Supporting Information

Bioturbation Delays Natural Attenuation of DDT by Clean Sediment Cap but Promotes Sequestration by Thinly-layered Activated Carbon

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Method details

Flux Measurement Method Validation

The method used to measure flux with the flux measurement devices was validated by measuring the quiescent flux from sediment in a time series test as shown in Figure S1. The following calculations show that the amount of DDT lost to evaporation is insignificant compared to flux sorbed in the PE sheets. The maximum DDT concentration in the flux measurement device was 231 ng 4,4'-DDD/g PE. If we conservatively estimate the maximum air concentration that would be at equilibrium with the PE, based on the polyethylene-water partitioning coefficient ($LogK_{PE}$ = 4.93 L water/kg PE) (1) and the air-water partitioning coefficient ($H_{cc} = 10^{-3.49}$) (2), the equilibrium air concentration would be $9\ 10^{-7}$ ppb of 4,4'-DDD. This means that the air flow rate in each jar would need to be more than 100 L/day to account for 1% of the flux in the PE devices. We estimated the actual aeration rate to be approximately 20 L/d based on the observed bubbling rate. We also expect the water and air concentrations to be much lower than equilibrium concentrations.

The concentration of DDT in the flux devices was 0.2 μg/g PE, which is less than 10% of the concentration in PE placed in the sediment porewater for the same 28 d period. This supports the assumption that the PE is not saturated with PE, and can act as a sink for DDT into the overlying water.

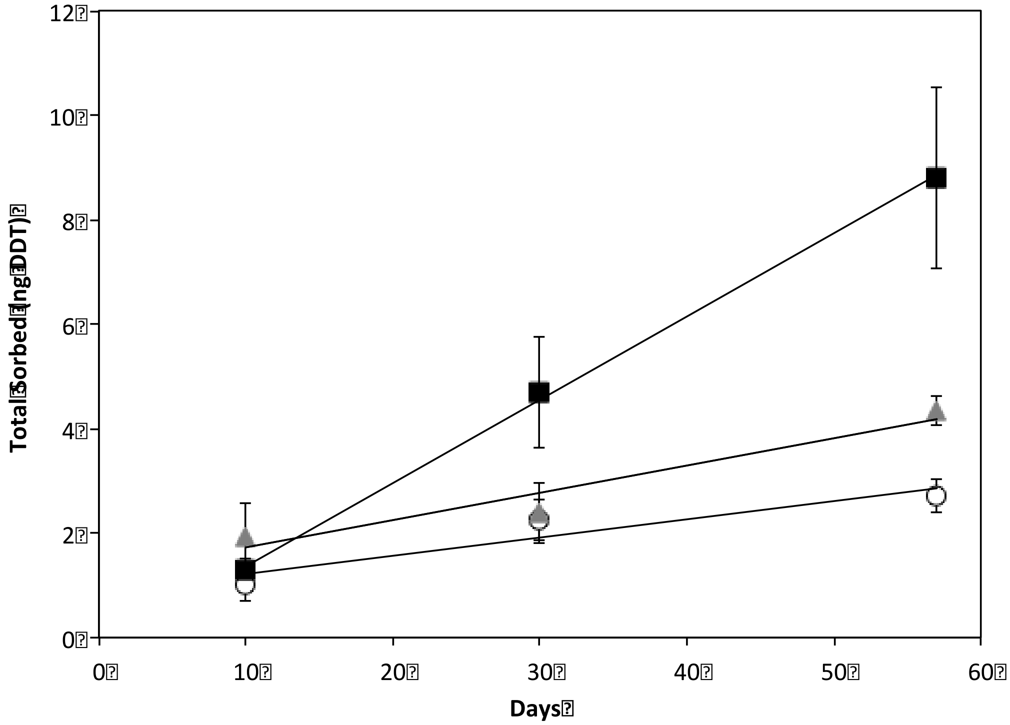

Figure S1. Cumulative amount of 4,4'-DDD (black square), 2,4'-DDD (gray triangle), and 4,4'-DDE (open circle), accumulated in the polyethylene (PE) flux measurement devices in quiescent microcosms tests with DDT-contaminated sediment (sediment sample collected from the same freshwater lake in Italy containing 0.10 ppm 4,4'-DDD, 0.04 ppm 2,4'-DDD, 0.10 ppm 4,4'-DDE). Error bars represent one standard deviation (n=3). The linear uptake profile ($p < 0.01$) confirms that the PE acted as an infinite sink for the DDT metabolites during the sampling period. Preliminary experiments showed that aeration increased the sediment-to-water flux by less than 30% compared to quiescent conditions.

Bioturbation and mass transfer model details

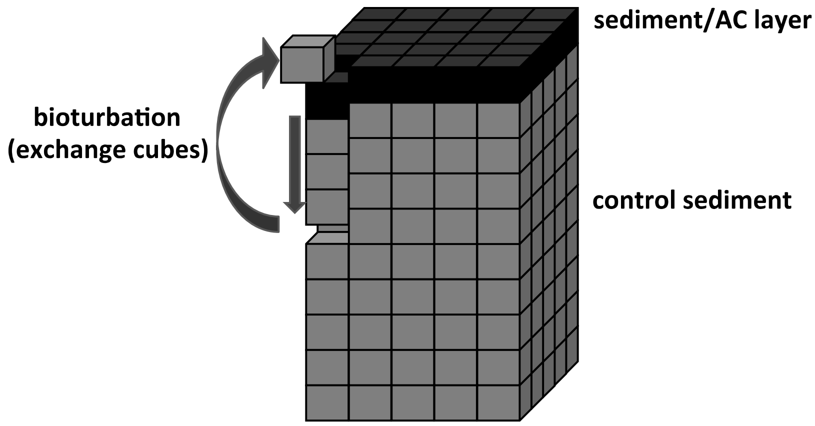

Figure S2. Schematic of how bioturbation activity was modeled in the mass transfer model. A randomly selected cube is placed at the top of the column, then the column is shifted down to fill the hole. This results in a depth-weighted movement of cubes, because the surface cubes are more likely to be moved than the bottom cubes.

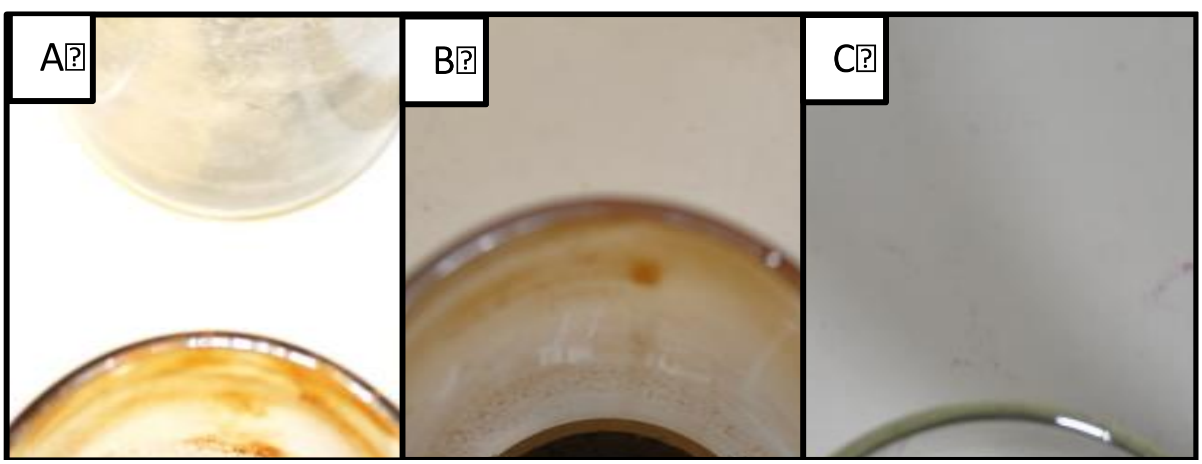

Figure S3. Sediment surface covered by *L. variegatus* feces after 28 d. The control and sediment systems (A and C) were covered by feces, while AC systems had only about 50% coverage by feces. Thus, the simulated bioturbation intensity in the AC system was estimated to be 50% less than control and sediment cap system.

Bioturbation Model Parameters.

The estimated bioturbation intensity of 3.6 cube exchanges per day can be converted to a turnover rate of sediment. Because the cubes are selected randomly, the average depth of the subsurface cube chosen for exchange is half the total depth. Therefore the average number of cubes moved per exchange is 50. The turnover rate (TR, kg d^{-1} m^{-2}) is calculated as:

$$TR = Exchange\ rate \cdot Cubes\ moved \cdot Cube\ dimensions \cdot \rho \cdot Surface\ area$$

where exchange rate = 3.6 cube exchanges per day, cubes moved = 50 cubes moved per exchange, cube dimensions = 8×10^{-6} cm^3, ρ = 1.5 g per cm^3, Surface area = 4×10^{-6} m^2. This calculation results in 0.5 kg m^{-2} d^{-1}. We can approximate an ingestion rate (IR) assuming all bioturbation activities are particle ingestion-related.

$$IR = TR \times Surface\ area \div worm\ dry\ mass$$

where TR = 500 g m^{-2} d^{-1}, Surface area = 9π cm^2, worm dry mass = 0.034 g, average dry mass of worms retrieved from microcosm. This results in a calculated ingestion rate of 4.8×10^{-4} g g^{-1} s^{-1}, which is consistent with previous studies (3).

The Matlab code used to implement the mass transfer model is available upon request.

Biodynamic Model Parameters. The biokinetic parameters of DDT in *L. variegatus* was conducted in another laboratory test with very similar conditions as the experiment discussed in this paper. In the previous experiment, eighty *L. variegatus* worms of 2-4 cm in length were placed in glass beakers filled with 125 mL of DDT-contaminated sediment (0.083 µg 4,4'-DDD g^{-1} sediment dw). To determine the uptake efficiency of 4,4'-DDD in *L. variegatus*, worms were exposed to sediment for 14 d, in triplicate. After removal, worms were allowed to depurate in aerated clean water for 6 h. The biodynamic equation

$$\frac{d}{dt}C_b(t) = k_{derm} \cdot C_{aq}(t) + \sum \alpha_j \cdot S_i \cdot IR \cdot C_{s,i}(t) - k_{elim} \cdot C_b(t)$$

from Sun et. al., 2009 (3) was fitted to the 14 d dataset for bioaccumulation in *L. variegatus*. Biodynamic parameters are in Table S1. In the summation term, we assumed that $\alpha_j * S_j * IR$ was the same for the fast and slow release particles. As a first order approximation to derive the value of the constant $C = \alpha_j * S_j * IR$, we assumed accumulation of 4,4-DDD was constant over the 14 d period, and calculated C as follows:

$$\frac{C_b(t_{14d}) - C_b(t_{0d})}{14d - 0d} = k_{derm} \cdot C_{aq} + C \cdot C_{sediment} - k_{elim} \cdot C_b(t_{14d})$$

The sediment concentration $C_{sediment}$ was assumed to be constant during the 14 d period, which is reasonable because we do not expect a significant amount of depletion of DDT from the sediment since the sediment TOC content to worm dry mass ratio is greater than 50:1. We also assumed C_{aq} was in equilibrium with $C_{sediment}$. The initial $C_b(t_{0d})$ and final $C_b(t_{14d})$ DDT concentration in the worm tissue after the 14 d bioaccumualtion experiment was one and 1,300 ppb of 4,4'-DDD in dw, respectively.

Additional Results

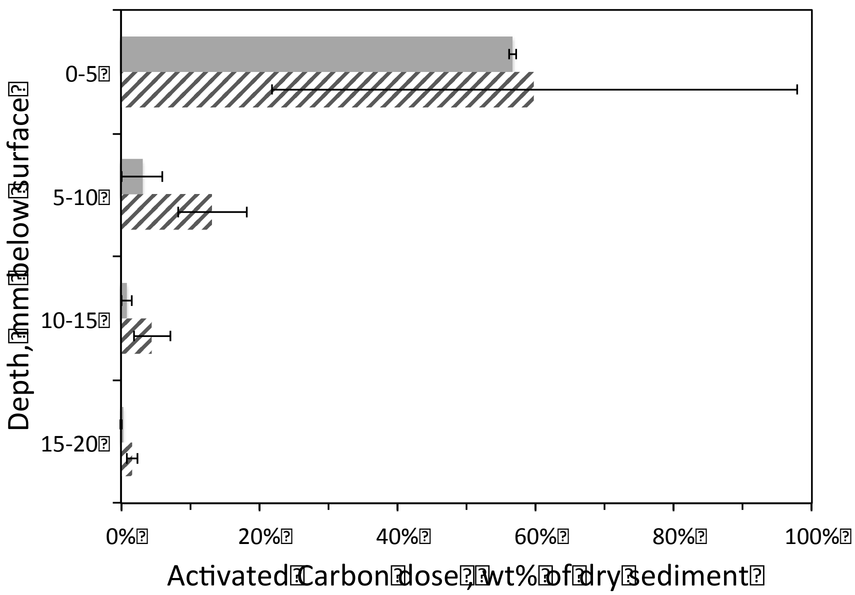

Figure S4. Activated carbon dose profile from AC cap (0.3 cm) microcosms without bioturbation (solid) and with bioturbation (striped) after 28 d. Error bars represent one standard deviation (n=3).

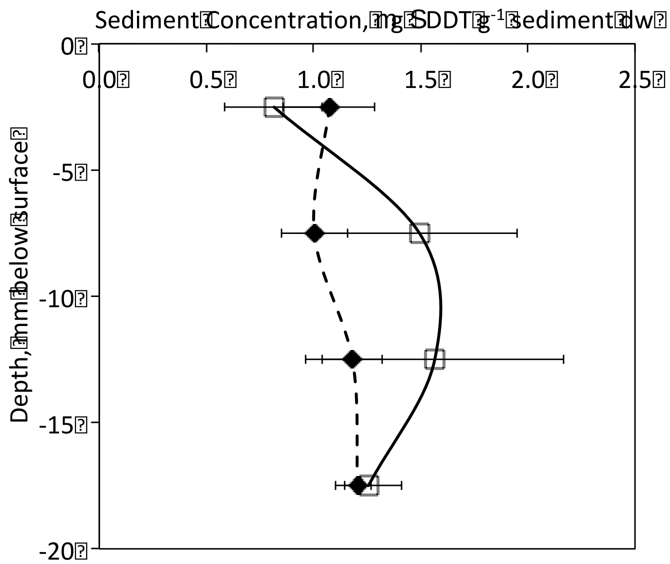

Figure S5. Sediment concentration profile of total DDT in top 2 cm of sediment column in sediment cap scenarios. Each point represents sediment section that were about 0.5 cm thick. Error bars represent one standard deviation (n=3).

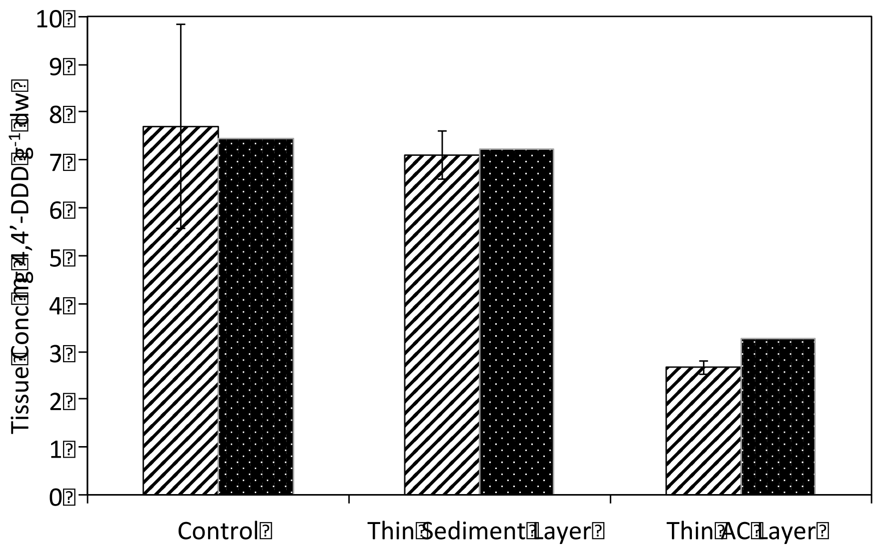

Figure S6. Comparison of measured (striped, n=3) and predicted (black) 4,4'-DDD concentration in *L. variegatus* after 28 d of exposure to DDT-contaminated sediment (0.9 µg/g 4,4-DDD). Error bars represent one standard deviation

Table S1. Biodynamic model input parameters.

Parameter	Parameter Annotation	Value[a]	Source
4,4'-DDD dermal absorption rate	k_{derm} ($cm^3\ g^{-1}\ s^{-1}$)	0.18	(3) [a]
4,4'-DDD elimination rate	k_{elim} (s^{-1})	6.65E-06	(3)[a]
fractional uptake efficiency * ingestion rate * selectivity index for Control and Sediment Cap Scenario	α * IR * S (s^{-1})	5.07E-05	measured[b]
fractional uptake efficiency * ingestion rate * selectivity index for AC Scenario	α * IR * S (s^{-1})	2.53E-05	measured[b]

[a]Values based on reported values in Sun et al., 2009 (3). Chemical specific parameters are based on reported values for PCB 64. PCB 64 has a Kow similar to 4,4'-DDD, with Kow of 5.95 and 6.0, respectively.

[b]Value based on a 14 d bioaccumulation test using k_{derm} and k_{elim} from Sun et al., 2009 (3). Ingestion rates for AC are estimated to be half of sediment scenarios because we observed 50% less egestion rates in microcosms.

References

(1) Hale S. E.; Tomaszewski J. E.; Luthy R. G.; Werner D. Sorption of dichlorodiphenyltrichloroethane (DDT) and its metabolites by activated carbon in clean water and sediment slurries. *Water Res.* **2009,** *43* (17) 4336-4346.

(2) Schwarzenbach R. P., Gschwend P. M., Imboden D. M. *Environmental organic chemistry;* Wiley: Hoboken, N.J., 2003.

(3) Sun X.; Werner D.; Ghosh U. Modeling PCB mass transfer and bioaccumulation in a freshwater oligochaete before and after amendment of sediment with activated carbon. *Environ. Sci. Technol.* **2009,** *43* (4) 1115.