Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts.

Supplemental Information

Passive sampling of DDT, DDE and DDD in sediments: Accounting for degradation processes with reaction-diffusion modeling

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Figure S2. Fraction of PRC remaining (empty symbols) and fraction of target compound accumulated (filled symbols) for static incubation of PE in CM and LM sediments for *4,4′*-DDE (top panels) and *4,4′*-DDD (bottom panels). Fractional accumulation calculated as the ratio of concentration of target analyte measured in PE from static incubation divided by the concentration of the same analyte in tumbled PE. Lines represent the diffusion model of Fernandez et al.[1] with K_d (L_W/kg_{SED}) for DDE of $10^{3.8}$ (CM), $10^{3.7}$ (LM) and for DDD of $10^{4.0}$ (CM), $10^{3.6}$ (LM). Error bars for fraction of PRC remaining calculated based on one SD of PRC concentration in T=0 PE, and for fraction of target accumulation based on one SD of instrument error.

Figure S3 Fraction of ^{13}C *2,4′*-DDT remaining in PE (empty symbols, left axis), and measured as its degradation product ^{13}C *2,4′*-DDD (filled symbols, right axis) as a function of time after incubation in CM (green triangles), LM (red squares) and F2 (blue diamonds). Lines are drawn to guide the eye and are not model fits.

Figure S4. Measured ^{13}C PCB 153 and d_8 4,4'-DDT remaining after incubation with sediment under tumbling conditions for 4 to 60 days. Concentrations normalized by the spiked concentrations. Exponential trendline suggested degradation is occurring at a rate of 0.04/d, but considering only the data at time = 0 and 4 days would imply the rate was faster (ca. 0.4/d).

Figure S5. Normalized concentration *versus* distance for DDT PRC inside the PE (-12.5 to 12.5 µm window) and in the sediment bed (note distance in sediment bed is in cm) as a function of deployment times of 0 through 35 days in increments of 1 day for various cases: A – no reaction ($K_d=10^{4.5}$), B – 0-10 cm ($K_d=10^{4.5}$, k_r=0.01/d), C – 20-30 cm ($K_d=10^{4.3}$, k_r=1.04/d) D- F2 lab ($K_d=10^{3.9}$, k_r=3.38/d). Input parameters (K_d and k_r) were those fitted from the DDT-PRC loss curves either from field deployments (panels B and C, 0-10 cm and 20-30 cm, respectively) or laboratory incubations with F2 sediment (panel D). Concentration in the PE was normalized by the initial concentration for the DDT PRC and concentration in the sediment was normalized by initial concentration in the PE divided by K_{PESED}.

Figure S6. Sensitivity analysis of model derived k_r relative to the value of K_d used for fitting the PRC loss data for each depth into the sediment bed. Panel A shows the correlation between the best fit k_r in log space *versus* log K_d and the associated trendline for each depth into the sediment. Panel B shows the RMSE of the reaction diffusion model fits for each depth into the sediment. The empty symbols represent the K_d value for DDE PRC which as discussed in the main text, were used as the K_d value for the DDT PRC in deriving the k_r values calculated in Figure 4. RMSE did not increase or decrease with log K_d suggesting that the fits could not have been consistently improved by using a higher or lower value of K_d for the DDT PRC relative to that measured for the DDE PRC.

Figure S7. Sensitivity analysis of best fit k_r relative to the value of K_d used for fitting the PRC loss data for each static *ex situ* laboratory incubation (CM, LM and F2). Panel A shows the correlation between the best fit k_r in log space *versus* log K_d and the associated trendline for each depth into the sediment. Panel B shows the RMSE of the reaction diffusion model fit for each sediment. The empty symbols represent the K_d value for DDE PRC which as discussed in the main text, was used as the K_d value for the DDT PRC in deriving the k_r values calculated in Figure 5. For these PRC data, RMSE appeared to increase with log K_d suggesting that although using a higher K_d would have decreased the estimated first order reaction rate, it would not have improved the model fit.

ESI-1. Derivation of Laplace solution for reaction diffusion model.
The general procedure for deriving Laplace domain solutions for the transfer between polymer membranes and various media has been described elsewhere (Fernandez *et al.*[1], and Tcaciuc *et al.*[2]), and we follow the same steps here.

<u>Solution for PRCs.</u> The governing equation are repeated here from the main text:
Governing equations:

$$\frac{\partial C_{PE}}{dt} = D_{PE}\frac{\partial^2 C_{PE}}{\partial x^2} \qquad \text{for} - L < x < L \tag{1}$$

$$\frac{\partial C_{SED}}{dt} = D_{SED}\frac{\partial^2 C_{SED}}{\partial x^2} - k_r C_{SED} \qquad \text{for } x < -L \text{ and } x > L \tag{2}$$

where x is the distance variable (cm, with the center of PE at x=0), C_{PE} and C_{SED} are the concentrations (mol/cm^3) in the PE and sediment, respectively, D_{PE} and D_{SED} are the diffusivities in the PE and in sediment (cm^2/s), k_r is the first order degradation rate of the chemical in the sediment (s^{-1}), and L is the PE half length (cm).

In addition, we write the following initial conditions (t=0):

$$C_{PE} = C_{PE}^0 \text{ for} - L < x < L \tag{3}$$

$$C_{SED} = 0 \text{ for } x < -L \text{ and } x > L \tag{4}$$

where C_{PE}^0 is the concentration in PE at t=0, and associated boundary conditions:

$$\frac{\partial C_{PE}}{\partial x} = 0 \qquad \text{at } x = 0 \tag{5}$$

$$C_{PE} = K_{PESED}\, C_{SED} \qquad \text{at } x = L \text{ and } x = -L \tag{6}$$

$$D_{PE}\frac{\partial C_{PE}}{\partial x} = D_{SED}\frac{C_{SED}}{\partial x} \qquad \text{at } x = L \text{ and } x = -L \tag{7}$$

$$C_{SED} = 0 \qquad \text{at } x = \infty \text{ and } X = -\infty \tag{8}$$

where K_{PESED} is the PE-sediment partition coefficient.
The first step in deriving the solution is to transform the equations and boundary conditions into nondimensional units. $\bar{C}, X, T$ are now unit-less variables for concentration, distance and time:

$$\overline{C_{PE}} = \frac{C_{PE}}{C_{PE}^0} \text{ and } \overline{C_{SED}} = C_{SED}\frac{K_{PESED}}{C_{PE}^0} \tag{9}$$

$$X = \frac{x}{L} \text{ and } T = t * \frac{D_{PE}}{L^2} \tag{10}$$

In non-dimensional terms the initial conditions for T=0 for a PRC diffusing out of PE become:

$$\overline{C_{PE}} = 1 \text{ for} - 1 < X < 1 \tag{11}$$

$$\overline{C_W} = 0 \text{ for } X < -1 \text{and } X > 1 \tag{12}$$

Similarly, at T>0, we have the following boundary conditions in nondimensional units:

- No flux at the center of sampler: $\frac{\partial \overline{C_{PE}}}{\partial T} = 0 \; at \; X = 0;$ (13)
- Chemical equilibrium at sampler/sediment interface:
  $\overline{C_{PE}} = \overline{C_{SED}}$ at $X = 1$ and $X = -1$ (14)
- No accumulation of mass at sampler-sediment interface

$$\frac{\partial \overline{C_{PE}}}{\partial X} = \frac{\psi}{K_{PESED}}\frac{\partial \overline{C_{SED}}}{\partial X} \text{ at } X = 1 \text{ and } X = -1, \text{ where } \psi = \frac{D_{SED}}{D_{PE}} \tag{15}$$

- At large distances away from the sampler, concentration equals to that of sediment, which is 0 for a PRC: $\overline{C_{SED}} = 0 \; at \; X = \infty$ and $X = -\infty$ (16)

Lastly, we perform the same change of variables for the governing equations:

$$\frac{\partial^2 \overline{C_{PE}}}{\partial X^2} = \frac{\partial \overline{C_{PE}}}{\partial T} \tag{17}$$

$$\frac{\partial^2 \overline{C_{SED}}}{\partial X^2} - \frac{\overline{k_r}}{\psi} C_{SED} = \frac{1}{\psi} \frac{\partial \overline{C_{SED}}}{\partial T} \tag{18}$$

where $\overline{k_r}$ is the reaction rate k_r normalized by D_{PE}/L^2. By taking Laplace transforms of the governing equations, we translate the equations from time domain to complex s domain, and thus reduce the complexity of the differential equations. $\widehat{C_{PE}}$ and $\widehat{C_W}$ denote the Laplace domain expression of concentration. It follows that we now have the following governing equations and boundary conditions that are independent of the time variable:

- governing equations:

$$\frac{\partial^2 \widehat{C_{PE}}}{\partial X^2} = s\,\widehat{C_{PE}} - 1; \tag{19}$$

$$\frac{\partial^2 \widehat{C_{SED}}}{\partial X^2} - \frac{\overline{k_r}}{\psi} \widehat{C_{SED}} = \frac{s}{\psi}\,\widehat{C_{SED}}; \tag{20}$$

- boundary conditions:

$$\frac{\partial \widehat{C_{PE}}}{\partial X} = 0 \qquad \text{at } X = 0 \tag{21}$$

$$\widehat{C_{PE}} = \widehat{C_{SED}} \qquad \text{at } X = 1 \tag{22}$$

$$\frac{\partial \widehat{C_{PE}}}{\partial X} = \frac{\psi}{K_{PESED}} \frac{\partial \widehat{C_{SED}}}{\partial X} \qquad \text{at } X = 1 \tag{23}$$

$$\widehat{C_{SED}} = 0 \qquad \text{at } X = \infty \tag{24}$$

The solutions found to satisfy both differential equations and the first and last boundary conditions above:

$$\widehat{C_{PE}} = A \cosh\left(X\sqrt{s}\right) + \frac{1}{s} \tag{25}$$

$$\widehat{C_{SED}} = Be^{\left(-X\sqrt{\frac{s+\overline{k_r}}{\psi}}\right)} \tag{26}$$

Using the second and third boundary conditions above, we can solve for A and B:

$$A = -\frac{1}{s} \frac{1}{\sqrt{\frac{s}{s+k_r}} \frac{K_{PEW}}{\sqrt{\psi}} \sinh\left(\sqrt{s}\right) + \cosh\left(\sqrt{s}\right)} \tag{27}$$

$$B = -A \sinh\left(\sqrt{s}\right) \frac{K_{PESED}}{\sqrt{\psi}} \sqrt{\frac{s}{s+k_r}}\, e^{\left(\sqrt{\frac{s+\overline{k_r}}{\psi}}\right)} \tag{28}$$

Since we are ultimately interested in the fraction of PRC which remains in the PE after a certain time, we can integrate the concentration in the PE across the thickness of the PE:

$$\widehat{M_{PRC}} = \int_0^1 \widehat{C_{PE}}\, dX \tag{29}$$

After plugging in A, and simplifying we are left with:

$$\widehat{M_{PRC}} = \frac{1}{s} - \frac{1}{s^{\frac{3}{2}}} \frac{1}{\frac{K_{PEW}}{\sqrt{\psi}} \sqrt{\frac{s}{s+k_r}} + \coth\left(\sqrt{s}\,\right)} \tag{30}$$

The expression cannot be inverted to the time domain using inversion tables. Instead we use a MATLAB numerical inversion algorithm invlap.m [3] to find the corresponding mass of PRC left in the PE as function of time T. A sample code to perform this operation is provided in SI-2.

Solution for target compounds. For target analytes diffusing into the PE, the governing equations remain the same as for the transport of PRCs, but the initial conditions and boundary conditions are different, written here directly in non-dimensional terms:

- Initial conditions at T=0:

$$\overline{C_{PE}} = 0 \text{ for} - 1 < X < 1 \tag{31}$$

$$\overline{C_{SED}} = 1 \text{ for } X < -1 \text{and } X > 1 \tag{32}$$

- Boundary conditions at $T > 0$

$$\frac{\partial \overline{C_{PE}}}{\partial X} = 0 \qquad \text{at } X\text{=0} \tag{33}$$

$$\overline{C_{PE}} = \overline{C_{SED}} \qquad \text{at } X\text{=1 and } X\text{=-1} \tag{34}$$

$$\frac{\partial \overline{C_{PE}}}{\partial \hat{x}} = \frac{\psi}{K_{PEW}} \frac{\partial \overline{C_{SED}}}{\partial X} \qquad \text{at } X\text{=1 and } X\text{=-1} \tag{35}$$

$$\frac{\partial \overline{C_{SED}}}{\partial T} = -\overline{\mathrm{k}}_{\mathrm{r}} T \qquad \text{at } X\text{= } \infty \text{ and } X\text{=-}\infty \tag{36}$$

We note that as opposed to the PRC case, the concentration is now normalized by C_{SED}^{0}, the initial concentration of the analyte in the sediment. Unlike a diffusion case, though, we can no longer assume that the sediment concentration stays constant over time. Instead, at a distance far away from the sampler the concentration in the sediment is only affected by the intrinsic rate constant.

The governing equations in Laplace domain are slightly different due to the change in the initial conditions:

$$\frac{\partial^2 \widehat{C_{PE}}}{\partial X^2} = s \ \widehat{C_{PE}}; \tag{37}$$

$$\frac{\partial^2 \widehat{C_{SED}}}{\partial X^2} = \frac{s+\overline{k_r}}{\psi} \widehat{C_{SED}} - \frac{1}{\psi}; \tag{38}$$

And the boundary conditions in Laplace domain are also slightly different:

$$\frac{\partial \widehat{C_{PE}}}{\partial X} = 0 \qquad at\ X = 0 \tag{39}$$

$$\widehat{C_{PE}} = \widehat{C_{SED}} \qquad at\ X = 1 \tag{40}$$

$$\frac{\partial \widehat{C_{PE}}}{\partial \hat{x}} = \frac{\psi}{K_{PESED}} \frac{\partial \widehat{C_{SED}}}{\partial X} \qquad at\ X = 1 \tag{41}$$

$$\widehat{C_{SED}} = \frac{1}{s+\overline{k_r}} \qquad at\ X = \infty \tag{42}$$

The solutions that satisfy the governing equations, and the first and last boundary conditions, take the form:

$$\widehat{C_{PE}} = D \cosh\left(X\sqrt{s}\right) \tag{43}$$

$$\widehat{C_{SED}} = E\ e^{\left(-X\sqrt{\frac{s+k_r}{\psi}}\right)} + \frac{1}{s+\overline{k_r}} \tag{44}$$

After solving for D and E using the second and third boundary conditions, we get:

$$D = \frac{1}{s+\overline{k_r}} \frac{1}{\cosh(\sqrt{s}) + \frac{\mathrm{K_{PEW}}}{\sqrt{\psi}} \sqrt{\frac{s}{(s+\overline{k_r})}} \sinh(\sqrt{s})} \tag{45}$$

$$E = -D \frac{\mathrm{K_{PEW}}}{\sqrt{\psi}} \sqrt{\frac{s}{(s+\overline{k_r})}} \sinh\left(\sqrt{s}\right) e^{\left(\sqrt{\frac{s+k_r}{\psi}}\right)} \tag{46}$$

Lastly, $\widehat{M_{target}}$ can now be calculated as:

$$\widehat{M_{target}} = \int_0^1 \widehat{C_{PE}}\, dX \tag{47}$$

$$\widehat{M_{target}} = \frac{1}{\sqrt{s}(s+k_r)} \frac{1}{\coth(\sqrt{s}) + \frac{\mathrm{K_{PEW}}}{\sqrt{\psi}} \sqrt{\frac{s}{s+k_r}}} \tag{48}$$

As expected, the solution reduces for $k_r = 0$ to that found by Fernandez et al. (2009)[1]:

$$\widehat{M_{target}} = \frac{1}{s^{\frac{3}{2}}} \frac{1}{\coth(\sqrt{s}) + \frac{\mathrm{K_{PEW}}}{\sqrt{\psi}}} \tag{49}$$

ESI-2. Additional materials and methods details

Solvents used for extraction of PE and sediment were purchased from VWR (JT Baker Ultraresi-analyzed). ^{13}C labeled PCBs (^{13}C PCB 28, ^{13}C PCB 47, ^{13}C PCB 111, ^{13}C PCB 153- used as PRCs, ^{13}C PCB 70, ^{13}C PCB 105, ^{13}C PCB 19, ^{13}C PCB 97,^{13}C PCB 170 and ^{13}C PCB 167- used as recovery or injection standards), ^{13}C labeled DDX (^{13}C *4,4′*-DDE, ^{13}C *2,4*'-DDT, ^{13}C *4,4*'-DDD – used as PRCs), and d_8 *4,4'*-DDD (used as a recovery standard) were purchased from Cambridge Isotope Laboratory (Tewskbury, MA). In addition, d_8 *2,4'*-DDT (used as a recovery standard) and d_8 *4,4'*-DDT (used only for spiking sediment) were obtained from C/D/N Isotopes (Pointe-Claire, Quebec). Polyethylene strips, used as samplers in the field and in laboratory experiments, were cut from PE sheets (25 µm, Film Guard 1 mil plastic drop cloth, Covalence Plastics, Minneapolis, MN), and cleaned by a sequence of overnight submersions in dichloromethane, methanol, and Milli-Q water (Aries Vaponics, Rockland, MA).

GCMS analysis of PE and sediment. All PE samples (retrieved from field deployment or incubated in the laboratory with sediment) were extracted according to procedures described in the main text and analyzed using an Agilent 6890 GC coupled with a mass spectrometer (JEOL GCmate, JOEL Ltd, Tokyo, Japan). For the GCMS analysis, the PE extracts were usually reduced to 250 uL – 1 mL volume, and aliquots of 1 or 2 uL of the same extract were injected directly onto an inert guard column (oven temperature of 55 ^{o}C), connected to a DB-5 XLB column (J&W Scientific DB-XLB, 30 m × 0.32 mm ID, 0.5 µm film thickness). The separation was done using He as carrier gas at a column flow of 2 mL/min. The oven temperature was ramped from 55 °C to 175 °C at 15 °C/min, and then to 270 °C at 4°C/min, followed by a 12 min hold. Similar GCMS conditions were used for the analysis of DDX in the sediment samples F1, F2, CM and LM.

Incubation of lake sediment with d_8 4,4′-DDT. Field-collected F2 sediment was used to determine if DDT could degrade in the laboratory conditions used typically for *ex situ* sampling (i.e., tumbling). Nine 50 mL, combusted, pear-shaped flasks were spiked with 1 µg ^{13}C PCB 153 and 5 µg d8 4,4′-DDT (25 µL of solution in hexane). To each flask about 20 g wet sediment and 40 mL of MilliQ water were added. The flasks were then put on a tumbler and removed after 4 (duplicates), 11, 14, 22, 30 (duplicates), 50, 60 days. The sediment slurry was poured off into an amber jar and frozen until freeze-dried, and the walls of the flask were washed with a mixture of methanol and DCM (to check that the PCB and DDT spike had mixed into the sediment slurry, as opposed to remaining on the walls). Aliquots of 1 g of the freeze-dried sediment were extracted using the procedure described previously for analysis of sediments.

Clarus GCMS analysis of d_8 *4,4′*-DDT spiked sediments. The analysis was performed with a programmable inlet and a DB-XLB column (30 m, 0.25 mm ID, 1 µm film thickness, Agilent Technologies, Lexington, MA). Injections of 1 µL were done at 70 °C, in splitless mode, and the inlet temperature was ramped to 275 °C at 200 °C/min. The split valve (20:1 split ratio) was open after 1.5 min. The column temperature was held at 75 °C for 1.5 min, then ramped to 200 at 25 °C/min, and to 275 °C at 4 °C/min. Helium was used as a carrier gas at 2 mL/min and the MS source temperature was held at 250 °C. For analysis of DDT in sediment samples, the inlet liner (deactivated liner, without glass wool, Restek, Bellefonte, PA) was periodically removed and cleaned, to prevent degradation of the DDT. Degradation was monitored by the loss of signal of ^{13}C *4,4′*-DDT spiked in each sample.

Results of d_8 *4,4'*-DDT sediment tumbling time course. We observed a marked decrease in DDT concentration compared to the spiked amount, but the data were not suitable for evaluating a reaction rate. Although more than 80% of the spiked DDT was lost in all sampled flasks, there was no correlation between DDT concentration and incubation time. However, we are fairly confident that the observed loss of DDT was not due to an experimental artifact, because both the PCB and DDT spikes were loaded into the tumbling flasks from the same solution (thus at a known and constant mass ratio to each other of 1:5 PCB:DDT). It is unlikely that DDT could have crystalized in the sediment, (which would have led to a heterogeneous concentrations), since the levels at which DDT were spiked were fairly low (<500 ng/g sediment). Even if crystals would have formed when the chemicals were spiked into the sediment, DDT and PCB 153 have similar chemical properties (MW 360 and 354, K_{OW} $10^{6.9}$ and $10^{6.9}$, melting points of 103 and 108 °C, respectively), and thus should have dissolved at the same rate. The loss to the walls of DDT was also negligible.

Fitting PRC losses with diffusion mass transfer models. For diffusion-controlled transport, the PRC loss data were fit with the model of Fernandez et al.[1] as well as with a simplified time-domain expression recently developed by Apell et al.[2] (see code in SI-3 "Sample_findKd.m"). The advantage of using the second time-domain model was that additional fit statistics could be obtained by using a Matlab built-in nonlinear fit function. However, as mentioned in Apell et al.[2], the time domain expression derived therein assumes that the contribution of the membrane to the mass transfer is negligible. In contrast, the Laplace domain model of Fernandez et al. takes into account diffusion through the membrane and the sediment bed, and is thus more general.

Using the model of Fernandez et al.[1], the best fit K_d was determined iteratively as the K_d value that minimized the sum of the squared differences between the measured and the model-calculated fraction of PRC remaining, across the sampling time points (e.g., 10 and 30 d for the field deployment).

For the model of Apell et al.,[2] which describes the fraction of the PRC remaining as a function of time, t and one parameter, T_{sed}:

$$f_{PRC,remaining} = \exp\left(\frac{t}{T_{sed}}\right) erfc\left(\sqrt{\frac{t}{T_{sed}}}\right) \quad (49)$$

the Matlab built in nonlinear fit function (NonLinearModel.fit) was used to evaluate T_{sed} and the standard error in T_{sed}. From T_{sed}, the K_d was calculated according to the expression[2]:

$$K_d = \frac{K_{PEW}^2 L^2 \tau}{T_{sed} D_W \phi} \quad (50)$$

where K_{PEW} is the PE-water partition coefficient (L_W/L_{PE}), L is the PE half-thickness (12.5 µm throughout), φ is the porosity of the sediment, τ is the tortuosity (calculated as $1-\varphi^2$, as in Fernandez et al.[1]) and D_W is the diffusivity of the compound in water (cm^2/s).

We note here that both models gave the same best fit log K_d results to within 3 decimal points, supporting the findings in Apell et al. [2], that the diffusion through the sediment bed dominated the mass transfers.

Fitting PRC losses with the reaction-diffusion model. For the DDT PRC, the best-fit reaction rate was determined by minimizing the sum of the squares of the differences between model-calculated and measured PRC losses for the various sampling time points (see code in SI-3 "Sample_main.m"). The K_d value of DDT was assumed to be equal to that of DDE (see main text) and changing the K_d value did affect the value of the best fit degradation rate (i.e., doubling the K_d halved the fitted k_r value and vice-versa).

ESI-3. Sample Matlab code used for fitting PRC loss data.

A. Laplace domain solution for PRCs diffusing out of PE

```
% Mass_out_rxn.m
% Laplace-space expression for the mass of PRC transfered from
% polymer to porous medium
%   K12 is partitioning coefficient between phase 1 (polymer) and phase 2
%   (porous medium)
%   Y is ratio of diffusivities (D(porous medium)/D(polymer))
%   krxn is the reaction rate in the sediment normalized to Dpe/L^2
%   s is the Laplace parameter



function F = Mass_out_rxn(s);
global K12 Y krxn;
 % rxn in sed
   F = (1./(s))-1./((s).^(3/2))./((K12)./(Y.^0.5).*sqrt(s./(s+krxn))+coth(sqrt(s)));
end
```

B. Laplace domain solution for target analytes diffusing into PE

```
% Mass_in_rxn.m
% Laplace-domain expression for the mass of target chemical taken up by
% polymer from porous medium
%   K12 is partitioning coefficient between phase 1 (polymer) and phase 2
%   (porous medium)
%   Y is ratio of diffusivities (D(porous medium)/D(polymer))
%   krxn is the reaction rate in the sediment normalized to Dpe/L^2
%   s is the Laplace parameter

function F = Mass_in_rxn(s);
global K12 Y krxn;
  F=1./((s.^0.5).*(s+krxn).*(coth(sqrt(s))+(K12./(Y.^0.5)).*((s./(krxn+s)).^0.5)));
end
```

C. Sample Matlab routine used to fit PRC loss data for DDE, DDD, and PCB PRCs and evaluate their respective K_d's using the diffusion model of Fernandez et al. (2009) and the simplified time domain solution of Apell et al. (2015).

```
%sample_findKd.m
%Sample code for fitting PRC loss data and determining best fit Kd
%This calculation needs the function invlap.m which can be downloaded at
%www.cambridge.org/us/engineering/author/nellisandklein/downloads/invlap.m
clear all
global phi krxn K12 Y;
time=32; % deployment time
phi=0.77; %porosity
L=12.75*10^-4; %half thickness of polymer (cm)

%properties for PCB PRCs used in this study
```

```
PCB_name={'PCB 28' 'PCB 57' 'PCB 111' 'PCB 153'};
MW_array_PCBs=[268 304 338 372]; %molar mass (g/mol) of 13C labelled
Dw_array_PCBs=(2.7*10^-4)./(MW_array_PCBs.^0.71);
Kpew_array_PCBs=10.^[5.22 5.57 6.76 6.92];
Dpe_array_PCBs=10.^[-8.81 -8.98 -9.16 -9.33]; %diffusivity in polymer (cm2/s)

%properties for DDT PRCs used in this study
DDT_name={'4,4-DDE' '4,4 DDD' '2,4 DDT'};
MW_array_DDTs=12+[320 318 354]; %molar mass (g/mol) of 13C labelled
Dw_array_DDTs=(2.7*10^-4)./(MW_array_DDTs.^0.71);
Kpew_array_DDTs=10.^[5.74 4.86 5.72];
Dpe_array_DDTs= 10.^[-9.33 -9.39 -9.55]; %diffusivity in polymer (cm2/s)
linespec_array=['m','c','g','y','b','k','r']; %matlab linespecs
t=0.0001:1:time; %days

%times of PE removal from sediment in days
Time_F2=[5 10 20 30];

%sample PRC loss from PE incubated in F2 sediment
Obs_PRC_rem_PCBs_F2=[0.86   0.70    NaN     0.54;
              1.02    0.82    NaN     0.81;
              0.95    0.96    0.93    0.89;
              0.86    0.89    0.92    0.81];
Obs_PRC_rem_DDTs_F2=[0.90   0.90    0.81    0.77;
              0.49    0.37    0.29    0.18;
              0.70    0.59    0.17    0.04];

%measured properties of the sediment
phi=0.77; %based on the fraction of water and density of solids of 2.5 kg/L
tau=1-log(phi^2); %Fernandez ES&T 2009 43 (8888-)

%% find Kd for DDTs iteratively
for i=1:length(Kpew_array_DDTs) % each compound
  Kdlow=0.1; % all Kd in the loop are Lw/Lsed
  for spacing=[0.2,0.02,0.002, 0.0002]
    for n=1:40 %each Kd value
      Kd=10^(Kdlow+(n-1)*spacing); %creates a vector of possible Kd's...
      ...based on the current spacing; choose for expected range
      Kdstore(n)=log10(Kd);
      K12=Kpew_array_DDTs(i)/Kd;
      Dsed=Deffective(Kd,MW_array_DDTs(i)); %calls function
      Y=Dsed/Dpe_array_DDTs(i);
      %calculate sampling times in non dimensional time
      Time_F2_ND=Time_F2*3600*24*Dpe_array_DDTs(i)/(L)^2;
      for j=1:length(Time_F2_ND) %calculate PRC loss for each sampling time
        krxn=0; %set reaction component to 0 to get the diffusion-only model
        Mstore(j,n)=invlap('Mass_out_rxn',Time_F2_ND(j)); %calls function
      end
    end
  for n=1:40 %for each Kd value
   %calculate sum square of the differences between observed PRC loss
   %and predicted using the model and nth Kd value
   Sum_Dev(n)=sum((Mstore(:,n)-Obs_PRC_rem_DDTs_F2(i,:)').^2,'omitnan');
  end
  [min_dev, index_min_dev]=min(Sum_Dev); %find minimum deviation
```

```
    Kdlow=Kdstore(index_min_dev)-spacing; %step back by one spacing
    end
    Kd_DDTs_iter(i)=log10(10^(Kdlow+spacing)/(1-phi)/2.5); %L/kg
    RMSE(i)=sqrt(min_dev);
end

%% find Kd for DDTs using time-domain equation in Apell et al. 2015
%model function with B as a fitted parameter and x as time, both in days
modelfun=@(B,x) exp(x/B) .* erfc((sqrt(x/B)));

for n=1:length(Kpew_array_DDTs) %each compound
    X=Time_F2; %define X vector (time in days)
    y=Obs_PRC_rem_DDTs_F2(n,:); %define y vector (PRC remaining in PE)
    %initial guesses for Kds (model performs best with a good initial guess
    %adjust initial guess to a better value if the output is complex
    Kd_array_DDTs=(1-phi)*2.5*10.^([3.9 4.1 5.6]); % for 4,4 DDE 4,4 DDD 2,4 DDT
    %calculate
    GuessB(n)=(Kpew_array_DDTs(n)^2*L^2*tau)/Kd_array_DDTs(n)/Dw_array_DDTs(n)/phi/3600/24;
    mdl = NonLinearModel.fit(X,y,modelfun,GuessB(n)); %model fit

    %use model fit to calculate Kd from B
    Kd_DDTs_NLF(n)=log10(1/(1-phi)/2.5*Kpew_array_DDTs(n)^2*L^2*tau/...
        mdl.Coefficients.Estimate/Dw_array_DDTs(n)/phi/3600/24); %L/kg

    %calculate SE of Kd from SE of B
    Positive_SE_DDTs_Kd_NLF(n)=log10(1/(1-phi)/2.5*Kpew_array_DDTs(n)^2*L^2*tau/...
        (mdl.Coefficients.Estimate-mdl.Coefficients.SE)/Dw_array_DDTs(n)/phi/3600/24)-Kd_DDTs_NLF(n);
    Negative_SE_DDTs_Kd_NLF(n)=Kd_DDTs_NLF(n)-log10(1/(1-phi)/2.5*Kpew_array_DDTs(n)^2*L^2*tau/...
        (mdl.Coefficients.Estimate+mdl.Coefficients.SE)/Dw_array_DDTs(n)/phi/3600/24);
end

%% find Kd for PCBs iteratively
for i=1:length(Kpew_array_PCBs) % each compound
    Kdlow=0.1; % all Kd in the loop are Lw/Lsed
    for spacing=[0.2,0.02,0.002, 0.0002]
        for n=1:40 %each Kd value
            Kd=10^(Kdlow+(n-1)*spacing); %creates a vector of possible Kd's...
            ...based on the current spacing; choose for expected range
            Kdstore(n)=log10(Kd);
            K12=Kpew_array_PCBs(i)/Kd;
            Dsed=Deffective(Kd,MW_array_PCBs(i)); %calls function
            Y=Dsed/Dpe_array_PCBs(i);
            %calculate sampling times in non dimensional time
            Time_F2_ND=Time_F2*3600*24*Dpe_array_PCBs(i)/(L)^2;
            for j=1:length(Time_F2_ND) %calculate PRC loss for each sampling time
                krxn=0; %set reaction component to 0 to get the diffusion-only model
                Mstore(j,n)=invlap('Mass_out_rxn',Time_F2_ND(j)); %calls function
            end
        end
    for n=1:40 %for each Kd value
      %calculate sum square of the differences between observed PRC loss
      %and predicted using the model and nth Kd value
      Sum_Dev(n)=sum((Mstore(:,n)-Obs_PRC_rem_PCBs_F2(i,:)').^2, 'omitnan');
    end
    [min_dev, index_min_dev]=min(Sum_Dev); %find minimum deviation
```

```
    Kdlow=Kdstore(index_min_dev)-spacing; %step back by one spacing
    end
    Kd_PCBs_iter(i)=log10(10^(Kdlow+spacing)/(1-phi)/2.5); %L/kg
end


%% find Kd using time-domain equation in Apell et al. 2015
modelfun=@(B,x) exp(x/B) .* erfc(real(sqrt(x/B)));

for n=1:length(Kpew_array_PCBs) %each compound
    clear X y mdl
    X=Time_F2; %define X vector (time in days)
    y=Obs_PRC_rem_PCBs_F2(n,:); %define y vector (PRC remaining in PE)
    %initial guesses for Kds (model performs best with a good initial guess
    %adjust initial guess to a better value if the output is complex
    Kd_array_PCBs_Guess=1/((1-phi)*2.5)*10.^[3.4 3.4 5 6]; %for PCB 28 47 111 153
    %calculate
    GuessB(n)=(Kpew_array_PCBs(n)^2*L^2*tau)/Kd_array_PCBs_Guess(n)/Dw_array_PCBs(n)/phi/3600/24;
    mdl = NonLinearModel.fit(X,y,modelfun,GuessB(n)); %model fit

    %use model fit to calculate Kd from B
    Kd_PCBs_NLF(n)=log10(1/(1-phi)/2.5*Kpew_array_PCBs(n)^2*L^2*tau/...
        mdl.Coefficients.Estimate/Dw_array_PCBs(n)/phi/3600/24);

    %calculate SE of Kd from SE of B
    Positive_SE_PCBs_Kd_NLF(n)=log10(1/(1-phi)/2.5*Kpew_array_PCBs(n)^2*L^2*tau/...
        (mdl.Coefficients.Estimate-mdl.Coefficients.SE)/Dw_array_PCBs(n)/phi/3600/24)-Kd_PCBs_NLF(n);
    Negative_SE_PCBs_Kd_NLF(n)=Kd_PCBs_NLF(n)-log10(1/(1-phi)/2.5*Kpew_array_PCBs(n)^2*L^2*tau/...
        (mdl.Coefficients.Estimate+mdl.Coefficients.SE)/Dw_array_PCBs(n)/phi/3600/24);
end



%%
disp('                    log Kd (L/kg)        ')
disp('                   Using iterations      ')
disp('   4,4 DDE   4,4 DDD   2,4 DDT   PCB 28    PCB 47    PCB 111   PCB153')
disp([Kd_DDTs_iter Kd_PCBs_iter])
disp('                  Using Nonlinear fit    ')
disp([Kd_DDTs_NLF Kd_PCBs_NLF])
disp('                 Positive standard error ')
disp([Positive_SE_DDTs_Kd_NLF Positive_SE_PCBs_Kd_NLF])
disp('                 Negative standard error')
disp([Negative_SE_DDTs_Kd_NLF Negative_SE_PCBs_Kd_NLF])
```

D. Sample Matlab routine used to determine degradation rate of DDT in sediments based on PRC loss data, and for evaluating PRC loss and target accumulation using the reaction-diffusion model.

```
%Sample_main.m
%Sample code for using the 1D reaction-diffusion model to evaluate
%(1) best fit reaction rate
%(2) PRC loss
```

```
%(3) target accumulation
%This calculation needs the function invlap.m which can be downloaded at
%www.cambridge.org/us/engineering/author/nellisandklein/downloads/invlap.m
clear all
global phi krxn K12 Y;

%polymer properties
L=12.5*10^-4; %half thickness of polymer (cm)
%sediment porosity, based on the measured water content of the sediment
phi=0.77; %assumed constant with depth into sediment bed

time=32; % deployment time in days
t=0.0001:0.5:time; %time vector in days

%properties of DDT PRC
Kpew_array=10.^[5.76]; %L/L, from Hale et al. 2010 Env Pollut 158 (2511-2517)
Dpe_array=[2.62]*10^-10; %diffusivity in polymer (cm2/s) of 2,4 DDT PRC
linespec_array=['r','b','g','k','c','m','r','b','g']; %matlab linespecs
MW_array=[354]+12; %molar mass (g/mol) of 13C labelled 2,4 DDT
%Kd value assumed to be equal to best fit Kd value of DDE calculated with
%the diffusion model and a routine similar to sample_findKd.m
Kd=[4.5 4.3 4.3 4.4]; %log space LW/kgdw
Kd_array=(1-phi)*2.5*10.^Kd; % Lw/Lsed

%% determining best fit reaction rates and calculating PRC losses
%measured fraction of PRC remaining after 10 and 30 d deployments at each
%depth into sediment
Sampl_Time=[10 30]; %days
fDDT=[0.68 0.40;  %0-10
    0.69 0.28;  %10-20
    0.52 0.15;  %20-30
    0.38 0.16]; %30-40

%find reaction rate k value that minimizes deviations between observed and
%model predicted fraction of PRC remaining
figure(1)
for i=1:4 %each sediment depth
   K12=Kpew_array(1)/Kd_array(i);
   Dsed=Deffective(Kd_array(i), MW_array(1));%cm^2/s
   Y=Dsed/Dpe_array(1);
   Sampl_Time_ND=Sampl_Time*24*3600*Dpe_array(1)/(L^2);
   krlow=-7; % in log space, units of per s
   for spacing=[1,0.1,0.01,0.001]
      for n=1:40 %each kr value
         kr=10^(krlow+(n-1)*spacing); %creates a vector of possible kr's...
         ...based on the current spacing;
         krstore(n)=log10(kr); %in log space
         krxn=kr*L^2./Dpe_array(1);
         for j=1:length(Sampl_Time_ND) %calculate PRC loss for each sampling time
            Mstore(j,n)=invlap('Mass_out_rxn',Sampl_Time_ND(j)); %calls function
         end
      end
   for n=1:40 %for each kr value
     %calculate sum square of the differences between observed PRC loss
     %and predicted using the model and nth Kd value
     Sum_Dev(n)=sum((Mstore(:,n)-fDDT(i,:)').^2,'omitnan');
```

```
   end
   [min_dev, index_min_dev]=min(Sum_Dev); %find minimum deviation
   krlow=krstore(index_min_dev)-spacing; %step back by one spacing
   end
   k_DDT(i)=10^(krlow+spacing)*3600*24;
     RMSE(i)=sqrt(min_dev);
   %calculate fraction PRC remaining for given Kd and fitted k_DDT
   krxn=k_DDT(i)*L^2./Dpe_array(1)/3600/24;
   T=t*24*3600*Dpe_array(1)/(L^2);
   for j=1:length(T) %calculate PRC loss for each sampling time
      M(j,i)=invlap('Mass_out_rxn',T(j)); %calls function
   end
   plot(t,M(:,i),'Color', linespec_array(i))
   hold on
  switch i
     case 1
      leg(i)={['k_0_-_1_0_c_m   ', sprintf('%.2f',k_DDT(i)),' d^-^1']};
     case 2
      leg(i)={['k_1_0_-_2_0_c_m ', sprintf('%.2f',k_DDT(i)),' d^-^1']};
     case 3
      leg(i)={['k_2_0_-_3_0_c_m ', sprintf('%.2f',k_DDT(i)),' d^-^1']};
     case 4
      leg(i)={['k_3_0_-_4_0_c_m ', sprintf('%.2f',k_DDT(i)),' d^-^1']};
  end
end
legend(leg);
%plot data on top of the model lines
plot([10 30],fDDT(1,:),'LineStyle','s','Color',linespec_array(1))
plot([10 30],fDDT(2,:),'LineStyle','x','Color',linespec_array(2))
plot([10 30],fDDT(3,:),'LineStyle','o','Color',linespec_array(3))
plot([10 30],fDDT(4,:),'LineStyle','^','Color',linespec_array(4))
xlabel('Time (d)');
ylabel('Fraction of DDT PRC remaining, C/C^0');

%% using the 1-D reaction model to evaluate target accumulation
figure(2)
for i=1:4 %each sediment depth
   K12=Kpew_array(1)/Kd_array(i);
   Dsed=Deffective(Kd_array(i), MW_array(1));%cm^2/s
   Y=Dsed/Dpe_array(1);
    krxn=k_DDT(i)*L^2./Dpe_array(1)/3600/24;
   T=t*24*3600*Dpe_array(1)/(L^2);
   for j=1:length(T) %calculate PRC loss for each sampling time
      M(j,i)=invlap('Mass_in_rxn',T(j)); %calls function
   end
   plot(t,M(:,i),'Color', linespec_array(i))
    hold on
end

legend(leg); xlabel('Time (d)'); ylabel('Fraction of target accumulation, C/C^0');
```

Table S1. Concentrations (ng/g dry weight) of DDT, DDE and DDD isomers measured in sediments collected from the study sites (F1, F2, CM and LM) and used in laboratory experiments.

Compound	**F1**	**F2**	**CM**	**LM**
2,4'-DDE	n.d.	15	6.3	46
4,4'-DDE	6.5	51	25	140
2,4'-DDD	3.4	21	16	100
4,4'-DDD	4.5	42	30	280
2,4'-DDT	n.d.	n.d.	n.d.	n.d.
4,4'-DDT	n.d.	n.d.	n.d.	n.d.

n.d.= below detection limit of ~0.7 ng/g dry weight

Table S2. Initial PRC concentrations (ng/g PE) measured in PE used in the field[a] and in laboratory incubations, as well as limits of detection (LOD, ng/g) determined as 3 times the standard deviation of peak areas measured from blank runs, adjusted by the appropriate response factor and assuming an average mass of PE extracted given in parentheses.

Compound	**Field PE (ng/g)**	**SD**	**%**	**LOD (60 mg)**	**Lab PE (ng/g)**	**SD**	**%**	**LOD (15 mg)**
^{13}C PCB 28	153	4	3%	0.1	266	35	13%	0.5
^{13}C PCB 47	152	2	1%	0.1	243	4	2%	0.7
^{13}C *4,4'*-DDE	192	4	2%	0.1	298	13	4%	1.2
^{13}C PCB 111	171	10	6%	0.1	230	26	11%	0.7
^{13}C *2,4'*-DDT	246	6	2%	0.2	380	31	8%	1.1
^{13}C *4,4'*-DDD	143	2	1%	0.1	284	12	4%	0.5
^{13}C PCB 153	115	3	2%	0.1	198	30	15%	0.9

Notes:

[a] Initial PRC concentrations for the PE employed in the field were measured using laboratory blanks as described in the main text. However, the concentration of ^{13}C DDE PRC was measured in trip blanks that accompanied the deployed PE. This analysis was done at Eni Donegani laboratory and the measured concentration (205 ng/g) agreed well with the result in this table (192±4 ng/g).

Table S3. Injection, recovery, PRCs and target analytes used for the PE exposed to sediment in the field

Compound	**Quant Ion**	**Retention Time (min)**
Injection compounds		
^{13}C PCB 97	338	15.20
^{13}C PCB 167	372	20.12
Recovery compounds		
^{13}C PCB 70	304	13.83
d_8 *2,4′*-DDT	243	16.87
d_8 *4,4′*-DDD	243	17.4
^{13}C PCB 105	338	18.07
PRCs		
^{13}C PCB 28	268	11.08
^{13}C PCB 47	304	12.08
^{13}C *4,4′*-DDE	260	15.55
^{13}C PCB 111	338	15.62
^{13}C *2,4′*-DDT	247	16.97
^{13}C *4,4′*-DDD	247	17.5
^{13}C PCB 153	372	17.65
Target analytes		
13C *2,4′*-DDD	247	15.85
2,4’ - DDE	318	14.22
4,4‘- DDE	318	15.55
2,4’ - DDD	235	15.85
2,4’ - DDT	235	16.97
4,4’ - DDD	235	17.5
4,4’ - DDT	235	18.68

Table S4. Injection, recovery, PRCs and target analytes used for the PE incubated in the laboratory

Compound	Quant Ion	Retention Time (min)
Injection compounds		
^{13}C PCB 167	372	20.70
Recovery compounds		
^{13}C - PCB 19	268	9.84
^{13}C - PCB 97	338	15.79
d_8 *2,4'*-DDT	243	17.47
d_8 *4,4'*-DDD	243	18.02
^{13}C PCB 170	406	23.14
PRCs		
^{13}C PCB 28	268	11.08
^{13}C PCB 47	304	12.08
^{13}C *4,4'*-DDE	260	15.55
^{13}C PCB 111	338	15.62
^{13}C *2,4'*-DDT	247	16.97
^{13}C *4,4'*-DDD	247	17.5
^{13}C PCB 153	372	17.65
Target analytes		
^{13}C *2,4'*-DDD	247	14.22
2,4' - DDE	318	14.84
4,4' - DDE	318	16.15
2,4' - DDD	235	16.46
2,4' - DDT	235	17.58
4,4' - DDD	235	18.11
4,4' - DDT	235	19.28

Table S5. Physicochemical properties used in the model for PRCs and target analytes

	log K_{PEW} (L_W/L_{PE})	*log D_{PE}* (cm^2/s)
^{13}C PCB 28	5.22	-8.81
^{13}C PCB 47	5.57	-8.89
^{13}C PCB 111	6.76	-9.16
^{13}C PCB 153	6.92	-9.33
^{13}C *4,4'*-DDE	5.74	-9.33
^{13}C *4,4'*-DDD	4.86	-9.39
^{13}C *2,4'*-DDT	5.72	-9.55

Sources:
K_{PEW}: Hale *et al.*[4] and Choi *et al.*[5]
D_{PE} calculated according to $-\log D_{PE} = 0.0145\ V_m + 6.1$ (Lohman[6])

Table S6. Fraction of PRC remaining in PE after field deployment in sediment bed.

Depth in sediment bed	0-10 cm		10-20 cm		20-30 cm		30-40 cm	
Time (days)	10	30	10	30	10	30	10	30
^{13}C PCB 28	n.a.	0.28	n.a.	0.34	0.42	0.28	0.37	0.30
^{13}C PCB 47	0.77	0.44	0.62	0.52	0.81	0.59	0.63	0.64
^{13}C PCB 111	0.87	0.84	0.98	0.87	0.97	0.89	0.94	0.91
^{13}C PCB 153	0.86	0.86	0.97	0.88	0.97	0.85	n.a.	0.86
^{13}C *4,4′*-DDE	0.75	0.66	0.81	0.67	0.82	0.68	0.71	0.70
^{13}C *4,4′*-DDD	0.46	0.19	0.52	0.25	0.47	0.27	0.48	0.31
^{13}C *2,4′*-DDT	0.68	0.40	0.69	0.28	0.52	0.15	0.38	0.16

n.a.= result was not included in the model fits because of analytical issue (poor recovery or suspected interference from another compound)

Table S7. Fraction of PRC lost and fractional target equilibration measured in PE from static incubations in the laboratory with F2, LM and CM.

	CM			LM			
Time (days)	4	20	40	4	14	20	40
Fraction PRC remaining in PE							
^{13}C PCB 28	0.73	0.55	0.50	0.68	0.56	n.a.	0.55
^{13}C PCB 47	0.88	0.77	0.66	0.87	0.81	n.a.	0.69
^{13}C PCB 111	0.91	0.85	0.87	0.98	1.05	0.91	0.91
^{13}C PCB 153	0.88	0.85	0.87	0.95	1.02	0.89	0.82
^{13}C *4,4'*-DDE	0.89	0.84	0.82	0.89	0.97	0.93	0.79
^{13}C *4,4'*-DDD	0.65	0.36	0.27	0.75	0.47	0.45	0.34
^{13}C *2,4'*-DDT	0.87	0.57	0.28	0.69	0.32	0.08	0.0
Fraction of target equilibration							
4,4'-DDE	0.08	0.16	0.23	0.08	0.13	0.17	0.23
4,4'-DDD	0.48	0.70	0.82	0.39	0.52	0.57	0.66

	F2			
Time (days)	5	10	20	30
Fraction PRC remaining in PE				
^{13}C PCB 28	0.86	0.70	n.a.	0.54
^{13}C PCB 47	1.02	0.82	n.a.	0.81
^{13}C PCB 111	0.95	0.96	0.93	0.89
^{13}C PCB 153	0.86	0.89	0.92	0.81
^{13}C *4,4'*-DDE	0.90	0.90	0.81	0.77
^{13}C *4,4'*-DDD	0.49	0.37	0.29	0.18
^{13}C *2,4'*-DDT	0.70	0.59	0.17	0.04
Fraction of target equilibration				
4,4'-DDE	0.09	0.17	0.19	0.26
4,4'-DDD	0.42	0.72	0.69	0.77

n.a.= result was not included in the model fits because of analytical issue (poor recovery or suspected interference from another compound)

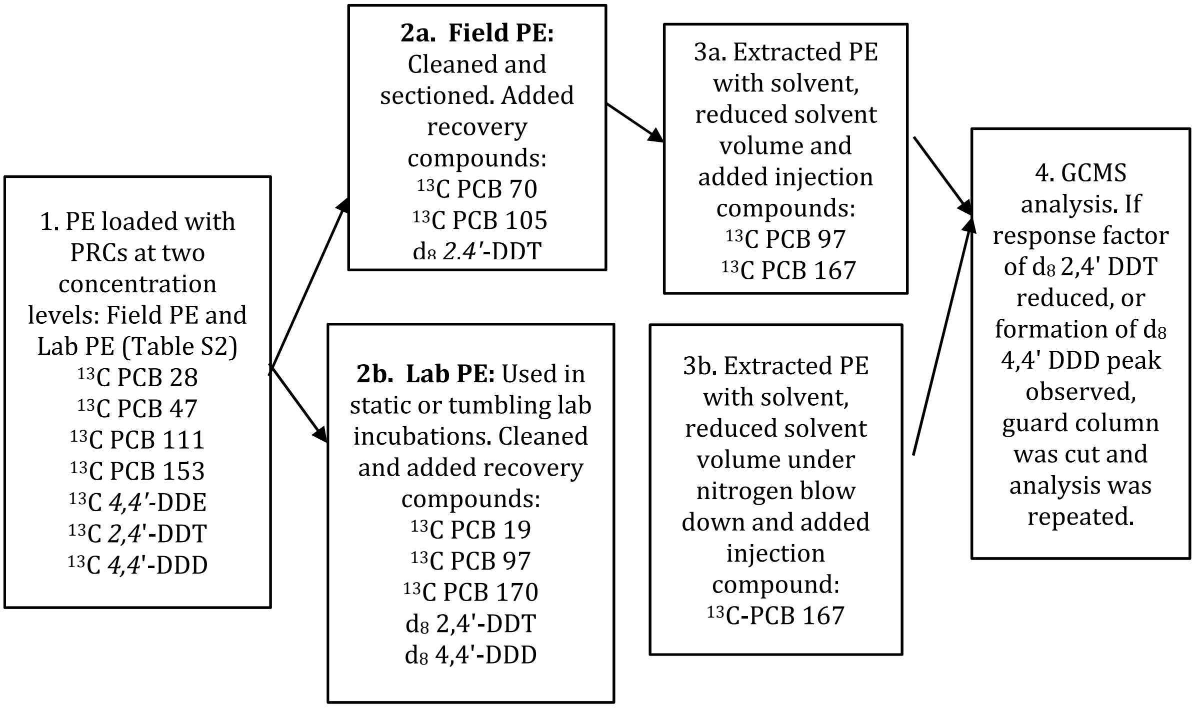

Figure S1. Flow chart of main steps involved in the processing of PE and the PRC, recovery standards, and injection compounds used in each step. The field and laboratory experiments were performed at different times, and the labeled PCB recovery standards were chosen to bracket the target analytes (native DDX analytes, as well as PRCs) and avoid coelutions. For reference, retention times for all analytes are provided in Tables S3 and S4.

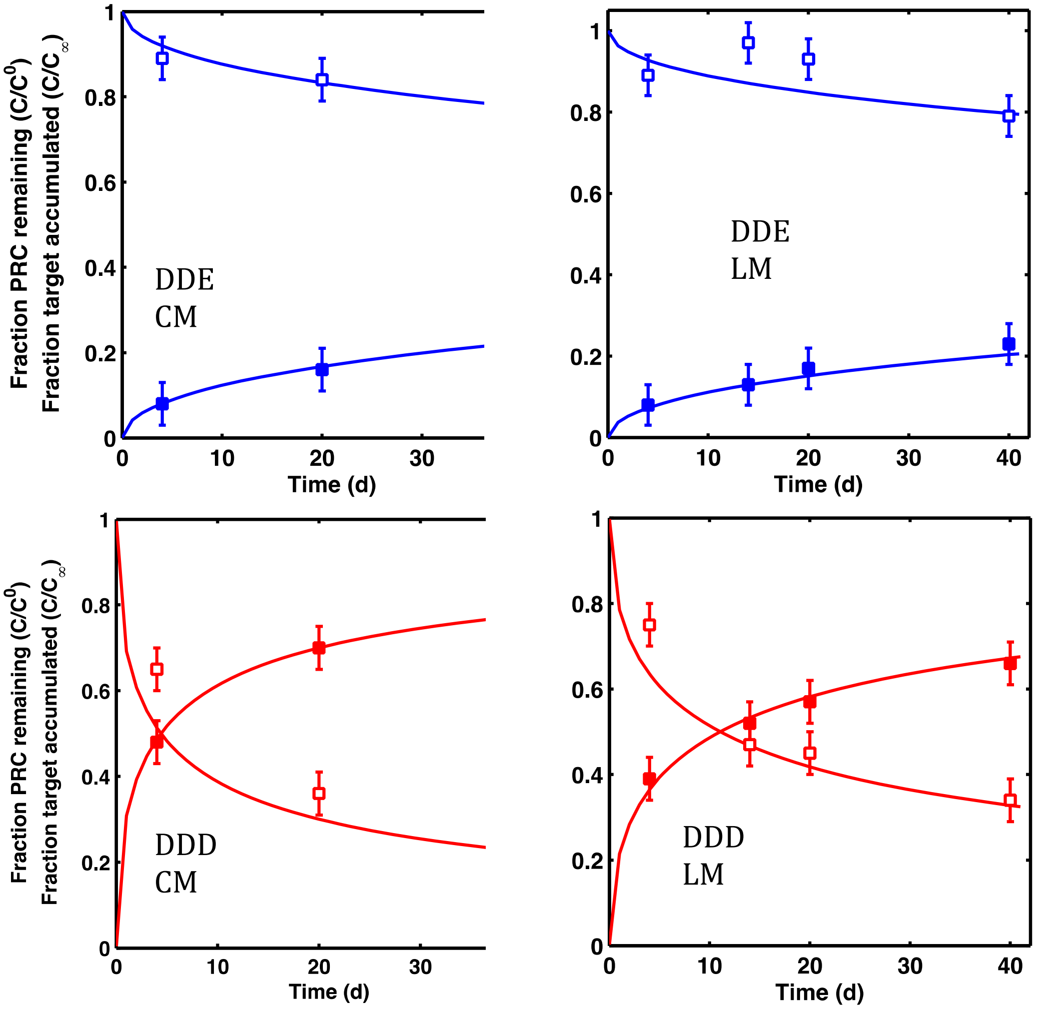

Figure S2. Fraction of PRC remaining (empty symbols) and fraction of target compound accumulated (filled symbols) for static incubations of PE in CM and LM sediments for *4,4′*-DDE (top panels) and *4,4′*-DDD (bottom panels). Fractional accumulation calculated as the ratio of concentration of target analyte measured in PE from static incubation divided by the concentration of the same analyte in tumbled PE. Lines represent the diffusion model of Fernandez et al.[1] with K_d (L_W/kg_{SED}) for DDE of $10^{3.8}$ (CM), $10^{3.7}$ (LM) and for DDD of $10^{4.0}$ (CM), $10^{3.6}$ (LM). Error bars for fraction of PRC remaining calculated based on one SD of PRC concentration in T=0 PE, and for fraction of target accumulation based on one SD of instrument error.

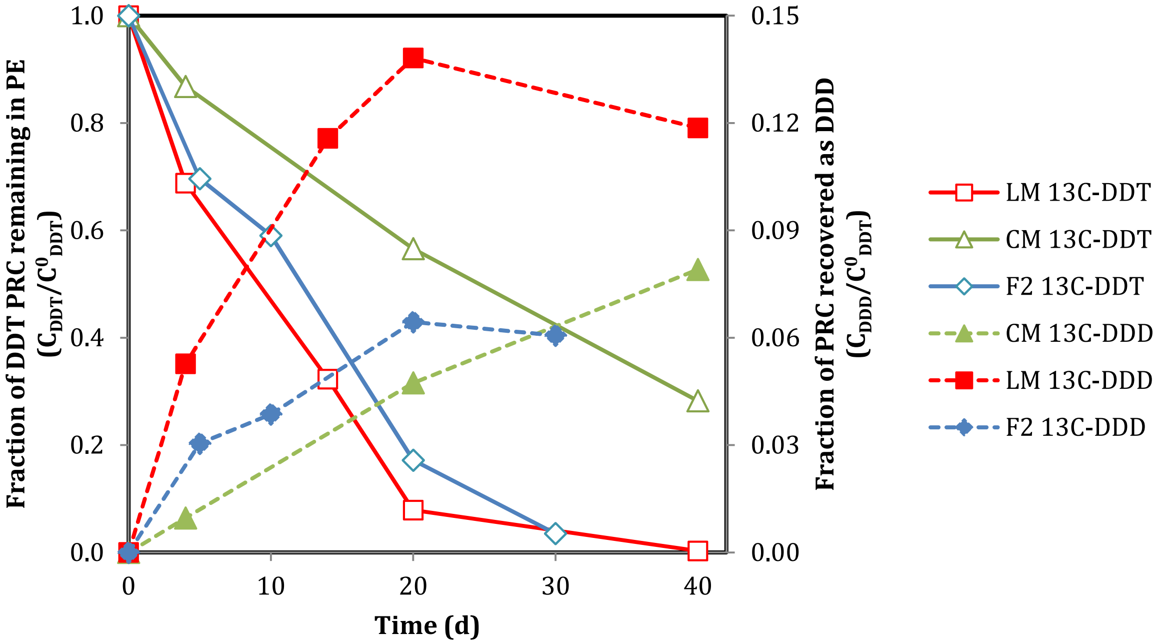

Figure S3 Fraction of ^{13}C *2,4'*-DDT remaining in PE (empty symbols, left axis), and measured as its degradation product ^{13}C *2,4'*-DDD (filled symbols, right axis) as a function of time after incubation in CM (green triangles), LM (red squares) and F2 (blue diamonds). Lines are drawn to guide the eye and are not model fits.

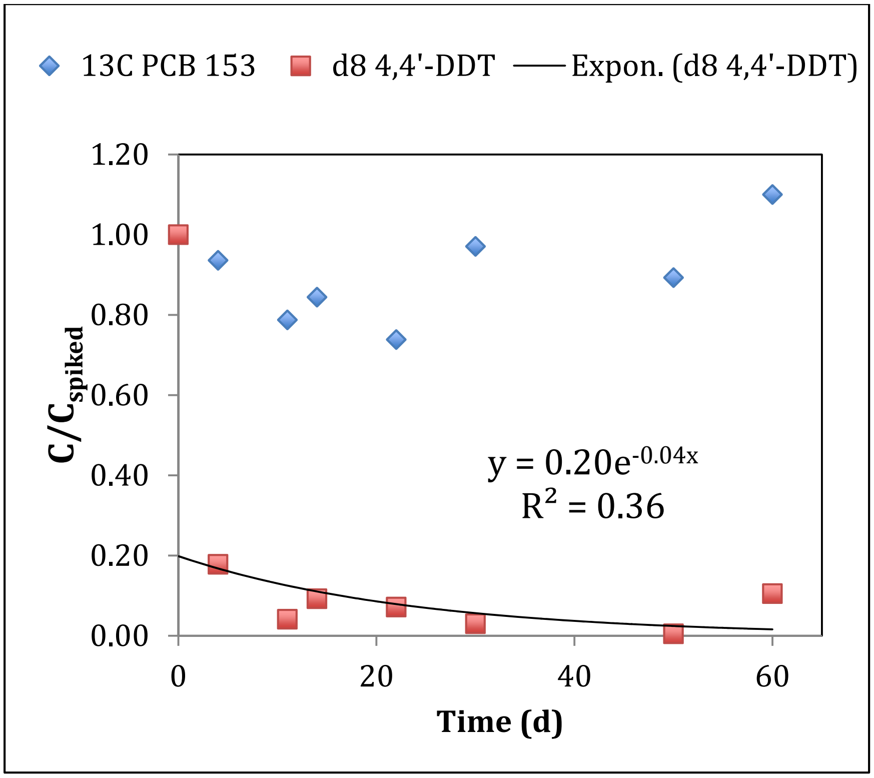

Figure S4. Measured ^{13}C PCB 153 and d_8 4,4'-DDT remaining after incubation with sediment under tumbling conditions for 4 to 60 days. Concentrations normalized by the spiked concentrations. Exponential trendline suggested degradation is occurring at a rate of 0.04/d, but considering only the data at time = 0 and 4 days would imply the rate was faster (ca. 0.4/d).

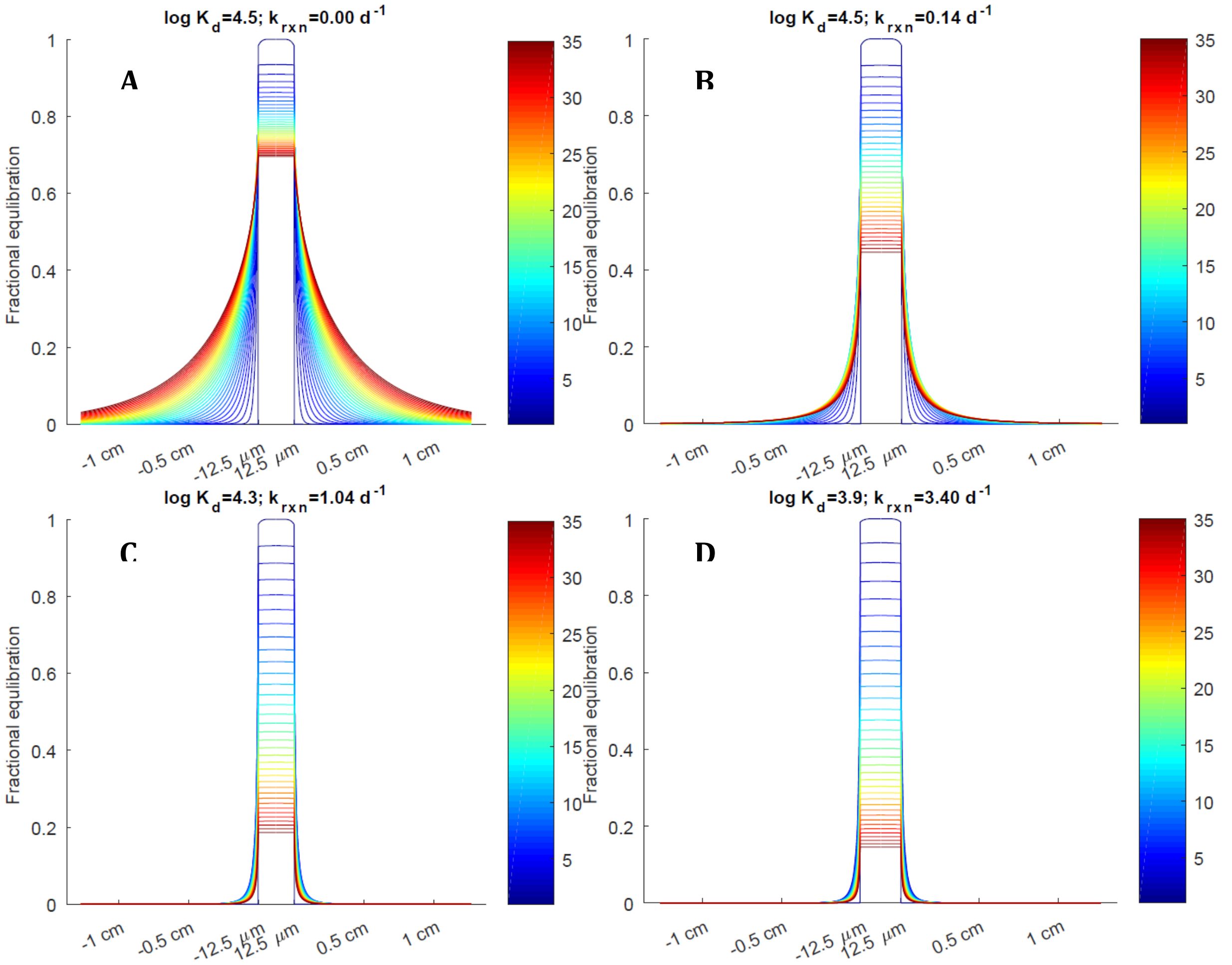

Figure S5. Normalized concentration *versus* distance for DDT PRC inside the PE (-12.5 to 12.5 µm window) and in the sediment bed (note distance in sediment bed is in cm) as a function of deployment times of 0 through 35 days in increments of 1 day for various cases: A – no reaction (K_d=$10^{4.5}$), B – 0-10 cm (K_d =$10^{4.5}$, k_r=0.01/d), C – 20-30 cm (K_d=$10^{4.3}$, k_r=1.04/d) D- F2 lab (K_d=$10^{3.9}$, k_r=3.38/d). Input parameters (K_d and k_r) were those fitted from the DDT-PRC loss curves either from field deployments (panels B and C, 0-10 cm and 20-30 cm, respectively) or laboratory incubations with F2 sediment (panel D). Concentration in the PE was normalized by the initial concentration for the DDT PRC and concentration in the sediment was normalized by initial concentration in the PE divided by K_{PESED}.

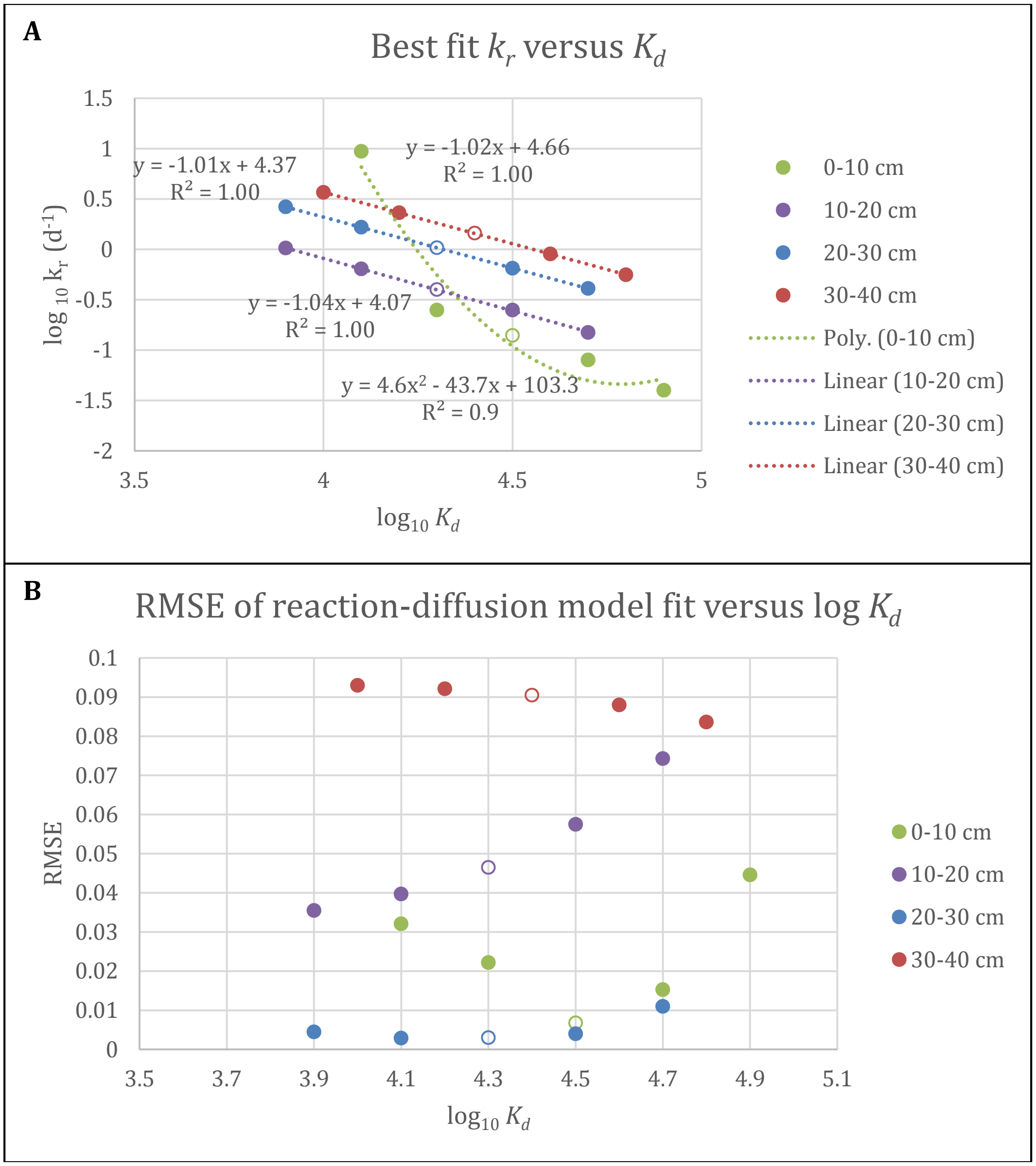

Figure S6. Sensitivity analysis of model derived k_r relative to the value of K_d used for fitting the PRC loss data for each depth into the sediment bed. Panel A shows the correlation between the best fit k_r in log space *versus* log K_d and the associated trendline for each depth into the sediment. Panel B shows the RMSE of the reaction diffusion model fits for each depth into the sediment. The empty symbols represent the K_d value for DDE PRC which as discussed in the main text, were used as the K_d value for the DDT PRC in deriving the k_r values calculated in Figure 4. RMSE did not increase or decrease with log K_d suggesting that the fits could not have been consistently improved by using a higher or lower value of K_d for the DDT PRC relative to that measured for the DDE PRC.

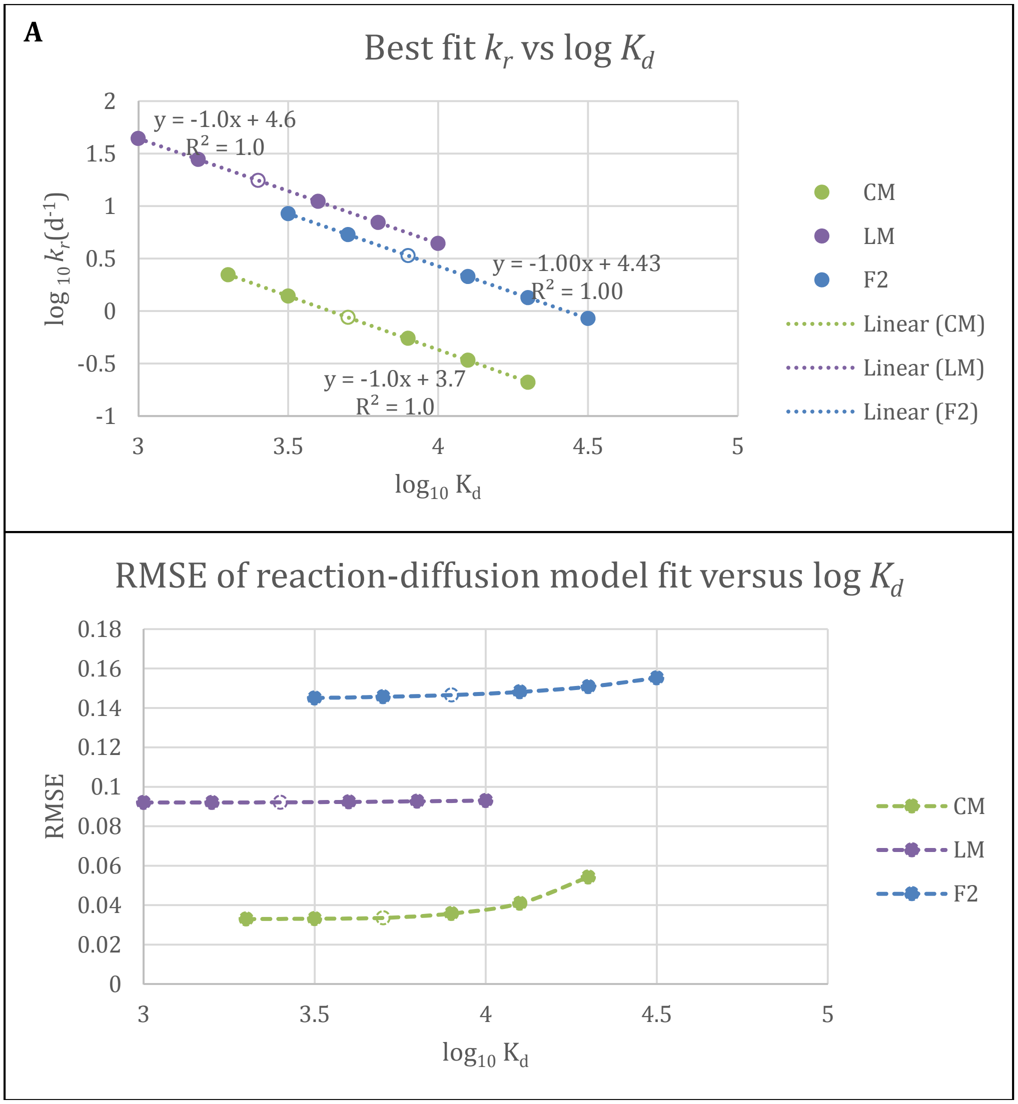

Figure S6. Sensitivity analysis of best fit k_r relative to the value of K_d used for fitting the PRC loss data for each static *ex situ* laboratory incubation (CM, LM and F2). Panel A shows the correlation between the best fit k_r in log space *versus* log K_d and the associated trendline for each depth into the sediment. Panel B shows the RMSE of the reaction diffusion model fit for each sediment. The empty symbols represent the K_d value for DDE PRC which as discussed in the main text, was used as the K_d value for the DDT PRC in deriving the k_r values calculated in Figure 5. For these PRC data, RMSE appeared to increase with log K_d suggesting that although using a higher K_d would have decreased the estimated first order reaction rate, it would not have improved the model fit.

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