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Bioturbation Facilitates DDT Sequestration by Activated Carbon against Recontamination by Sediment Deposition

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Abstract: We evaluated bioturbation as a facilitator for in-situ treatment with a thin-layer of activated carbon (AC) to treat dichlorodiphenyltrichloroethane (DDT)-contaminated sediment and contaminant influx by sediment deposition. Using the freshwater worm, *Lumbriculus variegatus* as a bioturbator, microcosm time-series studies were conducted for four months and monitored for DDT flux and porewater concentration profiles by passive samplers. With bioturbators present, the thin-layer AC amendment reduced DDT flux by >90% compared to the same simulated scenario without AC amendment. In contrast, a clean sediment cap without AC was ineffective in reducing flux when bioturbation was present. In simulated scenarios with contaminant influx through deposition of contaminated sediment, bioturbation facilitated in-situ AC treatment, reducing 4-month DDT flux by 77% compared to the same scenario without bioturbation. Porewater concentration profiles and AC dose profiles confirmed effective mixing of AC particles down to 1 cm depth. A mass transfer model was developed to predict flux with consideration of bioturbation and sediment deposition processes. Predicted flux values were consistent with experimental results and confirm that bioturbation activity helps reduce DDT sediment-to-water fluxes in AC-treated sediment with recontamination by contaminated sediment deposition. This is the first study to developed combined experimental and modeling results showing how bioturbation enhances AC amendment effectiveness against ongoing contaminant influx by sediment deposition.

Keywords: Sediment chemistry, Bioturbation, Persistent organic pollutants, Activated carbon amendment, Flux

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INTRODUCTION

In-situ treatment with activated carbon (AC) is a promising sediment remediation strategy. The technology utilizes AC as an amendment in which the strong sorption properties of the AC reduces the bioavailability of hydrophobic organic contaminants (HOCs) through reductions in porewater concentrations and biouptake by benthic organisms [1]. AC is considered an "active" material due to its physicochemical properties that strongly sequester HOCs; this is in contrast to non-active material, such as sand and clay that lack significant sorption capacity to sorb HOCs. Remediation studies with AC typically employ some form of mechanical mixing of AC with sediment to promote faster remediation benefits by decreasing HOC diffusion length scales for AC sorption [2,3]. However, mechanical mixing is often not feasible for deep water sediments or ecologically sensitive areas. In these situations, application of AC as a thin layer or in a pelletized form placed on top of the contaminated sediment has been proposed [4] and tested in the field [5–7]. In this case, bioturbation by benthic organisms is advantageous as an in-place and natural mode of mixing AC amendment with sediment within the bioactive layer. However, mechanistic models that combine the particle and porewater mixing processes with AC mass transfer processes are limited. Therefore, there is a need to investigate the effects of bioturbation on AC amendment for thin-layer applications.

To assess the effects of bioturbation on in-situ treatment with AC amendment, our previous microcosm studies simulated the deployment of a thin layer of AC cap placed above sediment contaminated with dichlorodiphenyltrichloroethane (DDT) [8]. That study showed that with bioturbation, the thin AC cap significantly reduced the time-averaged 28-day DDT flux, porewater concentration, and 28-day biouptake in *Lumbriculus variegatus* compared to untreated

sediment. In contrast, a thin clean sediment cap was ineffective in reducing DDT flux in the presence of bioturbation [8], which agrees with previous findings [9–11].

Studies by Cornelissen et al. provide the most recent evidence that adding a layer of non-active material to cap contaminated sediment, such as limestone and clay, may be less effective in reducing HOC flux from contaminated sediment under long-term field conditions with bioturbation and sediment influx compared to caps using active material such as activated carbon [12]. This conclusion was in contrast to initial studies indicating the reverse, where non-active caps were more effective than active caps [7]. This highlighted the need to investigate how bioturbation affects remediation strategies over time as well as the effects of continuing sediment influx, both of which were inferred to explain the trends observed in the field.

Incoming sediment deposition complicates remediation efforts [13,14]. Although sediment management guidance documents [15,16] state the importance of making sure all sources of contamination are identified and controlled before initiating any remediation, this may not be feasible at complex urban sites where industrial activities or widespread off-site contamination will continue to be a source of contaminant influx. Incoming contaminated sediment deposition can reverse the benefits of natural attenuation or costly remediation activities [16–18]. Therefore, in this study, we investigated whether in-situ treatment with AC amendment has a potential buffering capacity against recontamination by sediment influx after a remediation activity. Since bioturbation was previously shown to help facilitate contact between a thin AC layer and the underlying sediment [8], we hypothesized that bioturbation will be an important facilitator for also treating contaminant influx with the previously placed AC. The aim of this study is to investigate the effects of bioturbation on contaminant flux and porewater concentrations over time in a variety of dynamic field conditions, including natural attenuation

by clean sediment deposition and in-situ treatment with thin layer AC with ongoing clean and contaminated sediment deposition. A mass transfer model was developed to evaluate bioturbation and sediment deposition effects on contaminant flux.

MATERIALS AND METHODS

Experimental setup

Two different sediment samples collected from Lake Maggiore, an alpine lake in Italy with previous DDT-contamination history, were placed in glass jars to represent microcosms of different field scenarios. The concentration of DDT and DDT metabolites in the two sediment samples are shown in Table 1. Total DDT is represented as ∑DDT, which was measured as the sum of analytes 4,4'-DDT, 2,4'-DDT, 4,4'-DDE (dichlorodiphenyldichloroethylene), 2,4'-DDE, 4,4'-DDD (dichlorodiphenyldichloroethane), 2,4'-DDD, and DDMU (dichlorodiphenylmonochloroethylene). The control sediment contains 1.2±0.3 ∑DDT ppm and total organic carbon content (TOC) 1.9% dw). The control is used to represent a DDT-contaminated site. The background sediment was collected outside the contaminated area and contains 0.022±0.009 ∑DDT ppm, TOC 1.5%. The background sediment is used to represent clean sediment.

Both control and background sediment were placed in glass jars in order to represent different field conditions. Microcosm experiments were conducted in 500 mL glass jars (Thermo Scientific^{TM}, ICHEM-200 series, 6.5 cm inner diameter, 15 cm tall) at room temperature (21±1°C). Each microcosm contained 200 g ww (4.5 cm height in jar) of underlying control sediment to represent the bed sediment of a contaminated site, and additional AC and sediment were placed on top in layers to represent remediation with thin-AC amendment and sediment influx. Microcosms were set up in five scenarios:

1. Control (CTRL) comprised contaminated sediment only.
2. Simulated natural attenuation (NA) comprised contaminated sediment sublayer, with a thin layer of clean background sediment (12 g ww sediment, ~2.5 cm settled), and additional background sediment placed on day 60 and 90 from the beginning of the experimental period. Each additional layer of clean background sediment comprised 12 g ww, and was comparable to deposition rates measured in the Pallanza Bay, Lake Maggiore during a two-month period in the Autumn of 2012 [19].
3. Simulated AC in-situ treatment (AC), comprised a contaminated sediment sublayer, with a thin layer of virgin activated carbon (2.5 g dw AC, ~2.5 cm settled; TOG AC, Calgon Carbon, Pittsburgh, ground and sieved to 75-150 μm particle diameter);
4. Simulated AC in-situ treatment with subsequent natural attenuation (ACNA) comprised a contaminated sediment sublayer, thin AC layer (2.5 g dw AC), and clean background sediment layers (12 g ww) placed on day 0, 60, and 90.
5. Simulated AC in-situ treatment with subsequent recontamination (ACRE) comprised a contaminated sediment sublayer, thin AC layer (2.5 g dw AC), and layers of contaminated sediment (12 g ww) placed on day 0, 60, and 90.

Each sediment treatment was assessed for the effects of bioturbation, thus microcosm experiments were set up with *L. variegatus* (n=3 microcosms) and without worms (n=3).

Each microcosm was filled with wet control sediment, and polyethylene (PE) porewater sampling devices were placed three days later. Care was taken to fill any void space between the porewater device and sediment. AC was soaked in 10 mL of deionized water to obtain an AC slurry, and the slurry was carefully applied with a disposable pipette to the top of the control sediment. This technique was used to obtain a visually even layer covering the entire sediment

surface. The dry/wet sediment mass ratio was 50%. Therefore, the 2.5 g dw of AC was equivalent to a 2.5% dw dose to the 200 g ww of underlying sediment in each microcosm (calculated final TOC of 4.4% dw). The amount of sediment deposited in each time period (12 g ww) was designed to approximate the deposition rates measured in Pallanza Bay, Lake Maggiore, Italy during a high flow event in the river located upstream, which was typical of annual Autumn events in the region, i.e. 0.32 g/cm^2 [19]. The sediment deposition in the microcosms was carefully applied using the same method as AC placement.

On day 0, jars were filled with reconstituted freshwater [20], and fifty worms were added to each microcosm using a plastic pipette (worm density 1.5×10^4/m^2). This density was chosen to be consistent with previous studies [4,8,21,22]. Flux-measuring devices were put in place, and microcosms were gently aerated at the water surface. Microcosms were lightly capped to minimize evaporation, and 80 mL of water was exchanged twice a week during the 120-day study period.

Experimental organisms

Following the previous study [8], the freshwater worm, *Lumbriculus variegatus*, was selected as a bioturbator. *L. variegatus* acts as a vertical conveyor belt for sediment particles by feeding head-down and ingesting sediment at depth and depositing fecal pellets on the sediment surface. Previous studies have observed a significant presence of oligocheates in Pallanza Bay [23]. The organism has been used in other studies to assess bioturbation [8,22,24] and biouptake from sediment [4,8,20,25–27]. Worms 2-4 cm in length were selected for the experiment, and ten worms were added every 30 days to maintain the worm density. Using these protocols, survival rates in 28-day studies were >80% [8]. Worms were not fed additional food during the experiment.

DDT flux and porewater DDT concentration profile

DDT fluxes were measured by flux devices made of low-density polyethylene (LDPE) sheets as described previously [8]. Briefly, a stainless steel frame held 1.3 g of polyethylene sheets at the water surface, the LDPE was an infinite sink for DDT flux into the overlying water; LDPE was changed every 28 days, and the flux during the measured time period was calculated from the total amount of contaminant sorbed into the LDPE, sediment area, and time period. Images and a diagram of the sampling setup is shown in SI. Contaminant loss from aeration was calculated to be insignificant, as discussed previously [8]. The porewater concentration profile was measured using a PE sheet (0.2 g) wrapped around a frame (4 cm tall x 2 cm wide) made of stainless steel wire and removed after 120 days of exposure. Each PE sheet was cut into thin strips to separate portions exposed to different sediment layers: in the overlying water above the sediment, within the deposited layer, and at 0.5 cm depth intervals below the initial sediment layer down to 2 cm depth.

AC profile

TOC measurements ins sediments were used as a surrogate for AC dose [2,14] to assess whether bioturbation mixed the AC into the sediment. Triplicate profiles were collected from each jar by collecting a mini “core” with a stainless steel spatula and sectioning the sediment at 0.5 cm intervals. Results for this analysis are shown in Supporting Information (SI).

Numerical mass transfer model

A numerical mass transfer model developed in the previous study [8] was further expanded to simulate DDT flux under various treatment scenarios and continuous deposition. The compound 4,4'-DDD was selected as a model compound because it was the dominant DDT metabolite in samples and comprised 39-73% of total ∑DDT fluxes in all scenarios. Modeled

flux values were compared to experimental results to test the validity of the model and provide insights into the mass transfer mechanisms. The model input parameters were independently measured and assessed, and not fitted to the experimental data. We evaluated the variability in the modeled flux in each scenario by stochastically simulating the model 50 times with input parameters randomly chosen from the estimated normal distributions listed in Table 2. Based on the distribution of the model results after 50 simulations, we determined that 50 simulations were sufficient to estimate and bound the average flux. In the models without bioturbation, the standard deviation of the modeled flux after 50 simulations was less than 25% of the average flux; and in the models with bioturbation the standard deviation of modeled flux after 50 simulations was less than 55%. The 95% confidence interval for the average flux for n=50 for all scenarios was within 18% of the calculated average flux.

The basic modeling scheme is based on previous efforts by others to simulate intra-particle diffusion kinetics and porewater exchange through molecular diffusion and dispersion and is explained elsewhere [3,28]. The sediment-to-water flux was modeled by defining an infinite-sink boundary condition with an aqueous-side diffusion boundary layer thickness at the sediment surface [8]. Bioturbation activity was simulated by randomly selecting a cube within the bioturbation layer, placing it on the sediment surface, and shifting down the column of underlying cubes to fill the emptied space [8]. This simulates the "conveyor-belt" bioturbation induced by vertical feeding at depth and particle egestion at the sediment surface.

In this study, we expanded this model to simulate a dynamic system with ongoing sediment deposition by defining additional sediment volumes on top of the sediment. For example, the 0-30 day flux in the ACRE scenario is calculated by defining an infinite-sink boundary condition above the sediment sublayer, the AC layer, and the recontamination layer.

The 60-90 day flux is calculated by defining the boundary condition above an additional recontamination layer placed on the first recontamination layer. Thus the model can be used to simulate a range of dynamic conditions including clean sediment deposition, contaminated sediment deposition, changing deposition concentrations, no deposition, AC amendment, or combination of these events. Expanding the model to incorporate sediment influx was important to assess how bioturbation would affect AC treatment with sediment influx.

The bioturbation intensity in the model is defined by the parameter dt_{bio} which is the time interval between cube exchanges, and is the modeling parameter for the ingestion-egestion rate. In non-bioturbation scenarios, cubes are not moved. In the CTRL and NA bioturbated scenarios, the dt_{bio} was defined to correspond to an ingestion rate of 7×10^{-5} g/g/s using the equation

$$IR = \frac{1}{dt_{bio}} \times dz^3 \times \left(1 - V_{fsw}\right) \times d_s \div worm_{weight}$$

The ingestion rate value is consistent with other studies on ingestion rates of *Lumbriculus* [25,29]. The ingestion rate, (IR, g/g/s) is used to calculate the bioturbation parameter dt_{bio} (= 2400 s), where $1/dt_{bio}$ is the frequency of cubes ingested or moved to the surface in the model (cube/s), dz^3 is the cube volume (cm^3), $(1\text{-}V_{fsw})$ is sediment solids volume fraction (-), d_s is sediment particle density (g/cm^3), and $worm_{weight}$ is the scaled worm weight (0.04 g worms in microcosm × surface area in model (0.04 cm^2) ÷ surface area in microcosms (33.2 cm^2).

Some studies have shown that AC reduces the activity and growth for benthic organisms, while other studies have shown no negative effects from AC [26,27,30]. These effects likely depend on the type of organisms present, sediment characteristics, food source, and AC particle size and dose [26]. The AC particle size used in this study was fine (75-150 μm), and we did

observe reductions in worm activity in AC treated systems based on smaller amounts of feces deposited on the sediment surface in AC-treated systems compared to microcosms without AC. We estimated activity was reduced by 80% in AC-treated systems compared to control systems, based on the amount of feces deposited on the surface [8]. This is consistent with a separate study where *L. variegatus* in sediment amended with 1-5% AC showed 75-95% reduction in egestion rates compared to worms placed in unamended sediment [29]. To represent this in the model, the modeled ingestion rate for the AC treated scenarios (i.e., AC, ACNA, ACRE) was estimated to be 20% of the ingestion rate in the unamended systems. Potential ecological impacts from AC amendment should be considered within the framework of contaminant management strategies [26,27,31].

The parameter *biof* is the increase in porewater dispersion due to bioturbation activity relative to molecular diffusion. In non-bioturbated systems *biof* =1, and only molecular diffusion controls 4,4'-DDD movement between cubes in the model. For bioturbated systems, the movement of worms within the burrows should cause some porewater turbulence, such that *biof* ≥1.

In control microcosms, we observed the sediment on the surface had a thin light-brown oxygenated layer, and this layer was 0.7±0.1cm in non-bioturbated controls and 1.5±0.1 cm in bioturbated controls (measured on day 98). We hypothesized this difference was due to random dispersion caused by the moving worms. We made a coarse approximation that the value of *biof* was between 1 and 25 based on the difference in observed oxygen penetration depth in the microcosms, wherein the control had deeper oxygen penetration than the bioturbated scenario, indicating increased porewater dispersion.

The parameter *biof* was derived by fitting the model to the control experimental flux by changing the parameter biof. The model was run with biof = 1, 5, 10, 25, with all other parameters held constant at average values shown in Table 2 to understand the sensitivity of the mass transfer model to the *biof* parameter. The resulting one month time-averaged flux was 1.3, 4.8, 7.8, 13.5 μg/m^2/d, respectively. Therefore, the value of biof = 5, was determined to be the best estimate because it was the most consistent with experimental values. This increase in modeled dispersion in the porewater due to bioturbation is within the range of increase in apparent sediment-water mass transfer coefficients for a range of polychlorinated biphenyls measured due to *Lumbriculus* in untreated sediment (25th - 75th percentile range 2-100) in another study [24].

RESULTS AND DISCUSSION

Measured sediment-to-water DDT flux

The average flux over the 4-month experimental period showed that the effects of bioturbation on the flux were statistically significant (t-test, $p \leq 0.05$) in each scenario. The values used in the following comparisons are for ∑DDT flux, and the trends were consistent for ∑DDT and 4,4'-DDD (Figure 1 and Figure S2 in SI). In the control scenario (CTRL), bioturbation increased the average ∑DDT flux by a factor of four compared to that without bioturbation. The natural attenuation scenario (NA) significantly reduced flux by 92% compared to the control when there was no bioturbation. However, when there was bioturbation, natural attenuation was not effective in reducing flux and had a similar flux compared to the control with bioturbation. This is consistent with what we observed previously with a static cap [8]. This shows that bioturbation may delay natural attenuation even with continuing clean sediment deposition.

The AC thin cap was effective in reducing the flux with and without bioturbation. Without bioturbation, the flux from AC was reduced by 99% compared to the control without bioturbation. While DDT flux increased with bioturbation, the presence of AC still represented a 96% reduction compared to the control with bioturbation. The AC cap remained effective over the 4-month experimental period in reducing contaminant flux even with bioturbation present (Figure 2).

Our previous work demonstrated the effectiveness of the AC cap in reducing contaminant flux in the presence of bioturbation for one month [8]. The present study further investigated and assessed whether the benefits provided by the AC cap continued for a longer period (4 months) with and without surface deposition. This increase in AC cap effectiveness was also observed in the field [12], and it was inferred that bioturbation likely facilitated the sequestration of contaminants to AC over time. Moreover, the treatment efficiency of a thin AC layer cap measured in this study was consistent with our previous work [8].

The AC scenario was also a control for the additional treatment scenarios with sediment deposition, AC with clean sediment deposition (ACNA) and AC with contaminated sediment deposition (ACRE). The AC-treatment with natural attenuation (ACNA) showed very different patterns from natural attenuation, and looks similar to fluxes measured in AC treatment only. As expected, without bioturbation, ACNA exhibited the same minimal flux as natural attenuation. For ACNA, bioturbation increased the flux compared to the case with no bioturbation, but was still effective in reducing the flux by 96% compared to control with bioturbation. The effect of bioturbation on the flux from ACNA was much smaller than the effect of bioturbation on the NA scenario. For ACNA, bioturbation increased the time-averaged 4-month flux by a factor of three, while bioturbation increased flux by a factor of 45 for natural attenuation. This AC effect

could be due to both increased sequestration of contaminants when AC is amended to the sediment, as well as reduced bioturbation rates in ACNA compared to natural attenuation.

Without bioturbation, the AC-treatment with recontamination (ACRE) showed a 68% increase in flux compared to the control because fresh contaminated sediment was added on day 60 and 90. Notably, bioturbation did not increase the flux from ACRE, rather the presence of bioturbation reduced flux by 77% compared to the same sediment treatment without bioturbation and by 90% compared to the control with bioturbation. Previous laboratory and field studies have demonstrated that AC amendment with bioturbation reduces flux[12,24,32]; to our knowledge, this is the first study to specifically show the benefits of bioturbation in a recontamination scenario by facilitating the sequestration of contaminants from contaminated sediment deposited above the AC layer.

Modeled flux

Previous studies have noted the interaction between in-situ AC amendment with bioturbation in reducing HOC flux [8,10,24,33]. Those studies suggested that reductions in flux are due to both HOC sequestration by AC as well as reduced bioturbation activity. The development of the mass transfer model provided us with a tool to evaluate the interaction of AC sorption and bioturbation activity to determine whether contaminant flux is increased or decreased by bioturbation activity. The mass transfer model input parameters are given in Table 2.

The predicted average fluxes from the model fit relatively well with the experimental results (Figure 1). First, without bioturbation, the model accurately predicted the significant reduction in flux (≥95%) from addition of the sediment or AC cap in the natural attenuation (NA), activated carbon (AC), and activated carbon with natural attenuation scenario (ACNA). In

these cases, the model over-predicted the reduction in flux from the caps compared to experimental results. We believe this is due to artifacts in the experimental setup that may have elevated the flux, including holes in the sediment or AC cap and suspension of sediment particles during sediment deposition placement. In the recontamination scenario (ACRE) without bioturbation, the model correctly predicted an increase in flux compared to the control (CTRL).

The model successfully predicted the qualitative effects of bioturbation on the flux for all scenarios. Specifically, the model predicted a significant increase (>400%) in flux due to bioturbation in the control, natural attenuation (NA), and activated carbon treatment scenario (AC), and activated carbon with natural attenuation scenario (ACNA). In the activated carbon with recontamination scenario, the model also correctly predicted that bioturbation would reduce contaminant flux compared to that without bioturbation, confirming the experimental measurements that showed that bioturbation enhances the buffering capacity of activated carbon amendment to recontamination. The root mean square deviation between the 4-month average experimental flux and model flux for all sediment treatments with and without bioturbation was 0.6 $\mu g/m^2/d$. Given that the mean flux (and standard deviation) from the control with bioturbation was 4.7 (1.7) $\mu g/m^2/d$, this suggests the model was sufficiently accurate to predict how sediment treatments will affect flux compared to the control. We hypothesize that the difference between experimental and modeled flux values are due to simplification of processes in the experimental setup that are not modeled, including changes in bioturbation intensity, sediment resuspension from deposition placement and bioturbation activity, and variations in sediment porosity. Other studies [24] have also suggested that bioturbation can increase dissolved organic matter (DOM) in the water column which can facilitate mass transfer of contaminants across the diffusive boundary layer. While the current model does not include

DOM-facilitated mass transfer processes, this simplification is unlikely to account for the difference between experimental and modeled results because the differences are not consistent between sediment scenarios.

In general, the relatively close match between modeled and experimental values for various scenarios is encouraging and suggests that this is an appropriate modeling framework for further development. In addition, the model results clearly support our findings that bioturbation activity can help treat contaminated sediment deposited after the AC layer placement.

PE uptake profile

The total DDT uptake into PE samplers was measured as a surrogate for time-averaged porewater concentration profile (Figure 3). Only the PE measurements within the sediment were used for this analysis, because some of the PE measurements above the sediment in the overlying water likely came into contact with sediment particles, which would skew measurement of the truly dissolved concentration in the overlying water.

In the control scenario (CTRL), bioturbation increased the average PE uptake in the sediment by 81% (t-test, $p<0.001$). In the natural attenuation (NA) scenario, bioturbation increased average PE uptake in the sediment by 86% (t-test, $p=0.002$), which was also observed, previously [8].

The PE profile for all three AC-treated scenarios showed reductions in DDT porewater concentration from the control. Moreover, bioturbation was beneficial in all three AC treatments in that bioturbation helped reduce the PE concentrations further compared to the same sediment treatment without bioturbation. In the AC scenario, bioturbation had a positive effect of reducing the average PE concentration by 54% (t-test, $p=0.02$) compared to AC without bioturbation. In the ACNA scenario, bioturbation also reduced PE concentration by 34% (t-test,

p=0.08). A two-way analysis of variance (ANOVA) showed that the effect of bioturbation on the PE concentration profile was significant ($F(1,32) = 18.8$, $p=0.0001$). In ACRE scenario, average PE concentration in the sediment was also reduced by 32%, but this was not statistically significant because of the large deviations in the data (t-test, $p=0.2$, two-way ANOVA $F(1,22) = 1.15$, $p = 0.3$). PE concentrations in the sediment decreased towards the layer of AC, indicating that the AC layer acted as a sink for contaminants in the sediment above and below the AC layer.

In the PE concentration profiles, reductions in the surface porewater concentrations due to bioturbation would suggest that flux should decrease from bioturbation, although we measured and modeled increases in flux due to bioturbation for AC and ACNA. There were likely elevated DDT concentrations at the sediment surface that were much finer than the resolution of our passive samplers (5 mm). We observed a layer of worm feces on the sediment surface, which should elevate surficial porewater concentrations. Bioturbation activity would also be expected to move some of the contaminated particles at depth to the surface in all the bioturbated microcosms.

CONCLUSIONS

This study clearly showed that the presence and intensity of bioturbation has important implications for long-term flux of persistent organic contaminants in sediments. The results are based on 4-month microcosm studies using realistic sediment deposition rates and bioturbation intensities. This study confirmed that while bioturbation may delay natural attenuation through periodic clean sediment deposition, bioturbation can actually play a beneficial role in facilitating AC amendment placed as a thin layer on top of contaminated sediment. The buffering capacity of AC aged in sediment to further sorb additional influx of contaminants has been demonstrated under mechanical mixing in previous studies [24,32]. And the benefits of bioturbation in aiding

sorption in thin AC placement was inferred in field studies [12]. This experiment showed specifically that bioturbation aids a thin layer placement of AC in providing buffering capacity against recontamination. In other words, even with some amount of incoming contaminated sediment after initial placement of AC layer, the microcosms with AC and bioturbation still showed effective reduction in HOC flux compared to the control without treatment. The buffering capacity of in-situ remediation with AC should be considered a potential advantage of this remediation alternative compared to traditional methods such as dredging and capping with non-sorbing materials. Other studies have shown that both bioturbation and recontamination limit the effectiveness of remediation by dredging [13] and capping with passive materials [10].

In this study, we also developed a mass transfer model that simulates the sediment-to-water flux from contaminated sediment and captures the mixing activity from deposit-feeding *Lumbriculus variegatus* under various site conditions and remedial scenarios. The modeled results were comparable to experimental results, and the consistency between the model and experiment confirm conclusions from the experiment on the effects of bioturbation on sediment treatments with and without AC. Also, the close match between the model and experimental values are encouraging and support that this is a reliable framework for future improvement and developments for predicting contaminant flux under various field conditions.

In the case of AC treatment with recontamination, we expect that higher rates of bioturbation will reduce flux by further facilitating sequestration of contaminants by AC amendment. We used the mass transfer model to test this hypothesis by running the model with higher particle mixing rates by lowering the value of dt_{bio}. Holding all other parameters constant, lower values of dt_{bio} (more intensive bioturbation) resulted in lower values of predicted flux for

ACRE. Therefore, active bioturbation is an effective mechanism to facilitate sequestration from incoming contaminants from sediment in AC treatment with ongoing sediment deposition.

A future goal would be to validate and develop this model to predict long-term field conditions given site-specific field parameters including sediment characteristics, deposition rates, and bioturbation parameters to determine whether natural attenuation satisfies remedial goals as well as to evaluate remediation options with capping and AC amendment to optimize engineering parameters including modifying AC doses and deployment modes.

Supplemental Data—The Supplemental Data are available on the Wiley Online Library at DOI: 10.1002/etc.xxxx.

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Data Availability—Data and calculation spreadsheets are available from the corresponding author (luthy@stanford.edu).

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Graphical Abstract. Bioturbation enhances the performance of in-situ AC amendment against ongoing contaminant influx by reducing contaminant sediment-to-water flux.

Figure 1. Time-averaged 120-day flux for 4,4'-DDD in each sediment treatment scenario. Solid bars represent measured flux in microcosms without bioturbation (solid black) and with bioturbation (solid gray) (n=3 microcosms). Striped bars represent modeled flux from mass transfer model without bioturbation (black horizontal stripes) and with bioturbation (gray diagonal stripes) (n=50 simulations). Scenario abbreviations are defined as follows: CTRL = control, NA = natural attenuation, AC = AC layer placement, ACNA = AC layer placement with subsequent natural attenuation, ACRE = AC layer placement with subsequent recontamination.

Figure 2. Average 30-day flux measured in microcosms over four months without bioturbation (A) and with bioturbation (B), and flux predicted in model without bioturbation (C) and with bioturbation (D). Scenario abbreviations are defined as follows: CTRL = control, NA = natural attenuation, AC = AC layer placement, ACNA = AC layer placement with subsequent natural attenuation, ACRE = AC layer placement with subsequent recontamination. Error bar represents one standard deviation.

Figure 3. Time-averaged 120-day PE concentration profile in microcosms without bioturbation (open circles, solid line, n=3) and with bioturbation (filled diamond, dashed line, n=3) in each sediment treatment scenario: A) Control, B) Natural attenuation, C) AC thin layer placement, D) AC treatment with natural attenuation, E) AC treatment with recontamination. Error bars represent one standard deviation, n=3.

Table 1: Sediment DDT concentrations, n=5

	Contaminated Control	Clean Background
Chemical	Avg ± StDev (ppb)	Avg ± StDev (ppb)
DDMU	46±14	<2
2,4'-DDE	85±13	1±1
4,4'-DDE	187±32	7±2
2,4'-DDD	112±83	4±1
4,4'-DDD	596±139	5±1
2,4'-DDT	15±4	2±2
4,4'-DDT	153±52	3±1
∑DDT	1,170±296	22±9

Table 2. Mass Transfer Model Input Parameters: Uncertainty analysis conducted assuming normal distribution of uncertain model input parameters around specified mean and standard deviation values.

Model Parameter	Parameter Annotation	Value (StDev)	Source
	Model system		
time frame	months (30 days)	4	
modeled subvolume (cube) dimensions	dz, dx, dy (cm)	0.02	
deposition day 0 (NA, ACNA, ACRE)	Deposit1 (no. of cube layers)	11 (10%)	measured
deposition added day 60	Deposit2 (no. of cube layers)	11 (10%)	measured
deposition added day 90	Deposit3 (no. of cube layers)	11 (10%)	measured
AC thickness (AC, ACNA, ACRE scenario)	ACthickness (no. of cube layers)	10 (10%)	measured
	Bioturbation		
bioturbation frequency (CTRL, NA)	dt_{bio} (s)	2,400 (100%)	estimated
bioturbation frequency (AC, ACNA, ACRE)	dt_{bio} (s)	12,000 (100%)	estimated
bioturbation depth	Biodepth (cm)	1 (10%)	estimated
dispersion factor increase (CTRL, NA)	*biof* (-)	5 (10%)	calibrated
dispersion factor increase (AC, ACNA, ARE)	*biof* (-)	1 (10%)	estimated
no. cubes moved per exchange	$pellet_{\#\ of\ cubes}$	1	estimated
	Sediment-water physical properties		
sediment interparticle porosity	V_{fsw} (-)	0.5	measured
sediment intraparticle porosity	p_s (-)	0.1	
sediment particle density	d_s (g/cm3)	2	measured
sediment porewater tortuosity	$Tort_{sw}$ (-)	0.5	assumed same as V_{fsw}
	Physio-chemical properties for 4,4'-DDD		
bulk sediment partitioning coefficient	K_d (cm^3/g)	$8.9x10^3$ ($2x10^2$)	measured
fast release rate from sediment	$rate_{ss}$ (1/s)	$1.9x10^{-6}$ ($3.8x10^{-7}$)	measured
slow release rate from sediment	$rate_{sc}$ (1/s)	$1.5x10^{-8}$ ($3.0x10^{-9}$)	measured
mass fraction initially associated with $rate_{sc}$	f_{slow} (-)	0.63	measured
sediment conc. (control contaminated)	C_s (g/cm^3)	$6.0x10^{-7}$ ($1.4x10^{-7}$)	measured
sediment conc. (clean deposit)	C_d (g/cm^3)	$5x10^{-9}$ ($1x10^{-9}$)	measured
water-phase diffusion coefficient	D_{aq} (cm^2/s)	$4.5x10^{-6}$	measured
water-side diffusion boundary layer	DBL (cm)	0.09 (6%)	measured
	Activated Carbon properties		
AC particle radius	R_{ac} (cm)	0.0053	measured
AC solid-phase density	d_{ac} (g/cm^3)	1.96	
AC porosity	p_{ac} (-)	0.55	
4,4'-DDD AC-water partition coeff.	K_{ac} (cm^3/g)	2.95×10^8 (10%)	

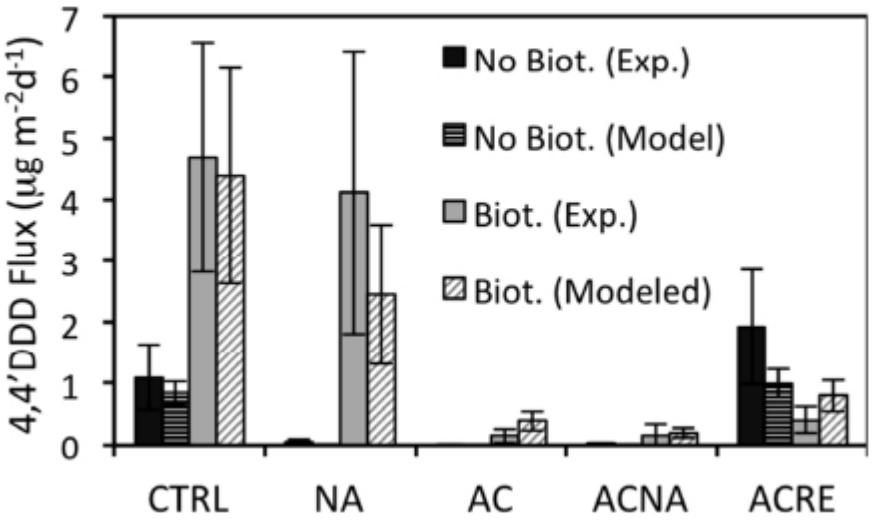


Figure 1

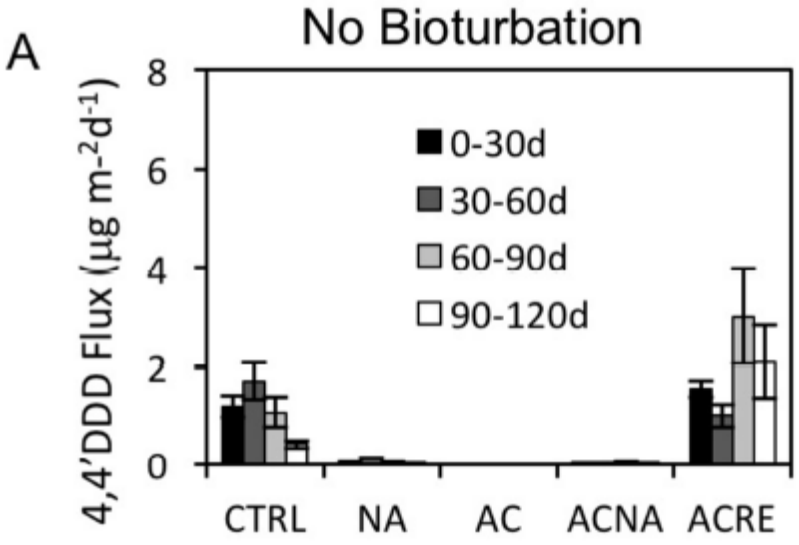
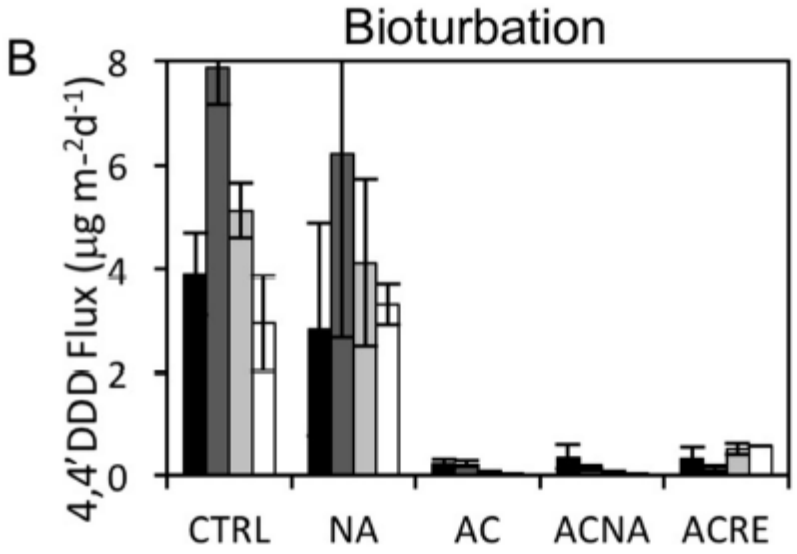


Figure 2A



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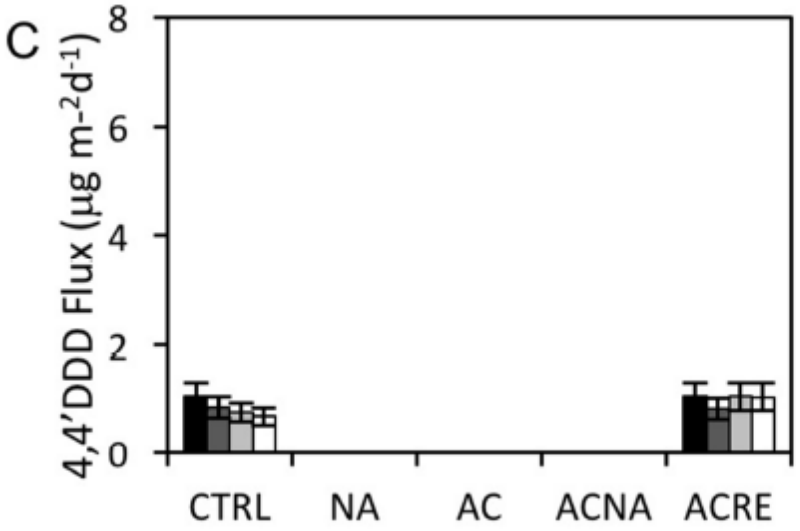

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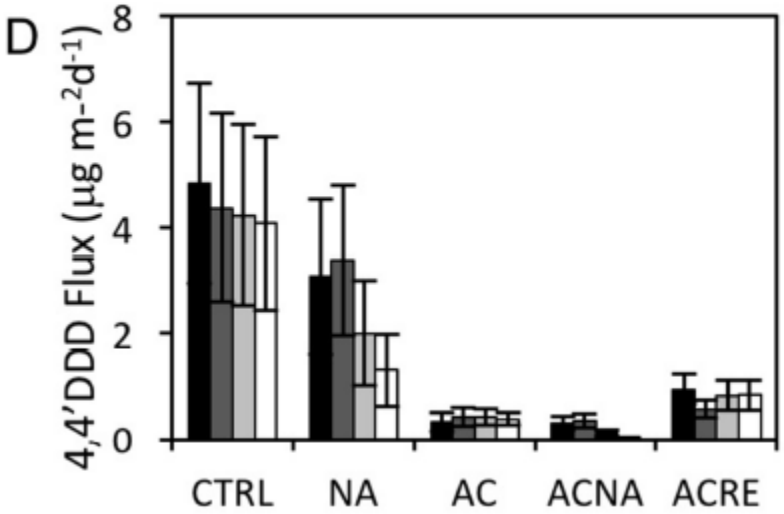

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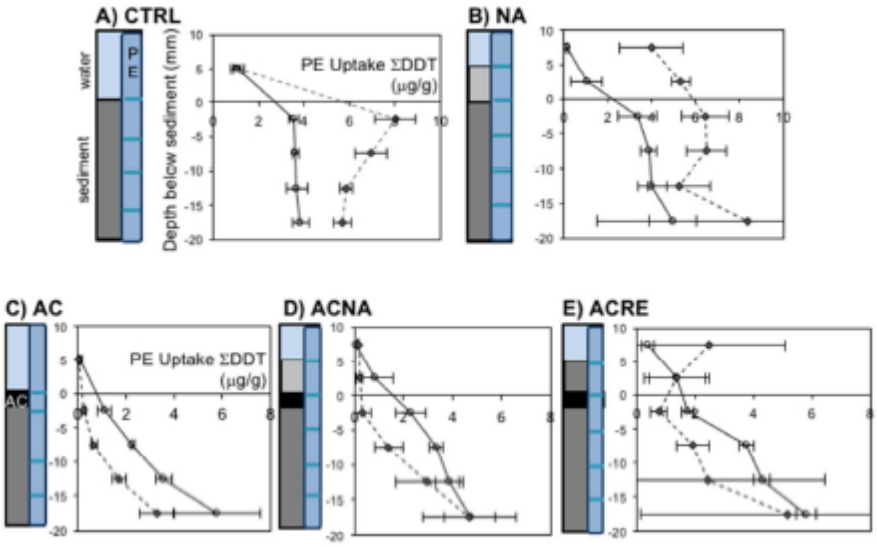

Figure 3