

Supplementary materials for “Influence of water exchange rates on toxicity and bioaccumulation of hydrophobic organic chemicals in sediment toxicity tests”

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Additional Descriptions for Materials and Methods

Determination of $K_{PDMS/w}$ for three polycyclic aromatic hydrocarbons (PAHs)

One piece of pre-cleaned 4-cm PDMS-coated glass fiber (10 μm coating thickness) was transferred to a glass tube containing 10 mL of Milli-Q water. The tube was spiked with 5 μL of methanolic stock solution of PAHs (i.e., Phe, Pyr, and BaP) at a concentration of 2 mg/L, resulting in a final concentration of 10 $\mu\text{g/L}$. The tube was then shaken at 25 $^{\circ}\text{C}$ and 150 rpm for 2 and 5 days. Five tubes were retrieved at each time point, and the water samples were diluted with an equal volume of acetonitrile. The PDMS fibers were wiped with moist lint-free tissues, extracted with 500 μL of acetonitrile, and diluted with 500 μL of Milli-Q water. PAH concentrations in the water and extracts were analyzed as described below. The determined $K_{PDMS/w}$ values for three PAHs were not significantly different after 2 and 5 days, indicating equilibrium was achieved between the fiber and water.

Instrumental analysis

Quantitative analysis of PAHs was performed by using an LC-VP series HPLC system (Shimadzu Corp.). The mobile phase was a mixture of acetonitrile and Milli-Q water (80:20 v/v) at a flow rate of 0.35 mL/min. The target chemicals were separated with a guard column (GVP-ODS, Shimadzu Corp.) and a silica-based C18 column (150 mm \times 2.0 mm i.d., VP-ODS, Shimadzu Corp.) at 40 $^{\circ}\text{C}$, and quantified with a fluorescence detector (RF-10A XL, Shimadzu Corp.). The excitation/emission wavelengths used were 265/380 nm for Phe and Pyr, and 365/410 nm for BaP. The instrumental limits of quantification (LOQ) were 0.39 $\mu\text{g/L}$ (Phe), 0.38 $\mu\text{g/L}$ (Pyr), and 0.04 $\mu\text{g/L}$ (BaP), as estimated from the residuals and slopes of regression lines of standard solutions according to DIN 32 645. The DOC concentrations were determined with a TOC-L total organic carbon analyzer (Shimadzu Corp.) using a non-purgeable organic carbon method. TOC content of sediment (f_{OC}) was determined with TOC-L equipped with a solid sample module (SSM-5000A, Shimadzu Corp.)

Table S1. Measured water quality in overlying water.

	Temperature (°C)	DO (mg/L)	pH	Conductivity (mS/m)	Total ammonia concentration (mgN/L) ^a	Unionized ammonia concentration (mgN/L) ^a
Condition 1	23.0 ± 0.2	8.5 ± 0.3	7.5 ± 0.2	38.3 ± 5.1	2.8 ± 3.4	0.05 ± 0.00
Condition 2	22.6 ± 0.2	8.1 ± 0.5	7.7 ± 0.2	32.6 ± 0.6	0.7 ± 0.5	0.01 ± 0.00
Condition 3	22.9 ± 0.2	8.2 ± 0.5	7.9 ± 0.1	31.6 ± 0.5	0.4 ± 0.1	0.01 ± 0.00
Condition 4	22.4 ± 0.2	8.4 ± 0.3	7.8 ± 0.1	32.1 ± 0.3	0.3 ± 0.1	0.01 ± 0.00
Condition 5	22.5 ± 0.2	8.6 ± 0.2	7.9 ± 0.1	31.8 ± 0.4	0.2 ± 0.1	0.01 ± 0.00

Mean ± standard deviation.

a: Measured only at the start and end of exposure (i.e., Day 0 and 10).

Table S2. Measured pH and ammonia in pore water at the end of exposure (i.e., Day10).

	pH	Total Ammonia concentration (mgN/L)	Unionized ammonia concentration (mgN/L)
Condition 1	7.8 ± 0.2	6.6	0.18
Condition 2	7.8	4.1 ± 1.0	0.12 ± 0.03
Condition 3	8.2 ± 0.2	2.4	0.16
Condition 4	8.1	2.8 ± 0.3	0.16 ± 0.02
Condition 5	8.5 ± 0.1	2.8	0.34

Mean ± standard deviation. The values with only one replicate ($n = 1$) are shown without standard deviation.

Table S3. Measured dissolved organic carbon (DOC) concentrations in overlying and pore water at the start and end of exposure.

	Overlying water		Pore water	
	Day 0	Day 10	Day 0	Day 10
Condition 1	3 ± 0	50 ± 2		100 ± 3
Condition 2	3 ± 0	6 ± 0		110 ± 15
Condition 3	3 ± 1	4 ± 0	96 ± 18	87 ± 16
Condition 4	3 ± 0	4 ± 1		91 ± 12
Condition 5	4 ± 1	3 ± 0		85 ± 0.3

Mean ± standard deviation ($n = 3$ for overlying water, $n = 4$ for pore water at Day 0; $n = 2$ for pore water at Day 10). Unit: mgC/L.

Table S4. Recovery ratio (%) of PAHs and organic carbon content (f_{oc} ; %) from spiked sediment (nominal: 30 mg/kg-dry).

		Recovery ratio (%)			f_{oc} (%)
		Phe	Pyr	BaP	
Day -1	—	57 ± 4	70 ± 6	84 ± 7	2.12 ± 0.13
	Condition 1	35 ± 9	44 ± 9	59 ± 10	2.26 ± 0.15
	Condition 2	27 ± 0	36 ± 1	50 ± 0	1.22 ± 0.11
Day 10	Condition 3	28 ± 5	36 ± 1	48 ± 3	1.91 ± 0.18
	Condition 4	31 ± 6	39 ± 0	50 ± 1	1.32 ± 0.17
	Condition 5	34 ± 2	43 ± 2	54 ± 1	1.36 ± 0.16

Mean ± standard deviation ($n = 3$).

Table S5. Measured total dissolved PAH concentrations in pore water ($C_{diss,pore}$) at the start and end of test.

	Phe		Pyr		BaP	
	Day 0	Day 10	Day 0	Day 10	Day 0	Day 10
Condition 1		46 ± 3		19 ± 1		15 ± 0
Condition 2		46 ± 9		25 ± 7		29 ± 10
Condition 3	42 ± 4	38 ± 8	14 ± 3	21 ± 13	9 ± 3	20 ± 19
Condition 4		44 ± 5		19 ± 7		16 ± 9
Condition 5		42 ± 0		16 ± 2		11 ± 3

Mean ± standard deviation ($n = 4$ for pore water at Day 0; $n = 2$ for pore water at Day 10). Unit: µg/L.

Table S6. Survival rate and dry weight of amphipods after 10-day exposure in five different water exchange conditions.

	Survival rate (%)	Dry weight (mg/amphipod)
Before exposure (Day -1)	—	0.02
Condition 1	100 ± 0	0.08 ± 0.01
Condition 2	70 ± 10	0.07 ± 0.02
Condition 3	83 ± 20	0.08 ± 0.02
Condition 4	97 ± 6	0.06 ± 0.02
Condition 5	73 ± 21	0.06 ± 0.00

Mean ± standard deviation ($n = 3$).

Table S7. PAH concentrations in survived amphipods (C_{org}) in five different water exchange conditions.

	Phe	Pyr	BaP
Condition 1	8 ± 1	66 ± 10	9 ± 3
Condition 2	14 ± 1	50 ± 5	9 ± 3
Condition 3	12 ± 6	49 ± 17	8 ± 3
Condition 4	16 ± 10	56 ± 34	8 ± 3
Condition 5	14 ± 7	43 ± 17	7 ± 1

Mean \pm standard deviation ($n = 3$). Unit: mg/kg-dry.

Table S8. Parameters used in the mechanistic model.

Parameter	Value	Description
C_{sed}	17.2 (Phe)	Sediment concentrations (mg/kg-dw). Experimental values measured before exposure were used in the model.
	19.5 (Pyr)	
	25.3 (BaP)	
	mg/kg-dw	
f_{OC}	0.021	Mass fraction of total organic carbon in the sediment. Experimental f_{OC} at the start of exposure was used in the model.
	kg-oc/kg-dw	
UWL thickness	1 mm	Thickness of unstirred water layer (UWL).
$K_{OC/W}$	$10^{4.2}$ (Phe)	OC-water partition coefficient (Lw/kg-oc). Calculated from C_{sed} , C_{free} measured by SPME in pore water, and corresponding experimental f_{OC} .
	$10^{5.1}$ (Pyr)	
	$10^{6.6}$ (BaP)	
	Lw/kg-oc	
$K_{DOC/W}$	$10^{3.0}$ (Phe)	DOC-water partition coefficient (Lw/kg-DOC). Calculated using experimental values from the following equation:
	$10^{4.1}$ (Pyr)	
	$10^{5.7}$ (BaP)	
	Lw/kg-DOC	
		$K_{DOC/W} = \frac{C_{diss,pore} - C_{free,pore}}{[DOC]_{pore} \cdot C_{free,pore}}$
		Water exchange rate.
		Day -1 to 0: 4 beaker volumes/day in all conditions.
k_{out}	4.62×10^{-5} /s	Day 0 to 10: 0 beaker volumes/day in Condition 1.
	(day -1-0)	Day 0 to 10: 1 beaker volumes at Day 1.00, 1.31, 3.00, 3.31, 6.00, 6.31, 8.00, and 8.31 in Condition 2.
	Depending on	Day 0 to 10: 1 beaker volumes at Day 1.00, 1.31, 2.00, 2.31, 3.00, 3.31, 4.00, 4.31, 5.00, 5.31, 6.00, 6.31, 8.00, 8.31, 9.00, and 9.31 in Condition 2.
	conditions (day 0-	Day 0 to 10: 1 beaker volumes/day in Condition 4.
	10)	Day 0 to 10: 2 beaker volumes/day in Condition 5.

More details are described in Fischer et al. (2021).

Table S9. Comparison of experimental and simulated total dissolved phenanthrene (Phe) concentrations in overlying water ($C_{\text{diss,over}}$) in Conditions 2 and 3.

		Day							
		1.01	3.30	6.00	6.30	8.00	8.26	9.30	10.00
Condition 2	Experiment	6 ± 3	6 ± 0	9 ± 0	6 ± 1	8 ± 0	6 ± 1	7 ± 0	8 ± 1
	Model I*	7	2	10	2	7	2	4	6
	Model II*	8	7	12	8	10	6	7	9
Condition 3	Experiment	7 ± 3	8 ± 0	9 ± 1	8 ± 0	9 ± 1	6 ± 0	7 ± 0	9 ± 1
	Model I*	5	2	3	2	3	1	1	3
	Model II*	7	5	5	4	5	4	4	4

Mean ± standard deviation ($n = 3$) for experimental values. Unit: $\mu\text{g/L}$.

* Model I and II indicates the simulation assuming that 100% and 50% of overlying water was replaced the timing of water exchange, respectively.

Table S10. Comparison of experimental and simulated total dissolved pyrene (Pyr) concentrations in overlying water ($C_{\text{diss,over}}$) in Conditions 2 and 3.

		Day							
		1.01	3.30	6.00	6.30	8.00	8.26	9.30	10.00
Condition 2	Experiment	2 ± 1	2 ± 0	3 ± 0	1 ± 1	2 ± 0	1 ± 0	2 ± 0	3 ± 0
	Model I*	3	1	4	1	3	1	2	3
	Model II*	3	3	5	3	4	2	3	4
Condition 3	Experiment	2 ± 1	2 ± 0	3 ± 0	2 ± 0	3 ± 0	2 ± 0	2 ± 0	3 ± 0
	Model I*	2	1	2	1	1	1	1	1
	Model II*	3	2	2	2	2	2	2	2

Mean ± standard deviation ($n = 3$) for experimental values. Unit: $\mu\text{g/L}$.

* Model I and II indicates the simulation assuming that 100% and 50% of overlying water was replaced the timing of water exchange, respectively.

Table S11. Comparison of experimental and simulated total dissolved benzo[*a*]pyrene (BaP) concentrations in overlying water ($C_{\text{diss,over}}$) in Conditions 2 and 3.

		Day							
		1.01	3.30	6.00	6.30	8.00	8.26	9.30	10.00
Condition 2	Experiment	<LOQ	<LOQ	0.4 ±	0.2 ±	0.1 ±	0.2 ±	0.1 ±	2.6
				0.2	0.1	0.0	0.1	0.0	
	Model I*	1.2	0.3	1.9	0.3	1.2	0.3	0.7	1.1
	Model II*	1.4	1.3	2.4	1.4	1.8	1.1	1.2	1.6
Condition 3	Experiment	<LOQ	0.1 ± 0.1	0.6 ±	0.6 ±	0.5 ±	0.4 ±	0.1 ±	0.2 ±
				0.1	0.2	0.2	0.2	0.0	0.0
	Model I*	0.8	0.2	0.5	0.2	0.5	0.2	0.2	0.5
	Model II*	1.1	0.8	0.9	0.7	0.8	0.6	0.6	0.7

Mean ± standard deviation ($n = 3$) for experimental values. Unit: µg/L.

* Model I and II indicates the simulation assuming that 100% and 50% of overlying water was replaced the timing of water exchange, respectively.

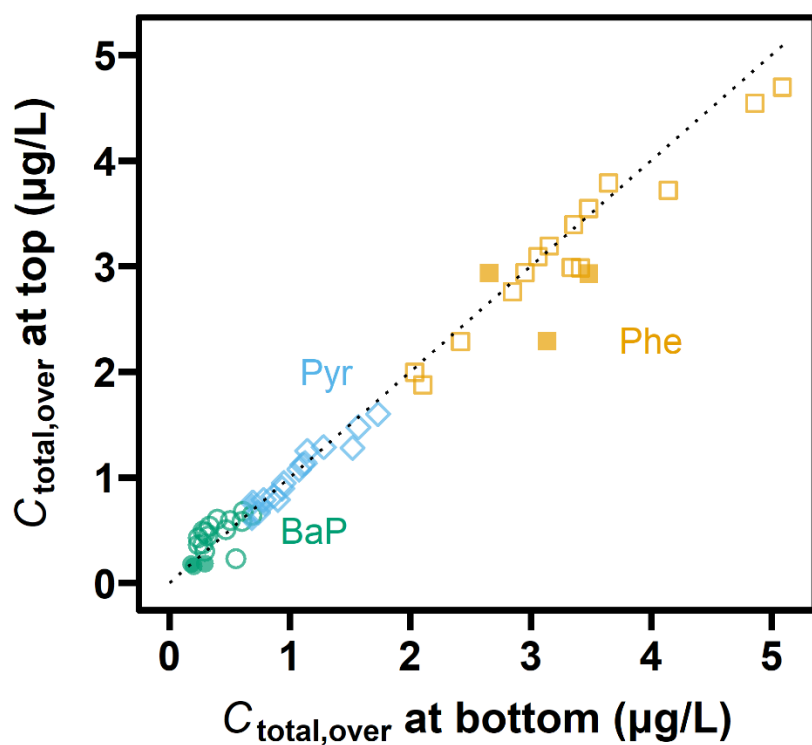


Figure S1. Relationship between total aqueous concentrations of Phe (yellow squares), Pyr (blue diamonds), and BaP (green circles) at bottom and top of overlying water in Conditions 2 (closed) and 3 (open). Overlying water at the bottom and top was taken from approximately 1 cm above the sediment and from <1 cm below the water surface, respectively. The dotted line indicates a 1:1 ratio.

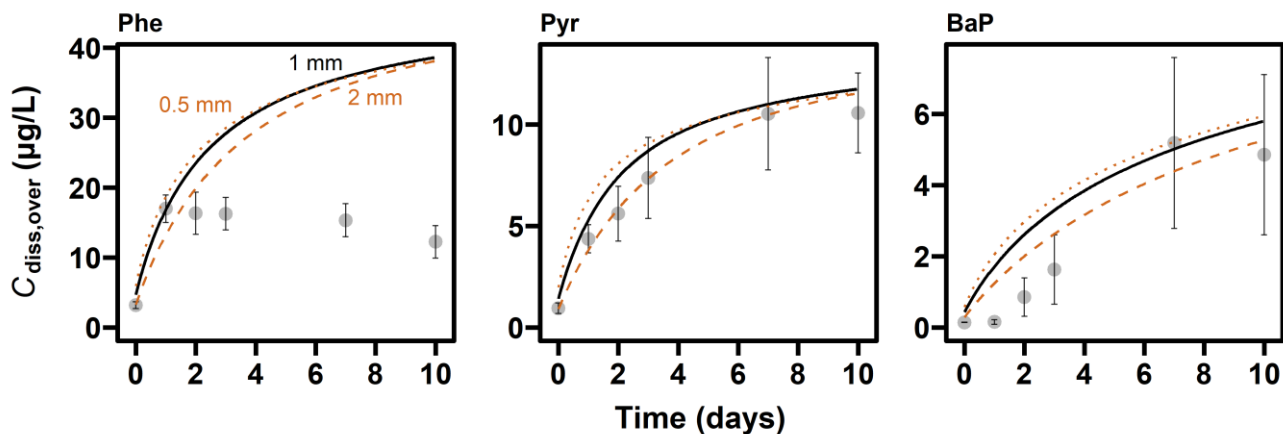
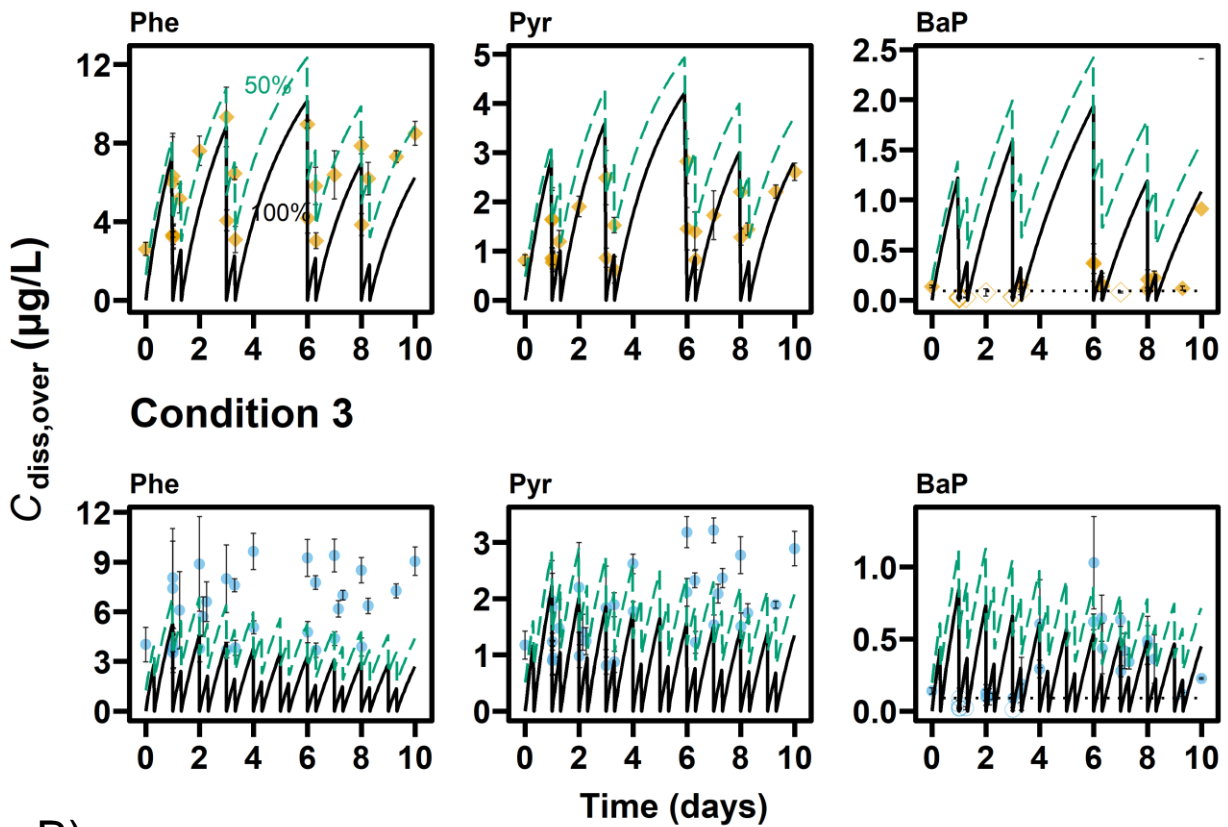


Figure S2. Total dissolved concentrations of phenanthrene (Phe), pyrene (Pyr), and benzo[a]pyrene (BaP) in overlying water under Condition 1, simulated with different thickness of unstirred water layer (UWL) (0.5, 1, and 2 mm). Solid and dotted lines represent simulated values by the mechanistic model, while dots represent experimental values ($n = 3$; mean \pm standard deviation).

A) Condition 2



B)

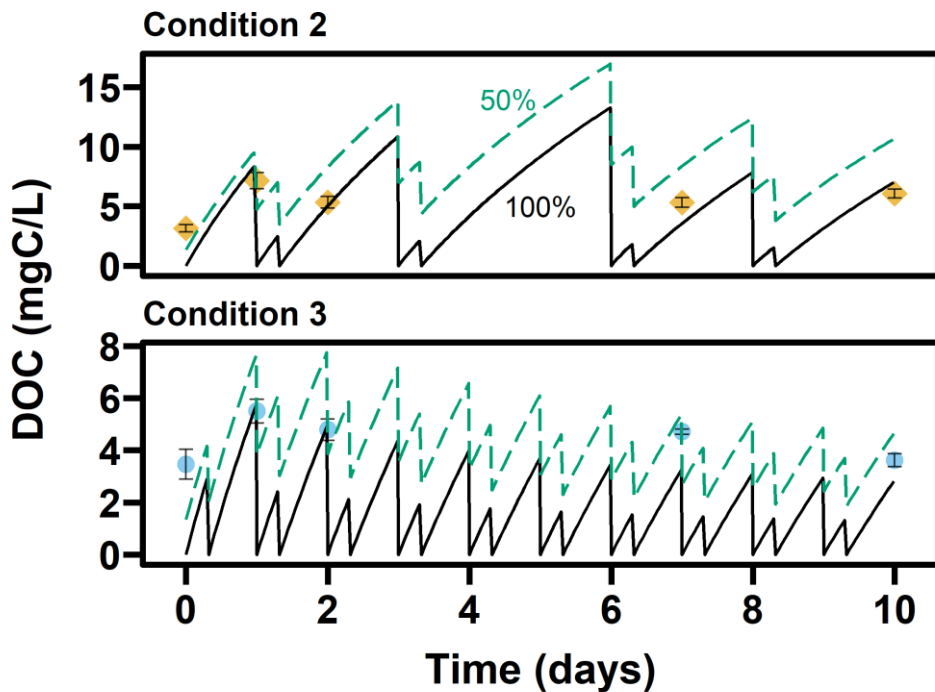


Figure S3. Simulated concentrations of (A) total dissolved phenanthrene (Phe), pyrene (Pyr), and benzo[a]pyrene (BaP) and (B) dissolved organic carbon (DOC) in overlying water under semi-static conditions. The model simulation was performed with different clearance ratio (50%: green dashed line, 100%: solid line). Dots represent experimental values ($n = 3$; mean \pm standard deviation). See Table S9 to S11 for more details of $C_{diss,over}$.

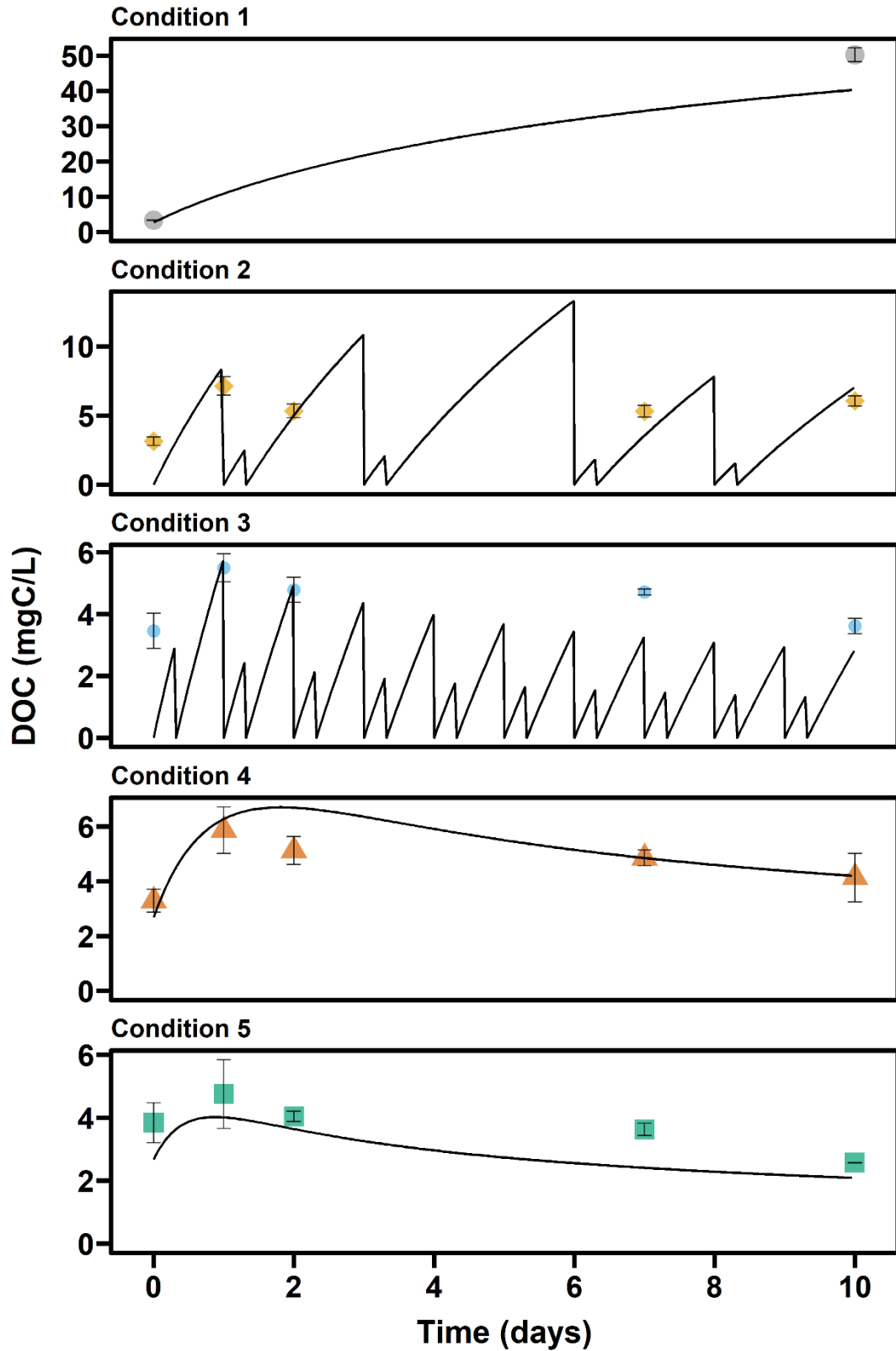


Figure S4. Time-course changes in dissolved organic carbon (DOC) concentrations in overlying water in five different water exchange conditions. Dots represent experimental values ($n = 3$; mean \pm standard deviation), while solid lines represent simulated values by the mechanistic model.

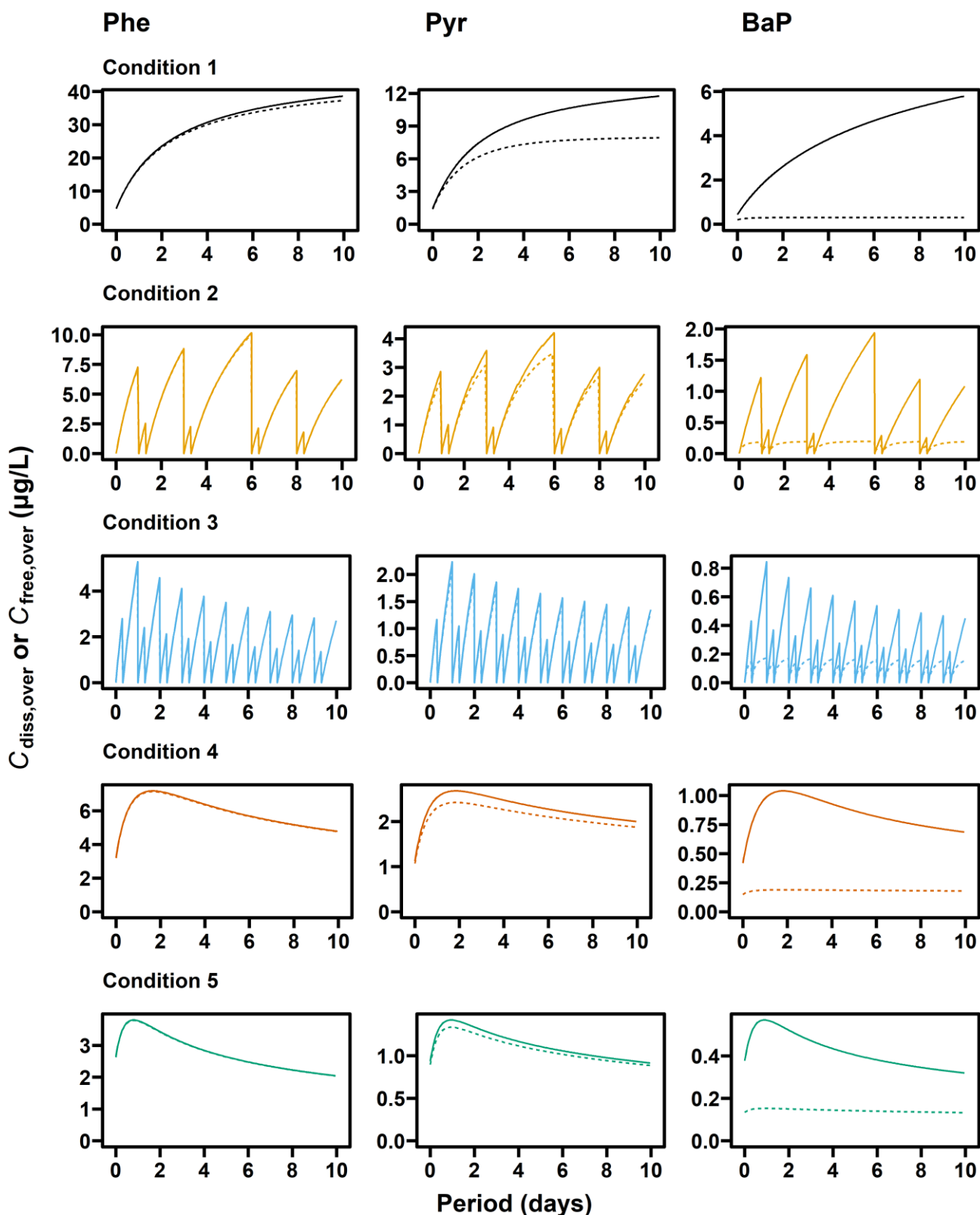


Figure S5. Time-course changes in total dissolved PAH concentrations ($C_{diss,over}$; solid line) and freely dissolved PAH concentrations ($C_{free,over}$; dotted line) in overlying water, simulated by the mechanistic model in five different water exchange conditions. Note that both lines overlap with each other for phenanthrene (Phe).

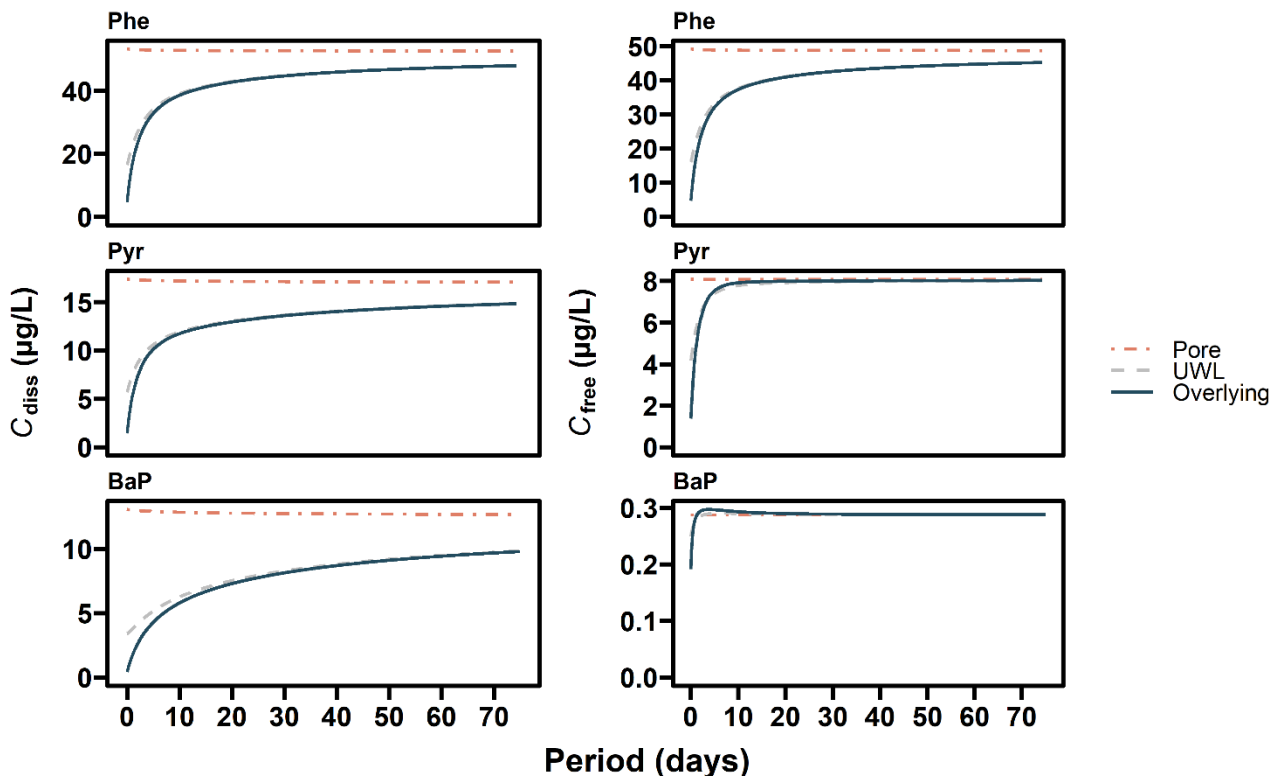


Figure S6. Extended time-course changes in total dissolved PAH concentrations (C_{diss} ; left panels) and freely dissolved PAH concentrations (C_{free} ; right panels) in pore water, unstirred water layer (UWL), and overlying water, simulated by the mechanistic model in the static condition (Condition 1).

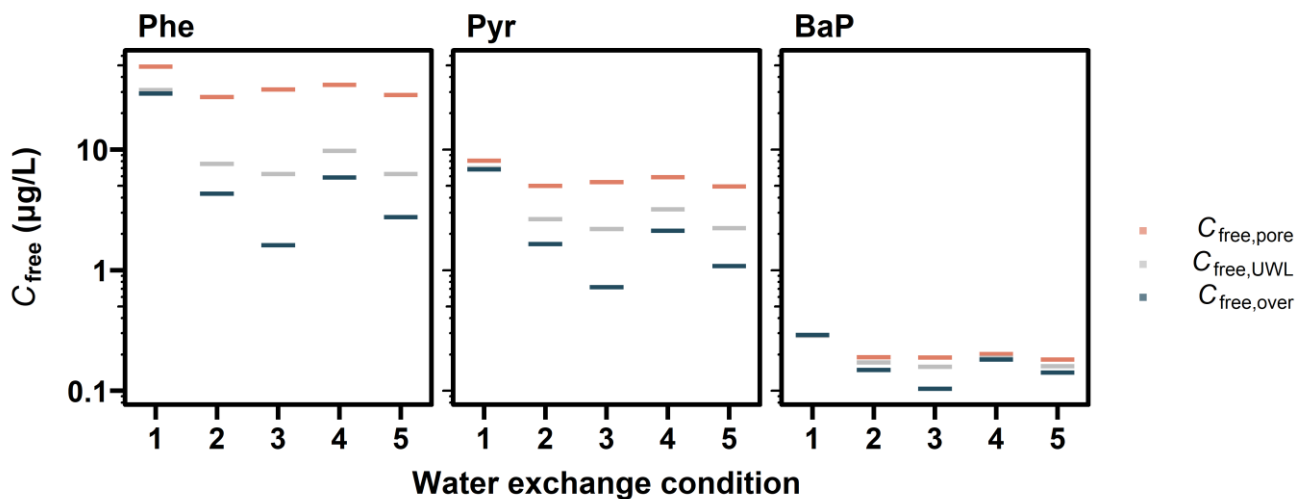


Figure S7. Simulated freely dissolved PAH concentrations under five different water exchange conditions. Different colors represent different positions (i.e., pore water, unstirred water layer [UWL], and overlying water). Concentrations represent the values at the end of exposure (i.e., Day 10) and depth-averaged values in each component.

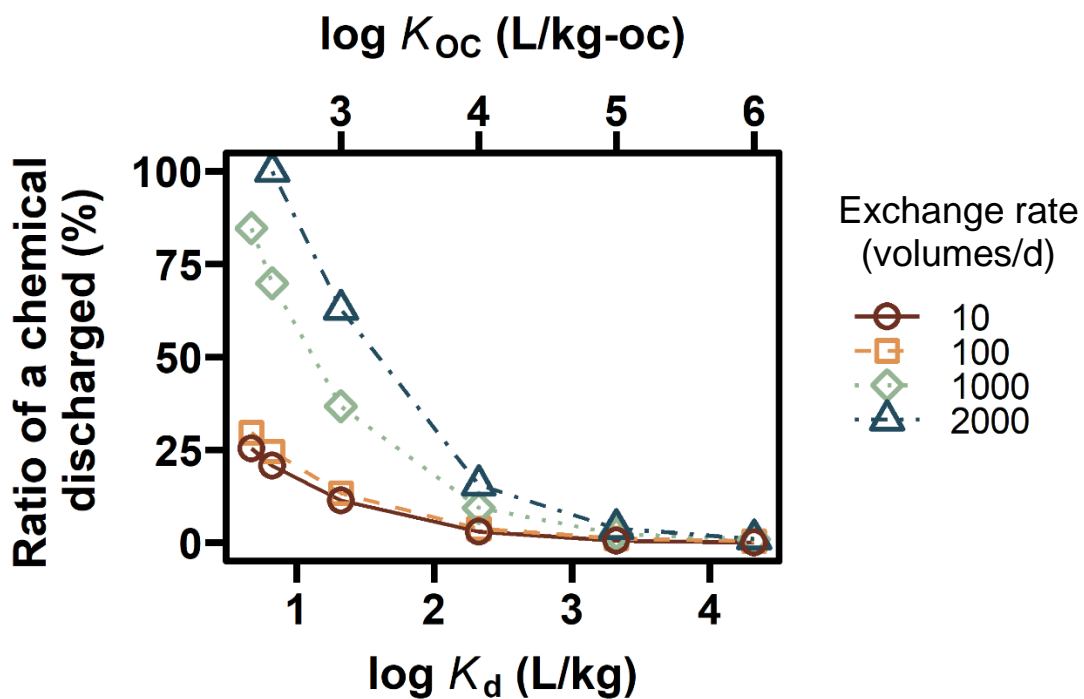


Figure S8. Dependence of the ratio of a chemical discharged from a beaker during 10-day test to the total installed amount on the log K_d values. Different symbols represent different water exchange rates (volumes/day). f_{oc} and K_{DOC} were set to 2% and 0.2 K_{oc} , respectively, for the model simulation.

REFERENCES

Fischer FC, Hiki K, Soetaert K, Endo S. 2021. Mind the Exposure Gaps—Modeling Chemical Transport in Sediment Toxicity Tests. *Environ Sci Technol.* 55(17):11885–11893. doi:10.1021/acs.est.1c03201.