Supporting information for: Novel Probe for In Situ Measurement of Freely Dissolved Aqueous Concentration Profiles of HOCs at the Sediment-Water Interface

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Pore water probe mooring schematic

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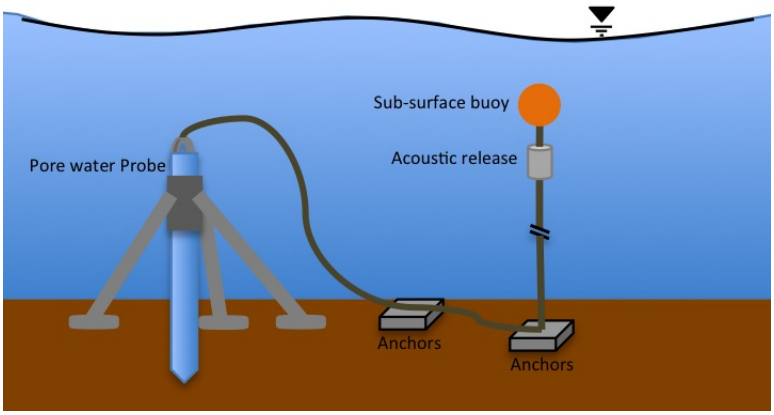


Figure S1: The pore water probe frame is attached to two anchors in series, and the end of the rope is attached to an acoustic release with additional 60 m of rope inside the canister, and finally to a buoy that is held below the water surface to avoid entanglement with boat traffic. When the probe is retrieved, an acoustic deck on board is used to release the acoustic transponder and the additional rope is released that allows the sub-surface buoy to come up to the water surface, and the whole mooring is carefully pulled onboard the boat.

Passive samplers

PE was obtained from Brentwood Plastics (St. Louis, MO, USA). PE strips were cleaned by solvent washing sequentially overnight with pesticide-grade hexane, acetone, and deionized (DI) water.[S1] Samplers used in the field were impregnated with PCB155 in two batches of 1-L 80:20 methanol: DI water solution spiked with $100\mu L$ of 100 ppm PCB155 standard solution in hexane (Ultra Scientific, N. Kingstown, RI, USA).[S2,S3] PRC batch solutions were placed on a shaker for two weeks for equilibrium to be reached. Afterwards, samplers were rinsed with DI water, gently wiped dry with Kimwipe, and stored in a clean 1-L amber jar at 4°C prior to deployment. Lab blanks were extracted to check for consistent PRC concentrations in passive samplers. Standard deviations in PRC concentration in the lab blanks were $< 5\%$ of total PRC concentration.

PE-water partition values for DDT and its metabolites were measured in the laboratory. PE strips were first impregnated with DDT its metabolites ($4,4'$-DDT, $2,4'$-DDT, $4,4'$-DDD, $2,4'$-DDD, $4,4'$-DDE, $4,4'$-DDE, DDMU) in a methanol-water solution spiked with a standard cocktail with the seven DDT analytes in hexane (Ultra Scientific). Specifically, a 200 mL solution of 80:20 methanol:DI water was spiked with $25\mu L$ of DDT metabolite standard in hexane, and six strips of PE (2.5 cm by 2.5 cm, 0.03 g each) were added.[S2] This solution was allowed to equilibrate on a shaker for 1 month, and strips were wiped dry with Kimwipe. In triplicate, one DDT-impregnated PE strip was added to a 1-L amber bottle filled with DI water and sodium azide (1 g/L) to avoid bacteria growth. This was allowed to equilibriate for 3-months on a shaker at 150 rpm. PE and water were extracted separately and analyzed to measure the DDT metabolite concentrations in each phase.[S4] Partition values were calculated by dividing PE concentrations by water concentrations. Measured partition values are presented in Table S1.

PE-water partition values (K_{PE}) values measured from other studies are also included Table S1 for comparison. All the DDT metabolite K_{PE} values are statistically the same as the other studies[S5,S6] (t-test $p > 0.05$) except for $2,4'$-DDE. Therefore, we have a high degree

of confidence in the K_{PE} values for the DDT metabolites, except for $2,4'$-DDE, which may be inflated based on comparison with the other two studies. However, since the measured $2,4'$-DDE in the overlying water and porewater were either below detection limits or less than 1% of total DDT concentrations, and potential error in the K_{PE} for $2,4'$-DDE did not affect results.

Since the temperature dependency of the partition value is mostly determined by the decrease in HOC solubility in water as the temperature decreases, the temperature relationship determined by Jonker et. al.[S7] for silicone-rubber samplers should be consistent for PE, and the adjustment to the laboratory-measured $\log K_{PE,i}$ would change by $\log 0.04$, which is well within the error expected.[S8] Even more conservative estimates, suggest the temperature dependence is expected to be between 0.1 and 0.2 log units.[S8,S9] The effects of temperature on partition values should not affect the shape of the concentration gradients and the calculated fluxes.

All PE samples were analyzed for DDT and PCB analytes using previously described cleanup and analytical methods.[S10]

Table S1: PE Partition Coefficients, Average $\log K_{PE}$ (L water/kg PE) measured at $20°C$, standard deviation in parenthesis.

Chemical	K_{PE} (this study)	K_{PE}[S5]	K_{PE}[S6]
DDMU	5.0 (0.2)	5.4 (0.3)	5.5 (0.1)
$2,4'$-DDE	6.6 (0.5)	5.7 (0.4)	5.8 (0.1)
$4,4'$-DDE	5.9 (0.2)	5.8 (0.3)	5.9 (0.1)
$2,4'$-DDD	5.1 (0.3)	5.0 (0.2)	4.8 (0.03)
$4,4'$-DDD	5.0 (0.4)	4.9 (0.2)	4.8 (0.04)
$2,4'$-DDT	5.6 (0.4)	5.8 (0.5)	5.9 (0.05)
$4,4'$-DDT	5.2 (0.3)	5.6 (0.3)	5.6 (0.05)
PCB69	5.35[S3]		
PCB103	5.78[S3]		
PCB155	6.1[S2]		

After retrieval, passive samplers were individually rinsed with DI water and wiped dry with Kimwipe to remove any sediment particles, biofilm, or organisms. Portions of passive samplers that were covered by the attachment plate (Fig. 2) were cut off. Samplers were

individually placed in 40 mL amber pre-cleaned glass vials that were pre-labeled, and stored at 4°C prior to and during shipment.

Determination of Aqueous Concentration

In general, a simplified first order equation is used to model passive sampler uptake rate (equation 1).[S1,S2]

$$C_{PE,i}(t) = K_{PE,i} \cdot C_{w,i} \cdot (1 - e^{-k_{e,i} \cdot t}) \tag{1}$$

where $C_{PE,i}$ is the target chemical concentration in PE after deployment period t (ng/g); $K_{PEW,i}$ is the target chemical PE-water partition coefficient (L/kg); $C_{w,i}$ is the target chemical concentration in water (ng/L); $k_{e,i}$ is the target chemical exchange rate coefficient (1/d); t is the deployment period (days). Equation 2 results by rearranging eq. 1, where the adjustment factor, $f_{adj} = \frac{1}{1-e^{-k_{e,i}t}}$. The exchange rate coefficient $k_{e,i}$ encompasses relevant environmental factors, such as hydrodynamics, temperature, and biofouling that control the uptake of HOCs through the aqueous boundary layer. Use of performance reference compounds utilizes the assumption that the uptake rate of chemicals is equivalent to the elimination rate. Thus, the elimination rate of the PRC is used to calculate the uptake rate of chemicals measured. If the PRC is not the isotopically labeled form of the compound of interest, then the exchange rate of the compound is related to the exchange rate of the PRC based on the empirical relation in equation 4 .

$$C_{w,i} = \frac{C_{PE,i}(t)}{K_{PE}} \cdot f_{adj} \tag{2}$$

$$C_{PE,PRC}(t) = C_{PE,PRC}(t = 0) \cdot e^{-k_{e,PRC} \cdot t} \tag{3}$$

$$\frac{K_{PE,i} \cdot k_{e,COC}}{K_{PE,PRC} \cdot k_{e,PRC}} \propto \left(\frac{D_{w,i}}{D_{w,PRC}}\right)^{2/3} \propto \left(\frac{M_{PRC}}{M_i}\right)^{1/3} \tag{4}$$

where $D_{w,i}$ and $D_{w,PRC}$ are the aqueous diffusivity of the chemical and PRC, respectively, and M is the molar volume.

Assessment of equilibrium in PE

We estimated that 90 days should be sufficient for near-equilibrium in deployed PE based on previous measurements with an earlier prototype of the pore water probe which involved attaching PE to stainless steel plates[S3] attached to an anchor and deployed for 2 months at the same location in Pallanza Bay (unpublished study). These PE samplers were spiked with $2,3',4,5$-tetrachlorobiphenyl (PCB 69) and $2,2',4,5',6$-pentachlorobiphenyl (PCB 103). The calculated average ($\pm$ st. dev.) exchange rate coefficient (k_e) for PE just above the sediment surface was approximately $0.015 \pm 0.004\ day^{-1}$ for the two PRCs (n=4). This k_e is a time-averaged uptake rate during the sampling period, and was calculated by solving for k_e in eq. 3 after a deployment period of t = 60 days, where $C_{PE,PRC}(t)/C_{PE,PRC}(0)$ is the fraction of PRC concentration remaining in the PE after the deployment period.[S1] The uptake rate of the target compounds (DDT metabolites) was calculated by adjusting the PRC depletion rates by the differences in molar volumes and PE-water partition values (eq. 4).[S1]

The calculated values of k_e for DDT metabolites ranged between 0.014 and 0.2 day^{-1}, where DDE compounds with higher K_{PE} values had a smaller k_e compared to DDD, which had lower K_{PE} and higher k_e values. The equilibrium fraction of each DDT metabolite compound in the PE ($f_{eq} = C_w(t=0)/C_w(t=\infty)$) can be calculated as $(1 - e^{-k_{e,DDT} \cdot t})$ based on eq. 1. Therefore, the fraction to equilibrium for target DDT metabolite compounds for a deployment of 93 days would range between $73-100\%$ for a k_e range between $0.015-0.1$ day^{-1}.

This estimate can be checked three ways:

Method 1. The PRC depletion rate of PCB155 used as a PRC in this study (93 day and 130 day deployment period) was lower than expected compared to the preliminary study (60 day deployment). During the April-July 2014 deployment period, PRC depletion in samplers above the sediment was $11 \pm 3\%$, while below the sediment this was $21 \pm 8\%$.

The PRC exchange rate coefficient, $k_{e,PRC}$ in equation 3 was calculated to be between $0.002 \pm 0.001 day^{-1}$ for samplers on the pore water probe above and below the sediment.

Using the PRC relationship in equation 4, the average exchange rate ($k_{e,i}$) for $4,4'$-DDD 0.03 ± 0.01, which is three times slower than exchange rates calculated for the 2012 60-day study. These values are also significantly less than values measured at a different site using the PE samplers on stainless steel plates.[S3] Therefore, we suspect that the depletion rates measured in this study are too low, and perhaps there were other processes that hindered the depletion of the heavier PRC from the PE. Nevertheless, using the conservative depletion rates measured in this study, the DDD metabolites, which account for most of the pore water concentration were within 90% of equilibrium for the 93-day deployment period. Since the major metabolites were near equilibrium, the calculated aqueous concentration using either method (with and without f_{adj}) showed similar results, where all values are within a factor of two (Fig. S2). More hydrophobic metabolites with greater values of log K_{PE}, like $4,4'$-DDE, were further from equilibrium where f_{adj} was on average 4.7 ± 2.4.

Method 2. Another method of modeling uptake rate of target compounds into the PE deployed in the sediment pore water is by modeling the diffusion of target compounds into PE from diffusion out of the sediment pore water.[S11] Parameters used in this model included DDT diffusivity in PE,[S6] K_{PE} (measured in this study), and sediment-water partition coefficients K_d. Sediment-water partition coefficients were measured by combining wet sediment (30 g archived grab sample from Pallanza Bay), PE (0.2 g of 51 μm thick PE), DI water (1 L), and sodium azide (1 ng/L) in a 1 L amber glass jar and allowing the system to come to equilibrium on a shaker for at least one month (n=15). K_d values for DDT and its metabolites were calculated by dividing sediment concentrations (C_{sed}) by PE concentrations (C_{PE}) and multiplying by PE partition-water partition values (K_{PE}). These measured values are shown in Table S2.

The dimensionless parameter $T = \frac{t \cdot D_{PE}}{l^2}$ for $4,4'$-DDD in a $51\mu m$ thick PE deployed for 130 days is 168. D_{PE} (m^2/s) is the diffusivity of the target compound in PE, t = deployment time period (s), and l is the PE thickness (m). By this approach, the calculated fraction of equilibrium f_{eq} for DDT metabolites ranged between $0.80 - 0.97$ for 130 days in 51 μm PE

Table S2: Average measured K_d (L/kg) in sediment samples collected from Pallanza Bay, standard devations in parenthesis, n=15 (triplicate analysis of 5 different sediment samples)

Chemical	K_d (L/kg)
DDMU	3.4 (0.1)
$2,4'$-DDE	4.4 (0.6)
$4,4'$-DDE	4.3 (0.2)
$2,4'$-DDD	4.0 (0.5)
$4,4'$-DDD	3.9 (0.3)
$2,4'$-DDT	4.9 (0.5)
$4,4'$-DDT	4.4 (0.6)

sheets. For the DDD metabolite compounds which account for over 80% of the total freely dissolved DDT concentration in the pore water, $f_{eq} > 90\%$. The f_{eq} for all DDT metabolites was $> 80\%$.

Method 3. A third method of evaluating equilibrium in PE in situ measurements is by comparing concentrations measured during different deployment periods or by comparing samplers with different surface to volume ratio measurements.[S12] Samplers deployed for longer time periods should measure higher concentrations that are closer to equilibrium until samplers converge when equilibrium is reached. Similarly, samples with higher surface to volume ratios should measure concentrations closer to equilibrium than samples with lower surface to volume ratios until equilibrium in reached. In Table S3, we compared calculated $C_w = C_{PE}/K_{PE}$ from different PE measurements at Site P2 in Pallanza Bay deployed in the overlying water. Measured DDD concentrations seem to be at equilibrium, since concentrations were consistent during April-July sampling period when samplers were either exposed one-sided or double-sided to the overlying water. Other DDT metabolites were not consistently measured in the overlying water.

Measured pore water concentrations measured at Site P2 during three different deployment period and deployment lengths are shown in Table S4. This data supports conclusions that PE samplers are at equilibrium for DDD metabolites. Whether $4,4'$-DDE with higher K_{PE} value was at equilibrium is not entirely conclusive based on this comparison, but these concentrations represent a small fraction of total DDT concentrations.

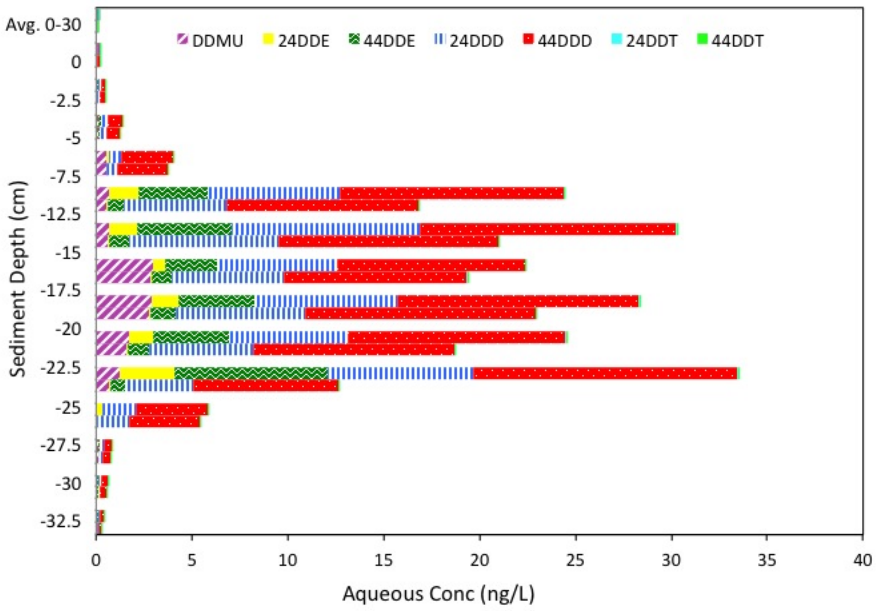
Table S3: Calculated $C_w = C_{PE}/K_{PE}$ from PE deployed in the overlying water for different deployment lengths (60 day (2012), 93 days (Apr-Jul 2014), 130 days (Jul-Nov 2014), and sampling configuration (single and double-sided exposure). Depth refers to height above sediment. Samplers attached to the pore water probe had only one side exposed to overlying water and pore water because samplers were wrapped tightly around the pore water probe. Double-sided samplers were attached to pore water probe frames with zipties so that both sides of the sampler were freely exposed to the surrounding water.

deployment period	60 days (double-sided)	93 days (single-sided)	93 days (double-sided)	130 days (single-sided)
depth (cm)	5-40	2.5-25	0-30	2.5-25
n	4	10	4	10
DDMU	< 0.01	0.03 (0.004)	0.01 (0.002)	0.02 (0.0008)
2,4'-DDE	< 0.01	< 0.01	< 0.01	< 0.01
4,4'-DDE	0.01 (0.002)	< 0.01	< 0.01	< 0.01
2,4'-DDD	0.02 (0.003)	0.02 (0.004)	0.02 (0.006)	0.05 (0.01)
4,4'-DDD	0.03 (0.004)	0.03 (0.004)	0.03 (0.008)	0.05 (0.02)
2,4'-DDT	< 0.01	< 0.01	< 0.01	< 0.01
4,4'-DDT	0.01 (0.001)	0.03 (0.006)	< 0.01	< 0.01

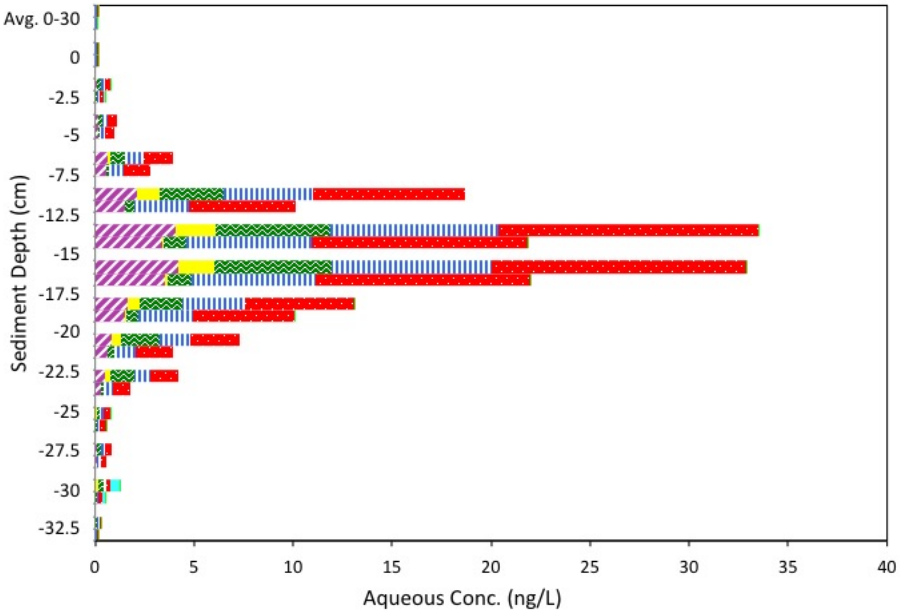
Table S4: Calculated $C_w = C_{PE}/K_{PE}$ from PE deployed in the pore water for different deployment lengths (Phase 1 = 60 days, Phase II = 93 days, Phase III = 130 days. Samplers were placed approximately two cm within the sediment. Samplers were attached to a stainless steel plate (63 days) or to the pore water probe (93 days and 130 days), so that samplers were only exposed on one side to the surrounding pore water DDT concentration.

	60 days (n=4)	93 days (n=1)	130 days (n=2)
DDMU	< 0.01	0.05	0.06
2,4'-DDE	0.004 (0.007)	< 0.01	< 0.01
4,4'-DDE	0.01 (0.002)	0.02	0.03
2,4'-DDD	0.1 (0.010)	0.1	0.1
4,4'-DDD	0.3 (0.019)	0.3	0.2
2,4'-DDT	< 0.01	< 0.01	< 0.01
4,4'-DDT	< 0.04	< 0.04	< 0.04

Based on these three methods of evaluating equilibrium in passive samplers, we conclude that the PE samplers were at or near equilibrium for DDD compounds for the 130 day deployment period, and the calculated freely dissolved aqueous concentrations in the overlying water and pore water concentrations are accurate within the error of the PE-water partition values, which is the largest source of uncertainty in the calculated concentrations.



(a) First deployment



(b) Second deployment

Figure S2: Aqueous concentration in pore water measured during both deployment periods assuming equilibrium (bottom bar of each pair) and with adjustment factor (f_{adj} from equations 2-4) (top bar of each pair). Measured DDT metabolites are $4,4'$-DDD (red, dots), $2,4'$-DDD (blue, vertical stripes), $4,4'$-DDE (green, squiggly), $2,4'$-DDE (yellow, solid), DDMU (purple, diagonal stripes).

Calculating diffusive flux in and from sediment

When considering diffusion in the overlying water, $D_{z,i}$ is equal to the molecular diffusivity of the compound i (D_i). In the sediment pore water, the diffusivity will be reduced both by less space available for diffusion (proportional to the porosity (ϵ) and longer paths for the components to travel (tortuosity (τ) related to ϵ by $\tau = \epsilon^{-1/3}$). Hence in the pore water D_z will be given by

$$D_z = \frac{\epsilon}{\tau} \cdot D = \epsilon^{4/3} \cdot D \tag{5}$$

Porosity was calculated from the water content in the sediment cores and diffusivities (D) of the different DDT metabolites was calculate from molecular weights and adjusted for temperature at $9°C$.[S13]

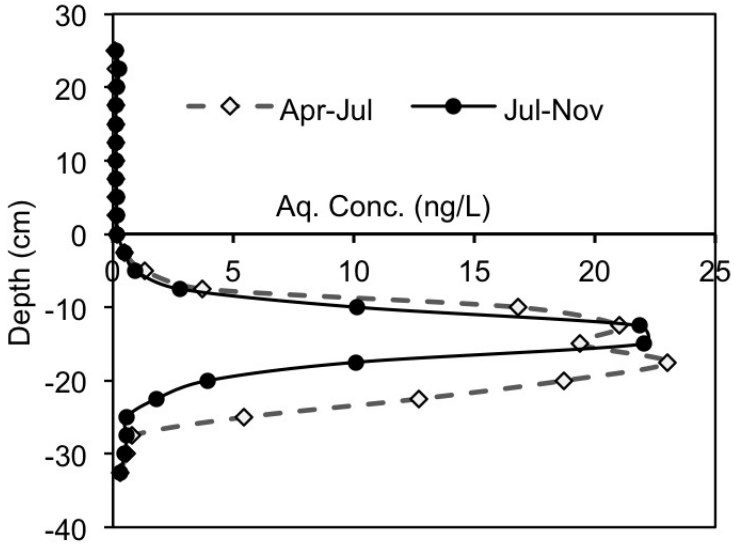
The diffusive flux, F can be calculated with the following equation:

$$F = D_{z,i} \left(\frac{C_{w_{z_1}} - C_{w_{z_2}}}{z_2 - z_1} \right) \tag{6}$$

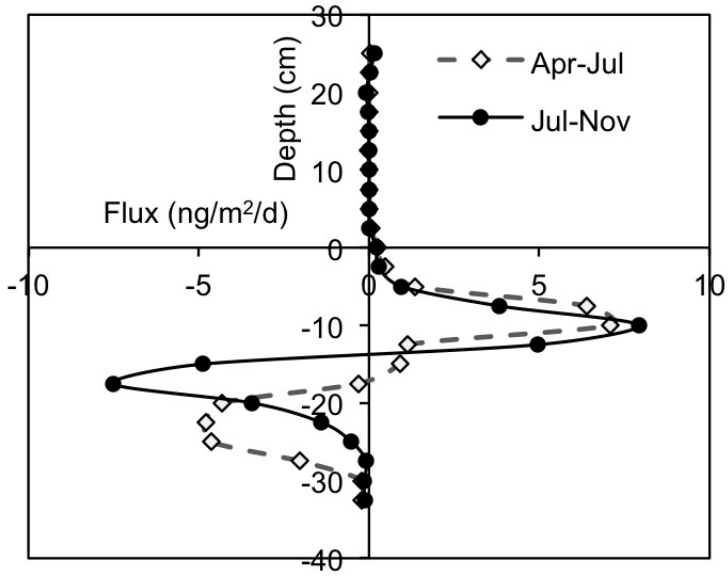
Where $D_{z,i}$ is the diffusivity of the compound of interest, i, at depth z. $C_{w_{z_1}}$ and $C_{w_{z_2}}$ is the concentration in the aqueous phase at depths z_1 and z_2.

A comparison of calculated flux from measured concentration profiles during the two deployment periods is shown in Fig. S3(b). The shape of the flux profile is the same between the two measurements. Difference in the concentration and flux profiles could be due to heterogeneity in the sediment at slightly different locations. Another possiblity is cross contamination in the pore water below the concentration peak due to the penetration of the probe.

Pore water profile measurements at other DDT-contaminated coastal sites in the U.S. and China showed a similar shape where the freely dissolved aqueous concentrations were lower above the sediment than within the pore water near the sediment surface.[S14,S15] At those sites, the pore water concentrations of the major DDT metabolites were much greater in the other studies than in Pallanza Bay, which resulted in greater calculated diffusive flux from the



(a) Total DDT concentration profile



(b) Total DDT flux profile

Figure S3: Comparison of calculated freely dissolved aqueous concentration (a) and flux (b) of total DDT during first (open diamond, dotted line) and second deployment periods (filled circle solid line).

sediment bed by at least an order of magnitude. The peak concentration profile measured at depth in this study is unique in showing DDT contamination that occurred during a specific historical period (approximately between 1960s and 1980s based on geochronological dating of cores, unpublished data). The sharp peak in the historical record of the sediment DDT

concentration was also not blurred by sediment resuspension events since Pallanza Bay is rather deep and mainly depositional with minimal resuspension.[S16]

Sediment Cores

Cores were collected by Carma® Quality Coring. The top 30 cm of the core was sectioned at 1 - 5 cm intervals, and sectioned sediment samples were placed in separate 125 mL amber glass jars (I-CHEM 200 series) for storage and shipment. Sediment samples were analyzed for DDT and its metabolites using previously published methods[S10] to measure total sediment concentrations.

Table S5: Sediment core concentration profile ($\mu g/kg$ dry).

Depth (cm)	DDMU	$2,4'$-DDE	$4,4'$-DDE	$2,4'$-DDD	$4,4'$-DDD	$2,4'$-DDT	$4,4'$-DDT	ΣDDT
0-1	0.6	0.6	4.7	3.6	3.2	¡0.4	1.7	15
1-2	1.3	0.7	5.3	4.5	5.6	¡0.4	1.4	19
2-3	3.0	1.4	7.4	7.5	13	¡0.4	2.6	35
3-4	1.7	1.5	5.5	6.0	13	¡0.4	4.7	32
4-6	5.4	7.0	24	14	28	1.2	3.6	82
6-8	16	16	64	31	65	1.8	19	212
8-10	< 0.5	154	424	220	651	0.3	54	1,505
10-15	124	224	833	597	1,330	12	61	3,190
15-20	< 0.5	5.9	12	19	19	0.4	2.4	60.

Table S6: Aqueous Concentration assuming equilibrium (ng/L water) for first deployment period (93 days).

Depth	DDMU	2,4′-DDE	4,4′-DDE	2,4′-DDD	4,4′-DDD	2,4′-DDT	4,4′-DDT	ΣDDT
25	0.02	< 0.0005	< 0.001	0.02	0.02	< 0.005	< 0.04	0.06
22.5	0.04	< 0.0005	< 0.001	0.02	0.02	¡0.005	< 0.04	0.08
20	0.03	< 0.0005	< 0.001	0.03	0.03	0.01	< 0.04	0.1
17.5	0.03	< 0.0005	< 0.001	0.02	0.03	< 0.005	< 0.04	0.08
15	0.03	< 0.0005	< 0.001	0.03	0.03	< 0.005	< 0.04	0.09
12.5	0.03	< 0.0005	< 0.001	0.02	0.03	< 0.005	< 0.04	0.08
10	0.03	< 0.0005	< 0.001	0.02	0.02	< 0.005	< 0.04	0.07
7.5	0.04	< 0.0005	< 0.001	0.02	0.02	< 0.005	< 0.04	0.08
5	0.03	< 0.0005	< 0.001	0.02	0.02	< 0.005	< 0.04	0.07
2.5	0.03	< 0.0005	0.003	0.03	0.03	< 0.005	0.05	0.1
0	0.03	< 0.0005	0.01	0.04	0.08	< 0.005	< 0.04	0.2
-2.5	0.05	< 0.0005	0.02	0.1	0.3	< 0.005	< 0.04	0.5
-5	0.13	0.002	0.05	0.3	0.7	< 0.005	0.06	1
-7.5	0.5	0.01	0.005	0.6	3	< 0.005	< 0.04	4
-10	0.6	0.07	0.8	5	10	0.01	< 0.04	17
-12.5	0.6	0.07	1	8	11	0.02	< 0.04	22
-15	3	0.06	1	6	10	0.02	< 0.04	19
-17.5	3	0.1	1	7	12	0.01	0.05	23
-20	2	0.08	1	5	11	0.02	< 0.04	19
-22.5	0.7	0.06	0.8	4	8	0.01	< 0.04	13
-25	< 0.02	0.03	0.01	2	4	0.01	< 0.04	5
-27.5	0.1	0.001	0.04	0.2	0.4	< 0.005	0.06	0.8
-30	0.07	< 0.0005	0.03	0.1	0.3	< 0.005	< 0.04	0.6
-32.5	0.05	< 0.0005	0.01	0.06	0.2	< 0.005	< 0.04	0.3
FB(n=3)	< 0.02	< 0.0005	< 0.001	< 0.008	0.004 ± 0.001	0.02 ± 0.003	0.02 ± 0.004	0.04

Table S7: Aqueous concentration assuming equilibrium (ng/L water) for second deployment period (130 days).

Depth	DDMU	2,4′-DDE	4,4′-DDE	2,4′-DDD	4,4′-DDD	2,4′-DDT	4,4′-DDT	ΣDDT
25	< 0.02	< 0.0005	0.01	0.04	0.04	0.01	< 0.04	0.1
22.5	0.02	0.001	0.01	0.08	0.1	0.01	< 0.04	0.2
20	0.02	< 0.0005	0.01	0.06	0.04	0.01	< 0.04	0.1
17.5	< 0.02	< 0.0005	0.01	0.04	0.04	0.01	< 0.04	0.1
15	< 0.02	< 0.0005	0.01	0.05	0.03	0.01	< 0.04	0.1
12.5	< 0.02	< 0.0005	0.01	0.04	0.03	0.01	< 0.04	0.09
10	< 0.02	< 0.0005	0.01	0.05	0.04	0.01	< 0.04	0.1
7.5	< 0.02	< 0.0005	0.01	0.05	0.04	0.01	< 0.04	0.1
5	< 0.02	< 0.0005	0.01	0.05	0.04	0.01	< 0.04	0.1
2.5	< 0.02	< 0.0005	0.01	0.05	0.04	0.01	< 0.04	0.1
0	< 0.02	< 0.0005	0.01	0.06	0.05	0.01	< 0.04	0.1
-2.5	0.06	0.001	0.03	0.2	0.2	0.01	< 0.04	0.5
-5	0.1	0.002	0.06	0.3	0.5	< 0.005	< 0.04	1
-7.5	0.5	0.01	0.2	0.8	1.3	< 0.005	< 0.04	3
-10	1	0.03	0.5	3	5	< 0.005	< 0.04	10
-12.5	3	0.09	1	6	11	< 0.005	< 0.04	22
-15	4	0.08	1	6	11	< 0.005	< 0.04	22
-17.5	2	0.04	0.6	3	5	< 0.005	< 0.04	10
-20	0.6	0.02	0.3	1	2	< 0.005	< 0.04	4
-22.5	0.3	0.01	0.1	0.5	0.9	< 0.005	< 0.04	2
-25	0.05	0.002	0.04	0.2	0.3	0.01	< 0.04	0.6
-27.5	0.07	0.002	0.04	0.2	0.3	< 0.005	< 0.04	0.6
-30	0.03	0.003	0.05	0.1	0.2	0.13	< 0.04	0.5
-32.5	< 0.02	0.001	0.01	0.06	0.07	< 0.005	< 0.04	0.1
FB (n=3)	< 0.02	< 0.0005	< 0.001	< 0.008	0.03 ± 0.001	0.01 ± 0.0002	0.03 ± 0.0006	0.07

References

(S1) Tomaszewski, J.; Luthy, R. G. Field Deployment of Polyethylene Devices to Measure PCB Concentrations in Pore Water of Contaminated Sediment. *Environ. Sci. Technol.* **2008**, *42*, 6086–6091.

(S2) Booij, K.; Hoedemaker, J. R.; Bakker, J. F. Dissolved PCBs, PAHs and HCB in pore waters and overlying waters of contaminated harbor sediments. *Environ. Sci. Technol.* **2003**, *37*, 4213–4220.

(S3) Oen, A. M. P.; Janssen, E. M.-L.; Cornelissen, G.; Breedveld, G. D.; Eek, E.; Luthy, R. G. In Situ Measurement of PCB Pore Water Concentration Profiles in Activated Carbon-Amended Sediment Using Passive Samplers. *Environ. Sci. Technol.* **2011**, *45*, 4053–4059.

(S4) Choi, Y.; Cho, Y.-M.; Gala, W.; Luthy, R. G. Measurement and Modeling of Activated Carbon Performance for the Sequestration of Parent- and Alkylated-Polycyclic Aromatic Hydrocarbons in Petroleum-Impacted Sediments. *Environ. Sci. Technol.* **2013**, *47*, 1024–1032.

(S5) 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*, 4336–4346.

(S6) Thompson, J. M.; Hsieh, C.-H.; Luthy, R. G. Modeling uptake of hydrophobic organic contaminants into polyethylene passive samplers. *Environ. Sci. Technol.* **2015**, *49*, 2270–2277.

(S7) Jonker, M. T. O.; van der Heijden, S. A.; Kotte, M.; Smedes, F. Quantifying the Effects of Temperature and Salinity on Partitioning of Hydrophobic Organic Chemicals to Silicone Rubber Passive Samplers. *Environ. Sci. & Technol.* **2015**, *49*, 6791–6799, PMID: 25978295.

(S8) Lohmann, R. Critical Review of Low-Density Polyethylene's Partitioning and Diffusion coefficients for Trace Organic Contaminants and Implications for Its Use as a Passive Sampler. *Environ. Sci. Technol.* **2011**, *46*, 606–618.

(S9) Adams, R. G.; Lohmann, R.; Fernandez, L. A.; MacFarlane, J. K. Polyethylene Devices: Passive Samplers for Measuring Dissolved Hydrophobic Organic Compounds in Aquatic Environments. *Environ. Sci. & Technol.* **2007**, *41*, 1317–1323, PMID: 17593736.

(S10) Tomaszewski, J. E.; Werner, D.; Luthy, R. G. Activated carbon amendment as a treatment for residual DDT in sediment from a superfund site in San Francisco Bay, Richmond, California, USA. *Environ. Toxicol. Chem.* **2007**, *26*, 2143–2150.

(S11) Fernandez, L. A.; Harvey, C. F.; Gschwend, P. M. Using performance reference compounds in polyethylene passive samplers to deduce sediment porewater concentrations for numerous target chemicals. *Environ. Sci. Technol.* **2009**, *43*, 8888–8894.

(S12) Mayer, P.; Parkerton, T. F.; Adams, R. G.; Gargill, J. G.; Gan, J.; Gouin, T.; Gschwend, P. M.; Hawthorne, S. B.; Helm, P.; Witt, G.; You, J.; Escher, B. I. Passive sampling methods for contaminated sediments: sceintific rationale supporting use of freely dissolved concentrations. *Integr. Environ. Assess. Manag.* **2013**, *10*, 197–209.

(S13) Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M. *Environmental Organic Chemistry*; Wiley: Hoboken, N.J., 2003.

(S14) Liu, H.-H.; Bao, L.-J.; Zhang, K.; Xu, S.-P.; Wu, F.-C.; Zeng, E. Y. Novel Passive Sampling Device for Measuring Sediment-Water Diffusion Fluxes of Hydrophobic Organic Chemicals. *Environ. Sci. Technol.* **2013**, *47*, 9866–9873.

(S15) Fernandez, L. A.; Lao, W.; Maruya, K. A.; Burgess, R. M. Calculating the Diffusive Flux of Persistent Organic Pollutants between Sediments and the Water Column on

229 the Palos Verdes Shelf Superfund Site Using Polymeric Passive Samplers. *Environ.*
230 *Sci. Technol.* **2014**, *48*, 3925–3934.

231 (S16) Scheu, K.; Fong, D.; Monismith, S.; Fringer, O. Sediment transport dynamics in a
232 large alpine lake. *Limnol. Oceanogr.* **2015**,