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Benchscale Assessment of the Efficacy of a Reactive Core Mat to Isolate PAH-spiked Aquatic Sediments

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Abstract

This paper describes the results of a benchscale testing program to assess the efficacy of a reactive core mat (RCM) for short term isolation and partial remediation of contaminated, subaqueous sediments. The 1.25 cm thick RCM (with a core reactive material such as organoclay with filtering layers on top and bottom) is placed on the sediment, and approximately 7.5 – 10 cm of overlying soil is placed on the RCM for stability and protection. A set of experiments were conducted to measure the sorption characteristics of the mat core (organoclay) and sediment used in the experiments, and to determine the fate of semi-volatile organic contaminants and non-reactive tracers through the sediment and reactive mat. The experimental study was conducted on naphthalene-spiked Neponset River (Milton, MA) sediment. The results show nonlinear sorption behavior for organoclay, with sorption capacity increasing with increasing naphthalene concentration. Neponset River sediment showed a notably high sorption capacity, likely due to the relatively high organic carbon fraction (14%). The fate and transport experiments demonstrated the short term efficiency of the reactive mat to capture the contamination that is associated with the post-capping period during which the highest consolidation-induced advective flux occurs, driving solid particles, pore fluid and soluble contaminants toward the reactive mat. The goal of the mat placement is to provide a physical filtering and chemically reactive layer to isolate contamination from the overlying water column. An important finding is that because of the high sorption capacity of the Neponset River sediment, the physical filtering capability of the mat is as critical as its chemical reactive capacity.

Keywords

Contamination; Sediment; Remediation; Reactive Mat; RCM; Organoclay

1. INTRODUCTION

Reactive core mats (RCMs) (Figure 1) represent a new class of sediment remediation tool, with the mat consisting of a reactive layer containing one or more neutralizing or otherwise reactive materials (i.e. organoclay, apatite, activated carbon) that is confined between two permeable geotextile filtering layers. With the inclusion of the reactive material, RCMs have the potential to not only physically sequester the contaminants in the underlying sediment by preventing transport of organic particle-associated contaminants (as in traditional geomaterial caps), but also have the potential to adsorb and immobilize the target contaminants in the sediment transported via advective and dispersive pore fluid flux, and

retard contaminant breakthrough to the overlying biologically active zone and water column (Sheahan et al., 2003). The RCM's reactive capacity, combined with the strength of the confining geotextiles, enables use of thin layers of reactive material with fewer physical stability concerns. RCM technology has been adopted in several U.S. EPA Superfund site projects (e.g., Grand Calumet River, Indiana; Bridgeport Rental & Oil Services (BROS) Site, Logan, New Jersey; Stryker Bay, Duluth, Minnesota; and West Doane Lake, Portland, Oregon; CETCO, 2010) as part of the overall remediation strategy in the last two years. However, isolation and remediation efficiency, as well as sorption capacity of the material are not well understood.

When placed on soft, aquatic sediments, the RCM and the overlying armoring soil layer (typically 8–10 cm thick) introduces a surcharge load that consolidates the sediment and creates a consolidation-induced pressure gradient and resulting advective flux that drives solid particles, pore fluid and soluble contaminants toward the RCM. The RCM is intended to provide a physical filtering and chemically reactive layer to isolate the contamination from the overlying water column.

This paper presents an experimental study on an RCM with a reactive core containing organoclay (PM-199, CETCO Corp., IL, USA) with a particularly high organic carbon fraction ($f_{oc} = 25\%$) to investigate the RCM's short term efficacy in isolating and partially remediating a natural sediment spiked with a specific polyaromatic hydrocarbon (PAH; naphthalene). The purpose of the experimental study is to obtain data that represents the sediment-RCM-overlying sand-water column behavior during the high flow, advective flux phase after RCM application. A new device was developed, the Integrated Contaminated Sediment Testing Apparatus Column (ICSTAC), to physically model the composite column. The ICSTAC device is first presented, after which the paper describes the field sampling of the sediment, storage and spiking protocols for the sediment, and the chemical and physical properties of the reactive organoclay. The testing program and results are presented, including use of the ICSTAC device for tests on sediment spiked with either with a non-reactive tracer or with the model PAH.

MATERIALS AND METHODS

2.1. Sediment & Soil

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.). Fifty liters of sediment were collected from the sampling location. Collected sediment was transferred into clean, non-translucent 18.9 L (5 gallon) HDPE buckets that were sealed, transported to the laboratory, and stored in a 10°C temperature room to minimize microbial activity. The samples were stored until settling of the solids had taken place. Collected sediment was classified as highly organic soil according to Unified Soil Classification System (USCS) due to the following characteristics: primarily composed of organic matter, dark in color, having a distinctive odor, and having limited variability. 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 (less than 1 ppm on average; Breault et al., 2004) and 10.6 ppm total PCB concentration.

At the conclusion of the settling period, the overlying water was decanted by siphoning. Organic debris and stones estimated to be larger than the opening of a 40 mL vial (18 mm diameter opening), were removed from the sediment by hand. Using one sample from each

bucket, tests were conducted on the remaining sediment to determine water content, organic matter content (ASTM D 2974,2007), specific gravity of solids (ASTM D 854,2010a), and hydraulic conductivity (ASTM D 2434,2006) of the sediment, on average, the test sediment contained 71.3% water by mass, 23% total organic matter (based on loss on ignition at 550 °C), 14.03% organic carbon fraction (EPA Method NCEA-C-1282, US EPA, 2002), a specific gravity of solids, $G_s = 2.3$, and an initial hydraulic conductivity of 4×10^{-5} m/sec. It should be noted that the organics content of the Neponset River sediment is higher than that reported for some other rivers studied for aquatic sediment contamination (e.g., Fox River 11.7–12.4% Hollifield et al., 1995; Anacostia River 2–10% MacAvoy and Bushaw-Newton, 2007; 0.6–19% in Hudson River, House and Denison, 2002) resulting in an increased sorption capacity for organic compounds.

For the ICSTAC tests using a non-reactive tracer, a natural silt (from another location) was used as the baseline soil due to its lower absorption, negligible organic content (0.23%), expected lower cation exchange capacity, and significantly lower organic carbon content compared to the Neponset River sediment. This sample was mixed to achieve a 39% water mass in total, which is twice the soil's liquid limit (ASTM D 4318,2010b), to simulate the physico-mechanical consistency of an aquatic sediment.

2.2. Spiking Compound and Method

2.2.1. Naphthalene Spiking of Neponset River Sediment—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 low cost. A nominal concentration of 250 mg/kg sediment was targeted, providing sufficient resulting concentrations above background values for measurement and modeling of reactive transport through the sediments and RCM.

Sediment samples were kept in their field-wet condition 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 mL/mg (volume of solvent:weight of compound) was adopted. Analytical grade acetone was used as the solvent with 1:8 mL/mg 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 in proportioning the solvent 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 (160 ± 2 mg), and 20 ml of analytical grade acetone solvent (Fisher Scientific, A 928-4, Pittsburg, PA) were first mixed, and the resulting solution (containing 160 mg naphthalene) was added to each sample jar containing 640 grams dry mass of sediment.

After the naphthalene spiking was completed, the jars were 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. Based on Reid et al. (1998) a mixing time of two weeks (14 days) was adopted, performed at 4 °C in a controlled cold room to minimize biological effects. At the end of spiking, the sediment-naphthalene mixture was immediately used in the experiment with no significant post-mixing storage duration. It has been shown that sorption/desorption chemistry and bioavailability of the spiked compounds differ from those in the native contaminants

(Alexander, 1995; Ten Hulscher et al., 1999), with higher mobility that would be advantageous considering the limited experimental durations.

2.2.2. Chloride and Bromide Spiking to Natural Silt—Chloride (Cl^-) and bromide (Br^-) were selected as the non-reactive tracers for ICSTAC tests because their anionic form reduces the likelihood of absorption on soil particles, thus maximizing the tracer's mobility. Inert silt was used as baseline soil in tracer tests to assure that no sorption or retardation of compounds occur within the porous media. This was done to better represent the baseline solute transport abilities of the testing device since it was anticipated that using the complex Neponset River sediment would have increased the uncertainty of baseline results. The baseline soil pore fluid in these experiments initially contained 175mg/L Cl^- natural concentration based on the analysis of saturation extract. Additional sodium chloride (NaCl) and sodium bromide (NaBr) salts were added to achieve an average nominal pore fluid concentration of 325mg/L Cl^- and 150mg/L Br^- for the non-reactive tracer tests. After spiking, the sediment was mixed for 24 hours to ensure homogeneous distribution of the tracer.

2.3. ICSTAC Testing Device

2.3.1. Description of Device—The ICSTAC device is a coupled, large-strain consolidation and contaminant transport device that can also be used to simulate upward submarine flow and groundwater discharge conditions. As shown in Fig. 2, the ICSTAC device is intended to be an accurate physical model of the aquatic sediment “stack” or column, including the contaminated sediment, the RCM, overlying clean sand layer (“biouptake zone”) and water column. The sand layer actually consisted of medium gradation sand mixed with 3% by mass Omega One® “trout chow” organic matter to promote retention of any contaminants that may break through the RCM, since the biouptake zone samples collected at the end of the tests are used in bioavailability tests with oligochaete worms (Meric et al., 2012). 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 ICSTAC's acrylic column (Fig. 2), 20.3 cm (8 in) diameter, 40.6 cm (16 in) high, serves as both the vertical flow-deformation process column for the testing, and a guide and sealing boundary for the loading piston to travel through. As described in Meric et al. (2010), porous ceramics are placed on top and bottom of the symmetrically channeled piston, and two O-rings are used on the piston perimeter to ensure that no preferential flow takes place in the device. Two independent pressurized water cylinders allow equal backpressure to be applied across the specimen for system saturation. 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 is actuated by deadweight loads. The development and proof-testing of this device is presented elsewhere (Yu et al., 2009; Meric et al., 2010).

2.3.2. Testing Procedures—Prior to testing, all device components were washed with industrial grade hexane (CQ Concepts Inc., CAS# 110-54-3) to dissolve any potentially adsorbed organic compounds from previous tests. Sediment was scooped and poured into the acrylic column to the desired initial height of 17.8cm to achieve a 1:1 height-to-diameter ratio for geotechnical aspect of the experiment. With the exception of control tests in which no reactive mat was used, a section of RCM with approximately the same diameter as the column was placed in the column on top of the sediment layer. The loading piston was then inserted, the sand-trout chow mixture placed onto the piston, and the system sealed.

Once the set-up procedures were completed, the system was back pressured to 200 kPa to ensure sediment saturation. Consolidation was initiated approximately 24 hours later, and performed using three stress increments of 10, 25 and 55 kPa (only 10 and 25 kPa were applied in the non-reactive tracer test), with each increment applied for 24 hours. It should be noted that except for 10 kPa, these are relatively high stress increments compared to what is expected in the field; they were selected to create higher pore fluid flux induced by consolidation for a more robust test of the RCM. As the consolidation load is applied, sediment pore fluid moves through the RCM and into the overlying water above the sand-trout chow layer (Fig. 2). 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, 60 min, 180 min, 360 min, 540 min, 720 min and 1440 min (samples were collected at $t = 0^-$, 180 min, 360 min, 720 min and 1440 min elapsed time for the non-reactive tracer test). Since the rate of consolidation is initially much faster and therefore provides higher initial advective flux than at later times during the stress increment, samples are collected more frequently in the early stage of each stress increment than later on. Collected water samples were placed in 20 ml glass vials and refrigerated at 4°C until analysis.

At the end of the test, the overlying water was drained into a sampling bottle, the sand-trout chow mix collected in a wide-necked sampling bottle, and the reactive core mat and the contaminated sediment each placed in individual, air-tight, zip-locked plastic bags (no RCM and sand layer were used in the non-reactive tracer test).

The collected materials all underwent subsequent analysis for total naphthalene content, and the sand-trout chow mixture was used for 28-day exposure tests on *Lumbriculus variegatus*, an oligochaete worm. The results of these bioaccumulation tests are presented elsewhere (Meric et al., 2012).

2.4. Chemical Analysis

2.4.1. Water Sample Analysis: Naphthalene—To analyze the concentrations of naphthalene in the ICSTAC water samples, EPA Method 8270C (US EPA, 1996), *Semi-volatile Organic Compounds by GC-MS*, was followed for sample preparation. A ratio of 1:1 hexane (Fisher Scientific, #H307-4) was added to each ICSTAC water sample for naphthalene extraction. Those mixtures were then shaken vigorously for 3 minutes and allowed to phase separate for 30 minutes. Following the separation, 1 ml of the non-aqueous top layer was removed and analyzed using a Varian™ 430GC-220MS. This GC-MS system is equipped with a 30×0.25 mm capillary column and was operated under the following chromatographic conditions: injector temperature of 270°C, split ratio of 20, and an oven temperature programmed as follows: 100°C for 1 minute increasing at 5°C per minute until reaching 150°C, where it remains for 1 minute. Helium under 70 kPa of pressure is used as the carrier gas.

2.4.2. Sediment and Biouptake Zone Analysis: Naphthalene—Upon completion of the ICSTAC tests, biouptake zone and sediment samples were analyzed for naphthalene content using the methods described in Vinturella et al. (2004) for naphthalene. Briefly, the sediment/biouptake zone 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.

Samples for naphthalene were analyzed on an Agilent Gas Chromatograph with mass selective detector in selected ion mode with a 30 m, 0.18 mm i.d., 0.18 μ m film thickness DB-KLB column utilized to quantify naphthalene. Quantification was based on external standards containing surrogates, the internal standard, and the analytes of interest. Method detection limits were calculated for each analyte by multiplying the procedural blank standard deviation value for each analyte by 3.

2.4.3. Water Sample Analysis: Chloride and Bromide—Ion chromatography was used for the analysis of the non-reactive tracers (Cl^- and Br^-) in water samples. EPA Method 300.0D (US EPA, 1993), *Determination of Inorganic Anions by IC*, was used as guideline for the analyses. Samples were filtered with 0.22 μ m filtration membrane under vacuum, and after each sample analysis, the filter membrane was changed to prevent cross-contamination. After the filtration, 5 mL of each sample was transferred into analysis vials and analyzed by a Dionex-120 IC.

2.4.4. Adsorption Tests—Adsorption isotherms were obtained for naphthalene adsorption on Organoclay PM-199TM (CETCO Corp.), the reactive material within the tested RCM, and Neponset River sediment. A protocol was developed based on EPA 712-C-08-009 (US EPA, 2008), *Fate, Transport and Transformation Test Guidelines OPPTS 835.1230 Adsorption/Desorption, (Batch Equilibrium)*. A saturated naphthalene solution (Acros Organics, #180902500) was prepared at a concentration of 32 mg/L. Preliminary tests were performed using this solution and the tested material to determine the proper ratio and equilibrium time of adsorption. Adsorption was then studied using different solution-to-adsorbent ratios. A constant 50 mL of naphthalene solution and varying masses of Organoclay adsorbent (6.2, 10.6, 16.1, 21.1, 25, 32.2, 74.7, 140.8, 198.3, 252.9, 321.8, 490.2, 690.4, 880.6 mg) were put into each glass flask. The flasks were tightly closed with stoppers and shaken at 150 rpm for the sample type's respective equilibrium time (48 hours was adopted for the given case). This mixture was then centrifuged at 6000 rpm for 5 minutes and the solution taken out and prepared for sample analysis using the GC-MS as described above. Adsorption curves were prepared to compare adsorbed naphthalene versus equilibrium naphthalene concentration in water.

3. RESULTS AND DISCUSSION

Results from the following tests are presented: sorption tests on Organoclay PM-199TM and Neponset River sediment, and tests using the ICSTAC device on spiked Neponset River sediment and on silt with non-reactive tracer compound added.

3.1. Adsorption Test Result

Adsorption testing was conducted on Organoclay PM-199TM, the material that is used in the RCM as a reactive layer, and unamended Neponset River sediment with a relatively high organic carbon content (25%). A linear isotherm is used to analyze these data, as shown in Figure 3 for Organoclay and Figure 4 for Neponset River sediment.

The sorption test conducted on Organoclay PM-199TM with naphthalene solution resulted in a sorption curve with upward curvature (Fig. 3a). The upward trending sorption curve, with a more dramatic increase in sorption capacity at higher equilibrium concentrations (C_e), follows neither Freundlich nor Langmuir isotherms, and differs from the manufacturer's reported sorption behavior. Initially, the last data point was assumed to be an outlier, and a linear isotherm was used to analyze the remaining data (Figure 3b; 8,890 L/kg, $R^2 = 0.907$). However since this type of sorption curves has been reported previously, and has been dubbed "cooperative sorption" (Li et al., 2006), indicating weak naphthalene-organoclay interaction at low concentrations and increasing sorption behavior with condensation of

hydrophobic organic compound in the sorbent's inner structure (Hundal et al., 2001). Similar upward trending sorption isotherms have been reported for various PAHs sorbing onto bentonite-based Organoclay PM-199 (Lee et al., 2012). Upward curvature has been widely observed with hydrophobic organic compounds, especially at high saturation concentrations in the vicinity of solubility limits (i.e., Yaron et al., 1967; Karickhoff et al., 1979; Weber et al., 1992; Li et al., 2004; Holbrook et al., 2004; Wang et al., 2007; and Oleszczuk, 2009). When the full data set is considered, due to upward curvature of the isotherm, the Freundlich equation failed to model the phenomena adequately. Consequently, the measured sorption isotherm was analyzed as a bilinear relationship with two different linear partitioning coefficients, one for $C_e < 0.5$ mg/L (9,180 L/kg, $R^2 = 0.928$), and one for $C_e > 0.5$ mg/L value (40,350 L/kg, $R^2 = 0.920$), with an overall C_e range of 0.2 to 0.8 mg/L. This compares with a previously reported linear partitioning coefficient for Organoclay PM-199 and naphthalene of 3,285 L/kg for C_e range of 0.5 mg/L to 4.0 mg/L (Reible et al., 2008). The difference is believed to be due to recent modifications of the surfactant and the pore structure of the organoclay compared to the previously used bentonite-based version of organoclay (Reible et al., 2008). For example, Organoclay PM-199 used in the presented study does not show swelling behavior when contacted with water as opposed to the swelling observed in the previous bentonite based Organoclay PM-199 version.

Adsorption tests conducted with the high organic content Neponset River sediment resulted in a K_d of 13,900 L/kg. It should be noted that high sorption capacity of the Neponset River sediment is associated with the case specific high organic carbon fraction and cannot be generalized for all aquatic sediments, which often have lower organic carbon contents. It is noted that organic carbon configuration of the sediment is as important as the organic carbon content, since different organic carbon particles (e.g., wood, partially oxidized coal, coke, lignite, charcoal, wood, cenospheres, char and pitch) have been reported to have different sorption capacities (Ghosh et al., 2003). In addition, K_d for the trout chow used in the overlying sand-trout chow layer was found to be 1,561 L/kg for naphthalene.

Theoretical approach was followed to back calculate the experimentally obtained partition coefficient values using the organic carbon fraction of the sediment and Organoclay and the octanol water partition coefficient (K_{ow}) of the naphthalene. Log K_{ow} and Log K_{oc} for naphthalene was estimated as 3.30 and 3.18 respectively by using KOWWIN (US EPA, 2012). Considering the organic carbon fraction of the sediment and organoclay, theoretical predictions of partition coefficients (211.9 L/kg for sediment and 378.4 L/kg for organoclay) are more than an order of magnitude smaller than experimental predictions. However, similar significant deviation was also observed in previously mentioned studies with naphthalene sorption onto organoclay (Lee et al., 2012). This indicates that the theoretical estimation of partitioning coefficients for hydrophobic organic compounds with high organic carbon fraction sediments may not be representative of measured values.

The presented results indicate that Organoclay PM-199TM has slightly lower sorption ability at lower concentrations and higher sorption capacity for higher equilibrium concentrations compared to highly organic sediment. Measured data also indicates that Organoclay PM-199TM has higher sorption capacity (9,180 L/kg for $C_e < 0.4$ mg/L and 40,350 L/kg for $C_e > 0.4$ mg/L) than the lipid based trout chow for naphthalene, a lipophilic compound (1,561 L/kg).

3.2. ICSTAC Tests Results

Nine ICSTAC tests were conducted using spiked Neponset River sediment under four different conditions, and one ICSTAC test was conducted with the non-reactive tracer-spiked silt. The hypothesis to be tested in these tests was two-fold: first, using non-reactive tracer tests, that the ICSTAC device itself will not significantly affect chemical transport

through the ICSTAC column components; and second, using naphthalene-spiked sediment tests, that the RCM will isolate the contaminants by reducing the concentration of naphthalene in the overlying biouptake zone or water when compared to tests in which no RCM is used. Each condition was duplicated to assess the precision of the findings for naphthalene-spiked tests, except for the case in which neither an RCM nor a biouptake layer was used (test no. NEP-20). Details of the testing conditions are summarized in Table 1.

3.2.1. Overlying Water and Pore Fluid Analysis—In tests NEP-13 to -22 samples were taken from the water overlying the sand or biouptake layer (or, if no such layer was used, above the loading piston) and from the sediment pore fluid, and chemically analyzed for naphthalene concentrations. These results are presented as follows. The overlying water (“top”) concentrations for NEP-13 and -14, (with sand and trout chow, no RCM) are compared to the sediment (“bottom”) concentrations for NEP-14 since a similar level and trend of normalized sediment pore fluid concentrations were observed in tests NEP-13 and -14. Similarly, the top concentrations of NEP-15 and -16 (with RCM, sand and trout chow) are compared to the bottom concentrations from NEP-16, and the top concentrations of NEP-18 and -19 (with sand only, no RCM and trout chow) with bottom concentration of NEP-18. Finally, the overlying water naphthalene concentrations of NEP-21 and -22 (repetition of test with sand and trout chow, no RCM) was presented by normalizing with the pore fluid concentration of NEP-21. In all cases, concentrations were normalized by the initial bottom total concentration, prior to the start of the 10 kPa increment, for a given test, which is explained by the initial “bottom” $C/C_0 = 1.0$ for all tests at $t=0^-$ in the 10 kPa data.

The non-reactive tracer test (NEP-23) results for chloride and bromide are given directly as concentrations for 10 kPa and 25 kPa stress increments (Fig. 5). However, for naphthalene-spiked tests, data are presented with dual y-axis plots (both normalized and direct naphthalene concentration) for all tests in Figure 6a, 6b and 6c for the 10 kPa, 25 kPa and 55 kPa stress increments, respectively.

It is useful to examine first the non-reactive tracer test results (NEP-23) as a baseline to interpret the other test results. Referring to Fig. 5, these tests indicate that the ICSTAC device physically allowed contaminant transport proportional to the flux occurring due to volume change in the tested soil. It is observed that both Cl^- and Br^- concentrations follow the same pattern and at the end of the 25 kPa stress increment, and the mass balance calculation (shown in Table 2) indicate no significant loss of mass due to physical sorption onto the device itself. However, low initial concentrations at the bottom for both compounds indicate that sediment was exposed to fresh water during the backpressure phase (as described in Section 2.3.2), thus initially lowering the sediment pore fluid concentrations of the tracer relative to initial levels.

Naphthalene concentrations measured in the pore fluid samples are similar for all tests (1.42 to 3.44 mg/L) except for lower values observed in the NEP-13 and -14 (with sand and trout chow, no RCM; average 0.42 ± 0.09 mg/L). Tests NEP-15 and -16 (RCM, sand and trout chow) showed the lowest average breakthrough concentration in the overlying water (0.036 ± 0.02 mg/L), a 63-fold reduction from the average pore fluid concentration measured (2.24 ± 0.51 mg/L). Tests NEP-13, -14, -21 and -22 (with sand and trout chow, no RCM) also had low overlying water concentrations (0.042 ± 0.03 mg/L), but only a 10-fold decrease, hypothesized to be related to the low initial pore fluid concentration. The overlying water samples in NEP-18 and NEP-19 tests (only sand, no RCM) yield slightly higher concentrations (0.23 ± 0.12 mg/L), an 11-fold reduction compared to pore fluid concentration (2.52 ± 0.54 mg/L), as in the NEP-13 and NEP-14 tests (sand and trout chow, no RCM). However NEP-20 test with no overlying barrier yield only a 6-fold difference between the pore fluid (3.08 ± 1.02 mg/L) and overlying water concentrations (0.52 ± 0.34

mg/L), which is related to dilution of upflowing pore fluid into initially clean overlying water. The very low standard deviation values for overlying water and pore fluid concentrations indicate that for all tests except for the NEP-20 (test with no barrier), there is little variation throughout the test. Consequently, the naphthalene transport data based on absolute and normalized concentrations from NEP-13 to -22 (Figs 6a,6b, and 6c) indicate the following: tests with the RCM layer (NEP-15 and -16) showed almost no naphthalene breakthrough to the overlying water layer. NEP-13 and -14 (sand and trout chow, no RCM) and NEP-18 and -19 (sand only, no RCM) provided similar results with limited breakthrough ($C/C_0 = 0.1\text{--}0.2$). However, NEP-20 (no RCM, sand layer or organic admixture) resulted in significant breakthrough ($C/C_0 = 0.3\text{--}0.6$).

3.2.2. Overlying Biouptake Layer and Sediment Analysis—Analysis of biouptake layers resulted in recovery values that were too low to be considered in data analysis (surrogate recovery less than 60%). Only 4 out of 10 tests yielded recoveries high enough to be considered valid (NEP-15, -16, -21, and -22). Similarly the comparison of naphthalene concentrations of the underlying sediment and the biouptake zone samples collected were analyzed for NEP-15 and -16 (RCM, sand and trout chow) and NEP-21 and -22 (sand and trout chow, no RCM). Analysis of the post-column experiment sediment from NEP-15, -16, -21 and -22 showed significantly lower naphthalene concentrations than the spiking concentration ($33,903 \pm 9,350$ ng/g versus 250,000 ng/g target spiking concentration). This may be due to the combined effects of the relatively low efficiency of the spiking process (Murdoch et al., 1997), desorption and dilution in pore fluid and/or overlying water (Meric et al., 2012), sorption by the RCM, and volatilization losses during sample handling and analysis. The biouptake zone naphthalene concentrations were 1.253 and 4.445 ng/g for NEP-15 and -16, respectively, and 2,300 and 3,700 ng/g for NEP-21 and -22, respectively (Figure 7). Background naphthalene concentrations of the biouptake layer and reference sediment for spiking were 0.51 and 65 ng/g respectively.

Based on the given sorption and ICSTAC tests data, experimental evidence shows that the RCM with an Organoclay PM-199 core provides an enhanced level of contaminant isolation of the overlying water from the sediment compared to tests in which no RCM was used. A limited change in biouptake layer naphthalene concentration was observed in tests with RCM, sand and trout chow (NEP-15 and -16) compared to background concentrations, whereas a 4,000 to 7,000 fold increase was observed in tests with sand and trout chow only (2,300 and 3,700 ng/g versus 0.51 ng/g). This enhanced isolation can be attributed to: the physical filtering capacity of the RCM, particularly in the early stages of each stress application when high advective flux may not allow the RCM to effectively chemically adsorb contaminants attached to dissolved organic matter; and, the chemical adsorption of the RCM, particularly at later, lower advective rate stages of the stress increments. Thus, it is concluded that the physical filtering capacity of the RCM is as important as its reactive capacity. Use of the sand layer alone was less effective than when the RCM was used, but sand alone provided fairly good isolation for naphthalene breakthrough from underlying sediment. However, no significant difference was observed between the tests with and without organic admixture. This indicates that even though the RCM with overlying sand and trout chow layer provides higher relative isolation of contaminants from overlying geomaterial and water column, the use of only a 7.6 cm (3 in.) thick layer of sand with organic matter can provide fairly good isolation when there is no additional significant submarine upflow. However, additional testing is underway to determine if such small differences in sequestration ability can be sustained over longer periods of time with upward flow introduced into the column experiments.

4. CONCLUSIONS

An upward trending sorption curve was observed for naphthalene in Organoclay PM-199, indicating that sorption ability increases with increasing naphthalene concentration, which is consistent with previously reported findings on organic amendments, i.e., the presence of multi-layered sorption sites leads to activation of additional sorption sites in saturated solutions. Based on contaminant concentrations measured in overlying water and the biouptake zone in consolidation-coupled contaminant transport (ICSTAC) tests (RCM versus no RCM tests), it can be concluded that the RCM provides more enhanced isolation over the use of sand isolation alone. In addition, the overlying water column concentrations from tests with no RCM showed no significant difference between the only sand and sand with trout chow tests. Further testing with submarine upflow should be conducted to investigate the long term efficacy and capacity of the RCM layer in more detail, and to assess longer-term differences in the sequestration abilities of the RCM-sand-organic mixture, and those of the sand-organic mixture alone.

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Fig. 1.
Schematic and Photo of the Reactive Core Mat (with courtesy of CETCO Corp., IL)

Fig. 2.
Schematic of the ICSTAC testing device

Fig. 3a.Adsorption isotherm for Organoclay PM-199™ with All Data Points

Fig. 3b.Adsorption isotherm for Organoclay PM-199™ with Linear Partition Analysis by Excluding the Last Data Point

Fig 3.

Fig. 3a. Adsorption isotherm for Organoclay PM-199™ with All Data Points

Fig. 3b. Adsorption isotherm for Organoclay PM-199™ with Linear Partition Analysis by Excluding the Last Data Point

Fig. 4.
Adsorption isotherm for Neponset River sediment

Fig. 5.
Bromide and Chloride concentration for 10 and 25 kPa stress increments

Fig.6a.

Fig.6b.

Fig.6c.

Fig. 6.
 Fig. 6a. Normalized and absolute naphthalene concentrations in overlying water and sediment pore fluid at 10 kPa stress increment for a) NEP-13 & -14; b) NEP-15 & -16; c) NEP-18 & -19; d) NEP-20; e) NEP-21 & -22
 Fig. 6b.. Normalized and absolute naphthalene concentrations in overlying water and sediment pore fluid at 25 kPa stress increment for a) NEP-13 & -14; b) NEP-15 & -16; c) NEP-18 & -19; d) NEP-20; e) NEP-21 & -22
 Fig. 6c.. Normalized and absolute naphthalene concentrations in overlying water and sediment pore fluid at 55 kPa stress increment for a) NEP-13 & -14; b) NEP-15 & -16; c) NEP-18 & -19; d) NEP-20; e) NEP-21 & -22

Fig. 7.
Naphthalene concentrations of the spiked sediment, overlying biouptake zone sampled at the end of NEP-15 and -16 (RCM, Sand and Trout Chow), NEP-21 and -22 (Sand and Trout Chow, no RCM), reference sediment and control biouptake zone

TABLE 1

Experiment List and Summary of Testing Conditions

Test Name	Testing Conditions		
	RCM	Sand	Organic Matter
NEP-13		•	•
NEP-14		•	•
NEP-15	•	•	•
NEP-16	•	•	•
NEP-18		•	
NEP-19		•	
NEP-20			
NEP-21		•	•
NEP-22		•	•

TABLE 2

Calculation of Mineral Loss During Non-reactive Tracer ICSTAC Tests

25 kPa Stress Increment 12 hour sample set		
Total Br ⁻ added initially	650	mg
Overlying water concentration	10.2	mg/L
Sediment pore fluid concentration	127.4	mg/L
Br ⁻ in overlying water	71.5	mg
Br ⁻ in sediment pore fluid	555.5	mg
Total Br ⁻ captured in sample set	627	mg