naphthalene	Spiked