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Mind the Exposure Gaps—Modeling Chemical Transport in Sediment Toxicity Tests

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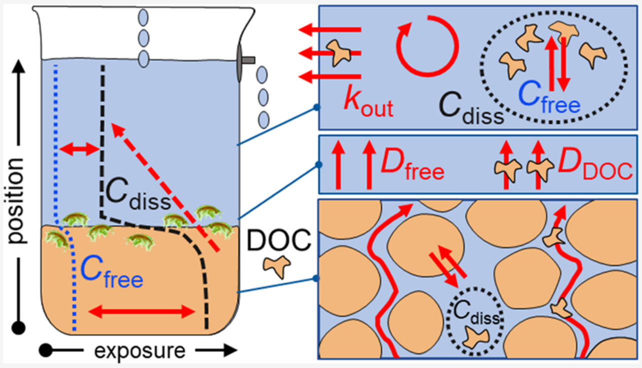
ABSTRACT: Chemical exposure in flow-through sediment toxicity tests can vary in time, between pore and overlying water, and amid free and bound states, complicating the link between toxicity and observable concentrations such as free pore ($C_{free,pore}$), free overlying ($C_{free,over}$), or the corresponding dissolved concentrations (C_{diss}, free + bound to dissolved organic carbon, DOC). We introduce a numerical model that describes the desorption from sediments to pore water, diffusion through pores and the sediment−water boundary, DOC-mediated transport, and mixing in and outflow from overlying water. The model explained both the experimentally measured gap between $C_{free,over}$ and $C_{free,pore}$ and the continuous decrease in overlying C_{diss}. Spatially resolved modeling suggested a steep concentration gradient present in the upper millimeter of the sediment due to slow chemical diffusion in sediment pores and fast outflux from the overlying water. In contrast to continuous decrease in overlying C_{diss} expected for any chemical, $C_{free,over}$ of highly hydrophobic chemicals was kept relatively constant following desorption from DOC, a mechanism comparable to passive dosing. Our mechanistic analyses emphasize that exposure will depend on the chemical's hydrophobicity, the test organism habitat and uptake of bound chemicals, and the properties of sediment components, including DOC. The model can help to re-evaluate existing toxicity data, optimize experimental setups, and extrapolate laboratory toxicity data to field exposure.



KEYWORDS: *numerical modeling, bioavailability and exposure, diffusion and partitioning, sediment toxicity, laboratory−field extrapolation, facilitated transport*

1. INTRODUCTION

Sediment toxicity tests are widely accepted tools to assess the chemical pollution of environmental sediment samples and to measure the toxicity of chemicals added to natural or artificial sediments.[1] Both endo- and epibenthic test organisms like copepods, amphipods, bivalves, and polychaetes are used for toxicity assessments,[2] most requiring a manual or (semi)-automated water exchange system to supply oxygen and to remove toxic byproducts for a typical test duration of 10−28 days. However, it has been observed that differences between test setups and protocols can lead to substantial alterations in chemical bioavailability,[3−5] emphasizing the need for methods to quantify and understand exposure for better interpretation of laboratory toxicity and extrapolation to field exposure conditions.

In spiked sediment toxicity tests, the apparent toxicity of chemicals is usually related to the dry-weight-based sediment concentration (C_{sed}), which is either calculated (nominal concentration) or measured by solvent extraction.[6] C_{sed}-based toxicity, however, carries uncertainty because it does not consider variabilities in sediment composition (e.g., carbon content and source).[3,5,7,8] The freely dissolved concentration in pore water ($C_{free,pore}$) has been shown to be a better exposure metric for organic chemicals because $C_{free,pore}$ considers varying chemical bioavailabilities across sediments,[9−11] as was demonstrated, e.g., for the endobenthic larvae of *Chironomus tentans*.[12] In equilibrium partitioning theory, $C_{free,pore}$ is estimated from C_{sed} and the sediment−water partition coefficient (K_d, L/kg$_{dw}$) and linked to water-only toxicity data.[13] The suitability of pore water concentrations as an exposure metric has been a matter of debate given the variable swimming and sediment burrowing behavior of test organisms under laboratory conditions,[14−16] implying the necessity to determine the free concentration in the water phase overlying the sediment ($C_{free,over}$) as well. Moreover, given the observation that test organisms ingest sediment particles (and possibly dissolved organic carbon (DOC)) in

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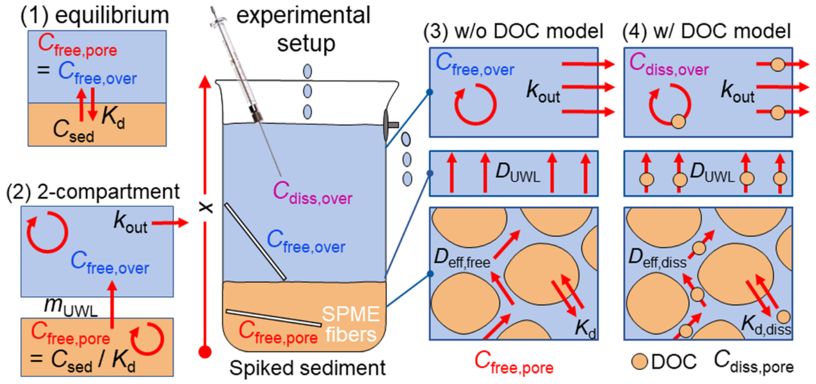

Figure 1. Experimental setup of the *H. azteca* sediment toxicity test and the corresponding C_{free} and C_{diss} sampling techniques that were applied in Hiki et al.,[23] as well as the chemical transport processes in the individual zones that were accounted for by the models (equilibrium, two-compartment, w/o DOC, and w/ DOC models). The chemical transport in the diffusion models was simulated in 1D, with the *x*-coordinate being representative of the entire cross section. Symbols are explained in the text.

the water column,[17,18] there may be cases where the total dissolved concentration (C_{diss}, i.e., free + DOC-bound concentrations) and/or the total aqueous concentration (free + DOC-bound + particle-bound concentrations) could better reflect the actual exposure. Following these observations and debates, there is a need to better understand chemical transport processes and distribution between bound and free species in sediment toxicity tests.

The chemical distribution in the sediment toxicity test system is the result of intertwined processes such as the partitioning and diffusion of chemicals in the sediment, interfacial transfer from the sediment to the overlying water, advection in the turbulent overlying water, and chemical outflux by water exchange. Overall mass transport kinetics can be influenced by the particle size of sediments and hence their mobility,[19] as well as facilitated by the cotransport of DOC-bound chemicals following the flux of DOC from the sediment to the overlying water, in addition to the transport of freely dissolved chemicals.[20,21] Recently, in the standardized 10-day sediment toxicity test with the amphipod *Hyalella azteca*,[22] we experimentally observed $C_{free,pore}$ that were by a factor of up to ~10 higher than $C_{free,over}$ and a decreasing trend of C_{diss} in the overlying water ($C_{diss,over}$) over time.[23] Moreover, a vertical concentration gradient of hydrophilic chemicals in the upper sediment was measured in static sediment toxicity tests with *Chironomus riparius* in the literature.[24] These observations indicate that the dynamic processes mentioned above lead to variable exposure conditions in space and time.

In this article, we propose to use mechanistic modeling to identify the process(es) and chemical properties that determine the establishment and temporal variability of $C_{free,over}$ and $C_{free,pore}$ and the corresponding C_{diss} in spiked sediment tests. The interrelated partitioning, diffusion, and outflux of chemicals in flow-through sediment toxicity tests could be simulated using numerical modeling following appropriate mathematical descriptions of these processes and derivation of the required model parameters (e.g., sediment OC content, water exchange rate). In recent years, various modeling efforts have been reported for in vitro toxicity tests, which shed light on the actual exposure in miniaturized test systems.[25−31] A recent study[24] adopted a similar approach and successfully modeled the chemical transport in a sediment−water test system. However, the focus was rather on relatively hydrophilic chemicals, and thus, C_{free} and C_{diss} in different water zones and DOC-facilitated transport, which are expected to be important for hydrophobic chemicals, were not considered in the simulations.

In this study, we developed a one-dimensional diffusion model to simulate the chemical transport over time and space in sediment toxicity tests. We applied the model to the standardized 10-day *H. azteca* sediment toxicity test and compared the model predictions to the experimental data set from Hiki et al.,[23] which included $C_{free,over}$, $C_{free,pore}$, $C_{diss,over}$, and dissolved concentrations in pore water ($C_{diss,pore}$) of four chemicals with moderate to high hydrophobicity. Following model validation, we performed model simulations for hypothetical chemicals with varying sorption properties to identify the system and chemical properties that drive the chemical transport and determine C_{free} and C_{diss} in the toxicity test. Finally, we discuss the re-evaluation of existing toxicity data, the optimization of existing protocols and procedures, the interpretation of toxicity on the basis of different exposure metrics, and the extrapolation of laboratory toxicity data to field exposure.

2. MODELS

For comparison and evaluation of the applicability domain, we present four models to calculate the chemical transport and distribution in the sediment toxicity test. (1) An equilibrium partition model (EqM) and (2) a two-compartment model serve as commonly applied reference models but could be too simplistic to represent the reality. (3) A simple kinetic diffusion model that considers only freely dissolved species (i.e., DOC-mediated transport not considered, thus "w/o DOC model") and (4) a more comprehensive model that accounts for both partitioning and transport of the freely dissolved and DOC-bound species ("w/ DOC model") are developed (Figure 1).

2.1. Equilibrium Partitioning Model (EqM).

The simplest approach in calculating C_{free} assumes chemical equilibrium between the sediment and the surrounding water, whereas no differentiation is made between pore and overlying water. C_{free} was estimated based on the chemical's sorption coefficient K_d and the initial total chemical concentration in the dry sediment $C_{sed,t0}$ (mg/kg$_{dw}$), assuming no depletion of the sediment after equilibration.

$$C_{free} = C_{sed,t0}/K_d \qquad (1)$$

K_d was calculated as $K_d = f_{OC,sed}K_{OC/w}$, with $f_{OC,sed}$ and $K_{OC/w}$ being the mass fraction of organic carbon (OC) in the sediment and the OC−water partition coefficient (L_w/kg_{OC}), respectively.

2.2. Two-Compartment Model. The two-compartment model presented here assumes (1) well-mixed overlying water and (2) well-mixed sediment compartments. The two compartments are connected over an unstirred water layer (UWL) with a thickness x_{UWL} of 1 mm, which is within the range that was measured for sediments in flow-through aquaria.[32] Instantaneous sediment particle−water equilibrium is assumed in the sediment compartment. The chemical transport over the UWL is described by the mass transfer coefficient m_{UWL} (cm/s), which was calculated as $m_{UWL} = D_w/x_{UWL}$, with D_w being the diffusion coefficient of the chemical in water (cm^2/s). The assumption here is that chemical diffusion is the sole driver of chemical transport over the UWL. The temporal changes in $C_{free,pore}$ and $C_{free,over}$ are calculated as

$$\frac{dC_{free,pore}}{dt} = -m_{UWL}\frac{\Delta C_{free}}{(x_{sed}\alpha_{free})} \tag{2}$$

$$\frac{dC_{free,over}}{dt} = \frac{m_{UWL}\Delta C_{free}}{x_{over}} - C_{free,over}k_{out} \tag{3}$$

where ΔC_{free} is the concentration difference between pore and overlying water ($C_{free,pore} - C_{free,over}$), t is the time (s), α_{free} is the capacity factor of the sediment for the free chemical (eq S3),[33] k_{out} is the water exchange rate in the overlying water (1/s), and x_{sed} and x_{over} are the height of the sediment and the overlying water (cm), respectively. Binding to DOC is not considered in this model.

2.3. Diffusion Models with and without DOC-Mediated Transport. *2.3.1. General Description.* Two diffusion models were applied that describe the transport in the sediment and the UWL as one-dimensional diffusion processes. The models divide the test system into three zones: (i) the sediment including sediment particles and pore water, (ii) the UWL, and (iii) an overlying water phase for which water exchange applies (Figure 1). The overlying water phase is assumed to be well mixed as for the two-compartment model. This assumption is supported by experiments that showed no concentration gradient between the top and bottom positions of the water phase.[23] The diffusion model without DOC-mediated transport (w/o DOC model) assumes that all chemicals released from the sediment are freely dissolved in each water phase, i.e., chemical transport in the sediment and UWL is solely dependent on the molecular diffusion of the chemical in water. The diffusion model with DOC-mediated transport (w/ DOC model) accounts for binding to and mediated transport by DOC in water, integrating the transport of free and DOC-bound chemicals. The temporal and spatial variabilities in DOC concentrations [DOC] in each water zone were considered. The w/o DOC model represents a special case of the w/ DOC model where the influence of DOC on chemical partitioning and transport is neglected. The mathematical description of the diffusion models is presented here only briefly. For details, we refer to Section S-1.

2.3.2. Governing Equations. The diffusive transport of chemicals in the individual water zones is dependent on the diffusion coefficient of chemicals, the concentration of DOC, and in the case of the pore water, physical properties of the sediment and the sorption of chemicals to sediment particles (Figure 1). Assuming local, instantaneous equilibrium between all phases involved and neglecting transport via suspended particles as well as intraparticle and surface diffusion of particle-bound chemicals in the sediment, the general diffusion equation applied in the w/o and w/ DOC diffusion models reads

$$\frac{\partial(\alpha C)}{\partial t} = D_{eff}\frac{\partial^2 C}{\partial x^2} \tag{4}$$

where C is the chemical concentration (C_{diss} in the w/ DOC model, C_{free} in the w/o DOC model), x is the distance from the bottom of the beaker (cm), and D_{eff} is the effective diffusion coefficient of the chemical in the respective water zone (cm^2/s) (including DOC-mediated transport in the w/ DOC model). The capacity factor α accounts for the retention of chemicals in the sediment following sorption and desorption to and from sediment particles and DOC (α_{diss} in the w/ DOC model, α_{free} in the w/o DOC model).

2.3.3. R Coding. The partial differential equations were solved numerically in discrete time steps (Δt) and a discrete space grid (Δx) using the open-source software *R* (version 3.6.2) with the aid of the package ReacTran.[34] The *R* code of the w/ DOC model is attached as a Word document. Details on the model geometry and derivation of system and chemical parameters can be found in Section S-2.

2.3.4. Parameterization of DOC Transport. For the implementation of the DOC-mediated transport (eqs S4−S6) and the calculation of C_{free} from C_{diss} in the w/ DOC model (eq S8), the DOC concentrations at all times and positions need to be simulated. Therefore, we ran the w/o DOC model for a hypothetical chemical that represents DOC (Figure S1). Chemical properties were adjusted so that the model results agree with experimental data for DOC concentrations in pore water ($[DOC]_{pore}$) after the 10-day test and in overlying water ($[DOC]_{over}$) over time.[23] See Section S-2 for more details. We note that this modeling was done to obtain time- and position-dependent $[DOC]_{pore}$ and $[DOC]_{over}$ that are consistent with measured values. The adjusted property values are thus fully empirical.

2.4. Experimental Data. Experimental concentration data considered are from ref 23. In ref 23, semi-flow-through sediment toxicity test systems were prepared according to standard protocols[22] for four chemicals (phenanthrene, pyrene, benzo[*a*]pyrene, chlorpyrifos). The experimental methods are summarized in Section S-3 and explained in detail in the cited article.[23] Briefly, artificial sediment was prepared following the OECD guideline,[35] spiked with the test chemical(s) and mixed on a roller shaker for homogenization. The spiked wet sediment was distributed to glass beakers, which were placed below a semi-flow-through water exchange system. Solid-phase microextraction fibers of polydimethylsiloxane (PDMS) were buried in the sediment and placed in the overlying water and collected at the test end (10 days) for measurement of $C_{free,pore}$ and $C_{free,over}$, respectively. Over the 10-day test duration, the overlying water was repeatedly sampled to measure $C_{diss,over}$. $C_{diss,pore}$ was measured at day 10. Additionally, the initial and final chemical concentrations and the total organic carbon content in the sediment were measured. The important observations in ref 23 include the following. First, the magnitude of concentrations was generally in the order $C_{diss,pore} \gtrsim C_{free,pore} > C_{diss,over} \gtrsim C_{free,over}$ (Figure S3). Only for benzo[*a*]pyrene was $C_{diss,over} > C_{free,pore}$ observed. This result suggests that the semi-flow-through water exchange reduced the concentration in the overlying water as compared

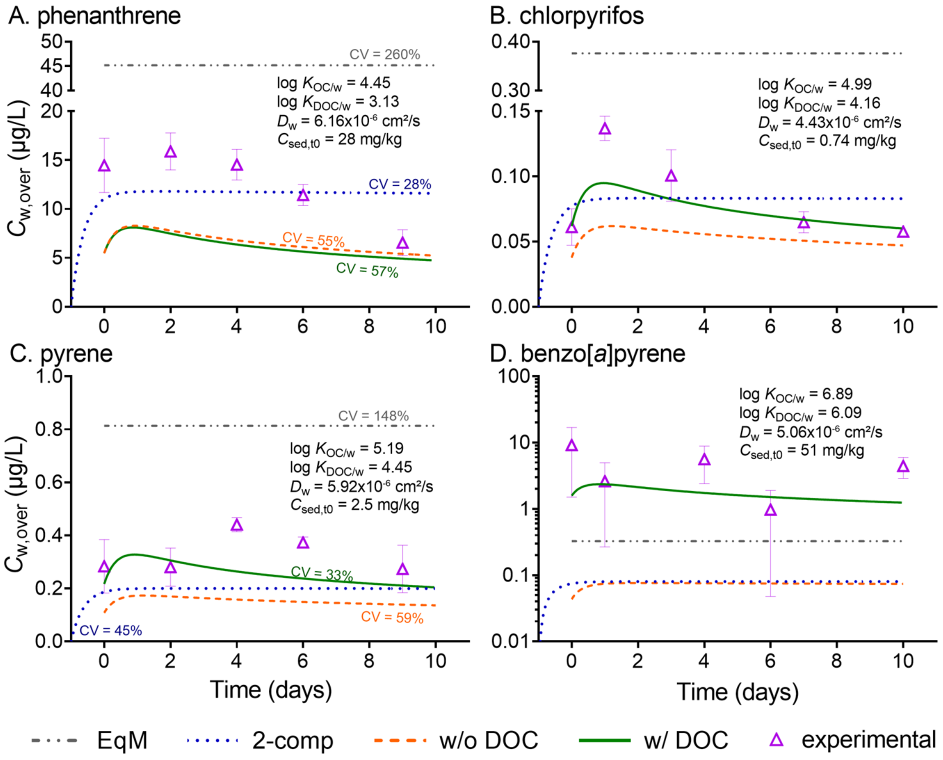

Figure 2. Experimental overlying water concentrations (purple triangles) of the test chemicals over the 10-day *H. azteca* semi-flow-through sediment toxicity test,[23] compared to predicted concentrations by the four models given model system parameters derived as described in Tables S1 and S2 and chemical parameters shown in the plots. Coefficients of variation (CV, %) between experimental and modeled data are shown in the plot.

to the pore water. Second, the time-series measurements of $C_{diss,over}$ showed an initial increase followed by a gradual decrease toward the end of the experiments (Figures 2 and S4). In the following, the models introduced in Section 2 were evaluated as to whether they can describe these trends and were used to identify the underlying mechanisms.

3. RESULTS AND DISCUSSION

3.1. Comparing Experimental Data with Model Predictions. Experimental overlying water concentrations ($C_{w,over}$) of four chemicals over the 10-day sediment test[23] were compared with simulations by the four models (Figures 2 and S4). Root-mean-square error (RMSE) was calculated using experimental (exp) and simulated values (sim) $\left(\mathrm{RMSE} = \sqrt{\frac{\sum_{i=1}^{n}(\exp - \mathrm{sim})^2}{n}}\right)$ and divided by the mean of experimental values to derive the coefficient of variation ($\mathrm{CV} = \mathrm{RMSE}/\overline{\exp}$). Note that the EqM, the two-compartment model, and the w/o DOC model consider only the free species and neglect the DOC-bound fraction, whereas the w/ DOC model accounts for both free and DOC-bound chemicals. The EqM predictions were significantly different (CVs ≥ 100%) from measured values and overestimated $C_{w,over}$ of phenanthrene, chlorpyrifos, and pyrene by a factor of 6.9, 6.6, and 3, respectively, at the end of the 10-day toxicity test. EqM cannot reproduce the time trends and extent of $C_{w,over}$ because the concentrations in the overlying water will never reach equilibrium due to the continuous outflux of chemicals by water exchange. In contrast to the three chemicals, the EqM largely underestimated $C_{w,over}$ of the most hydrophobic benzo[*a*]pyrene (by a factor of 14) because the EqM here does not consider DOC-bound species. The two-compartment model performed better in predicting the extent of $C_{w,over}$ (CVs = 28−116%) and the initial increase in $C_{w,over}$ after the start of the test (day 1 with increased water exchange). However, it did not match the decreasing $C_{w,over}$ that was observed in all experiments but rather predicted a quick attainment of a steady state within a day, which also did not match the experimental $C_{w,over}$ of most chemicals over 10 days. The two diffusion models simulated the decreasing trend of $C_{w,over}$. The $C_{w,over}$ was more accurately predicted by the w/ DOC model (CVs = 24−94%) than the w/o DOC model (CVs = 48−116%). Particularly for benzo[*a*]pyrene, the w/ DOC model was the only model that captured the order of magnitude of $C_{w,over}$. This result clearly indicates that the DOC in the water phase has a large influence on $C_{w,over}$ for very hydrophobic chemicals with a large log $K_{OC/w}$ (e.g., 6.89 for benzo[*a*]pyrene). All in all, these results point toward the necessity of considering the diffusive transfer in the sediment compartment and the DOC in the water phases to reproduce the experimental results and support the use of the w/ DOC model.

The agreement between experimental data and w/ DOC model-simulated concentrations was generally high for most of the experiments (Figures 2, S3, and S4), particularly after 10 days. A good agreement for $C_{free,pore}$ was expected because the $K_{OC/w}$ value used in the model was derived from the same set of experimental data.[23] Similarly, a good agreement for $C_{diss,pore}$ is no surprise, as $K_{DOC/w}$ was adjusted to the same data. In contrast, it is an encouraging finding that $C_{free,over}$ and $C_{diss,over}$ were predicted accurately by the w/ DOC model within one order of magnitude for most of the chemicals and concentrations tested. This result indicates that the w/ DOC model with appropriate parameters for OC and DOC sorption

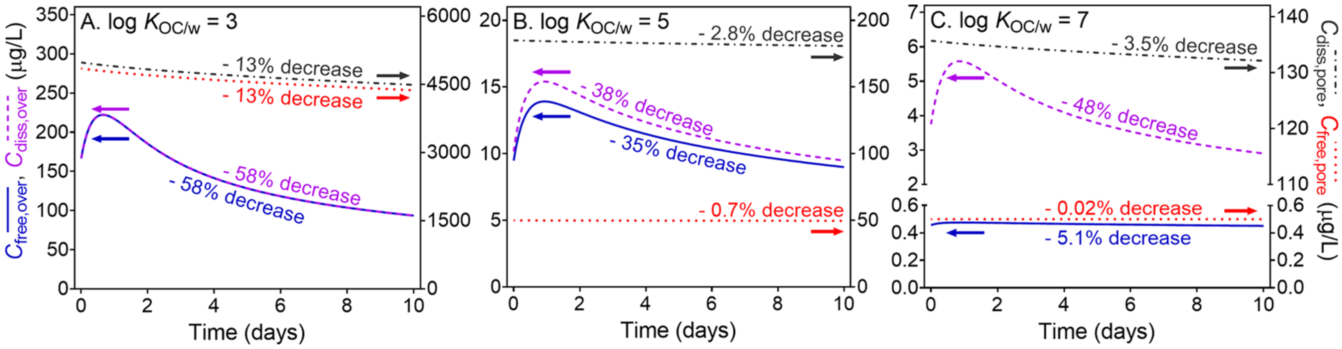

Figure 3. Dependence of $C_{free,over}$ (blue solid lines) and $C_{diss,over}$ (violet dashed lines), as well as depth-averaged $C_{diss,pore}$ (gray dash-dotted lines) and $C_{free,pore}$ (red dotted lines), over time on the log $K_{OC/w}$ of the chemical (ranging from 3 to 7 log units). Arrows indicate the axes that the data refer to. Percentage reductions from the highest value during the experiment are shown in the plot. D_w and $C_{sed,t0}$ were set to 5×10^{-6} cm^2/s and 100 mg/kg$_{dw}$, respectively. $K_{DOC/w}$ was defined as $0.2K_{OC/w}$. The system parameters correspond to those described in Tables S1 and S2. Note that the 24 h pre-equilibration period in which the water exchange rate was doubled is not shown (see Section S-3).

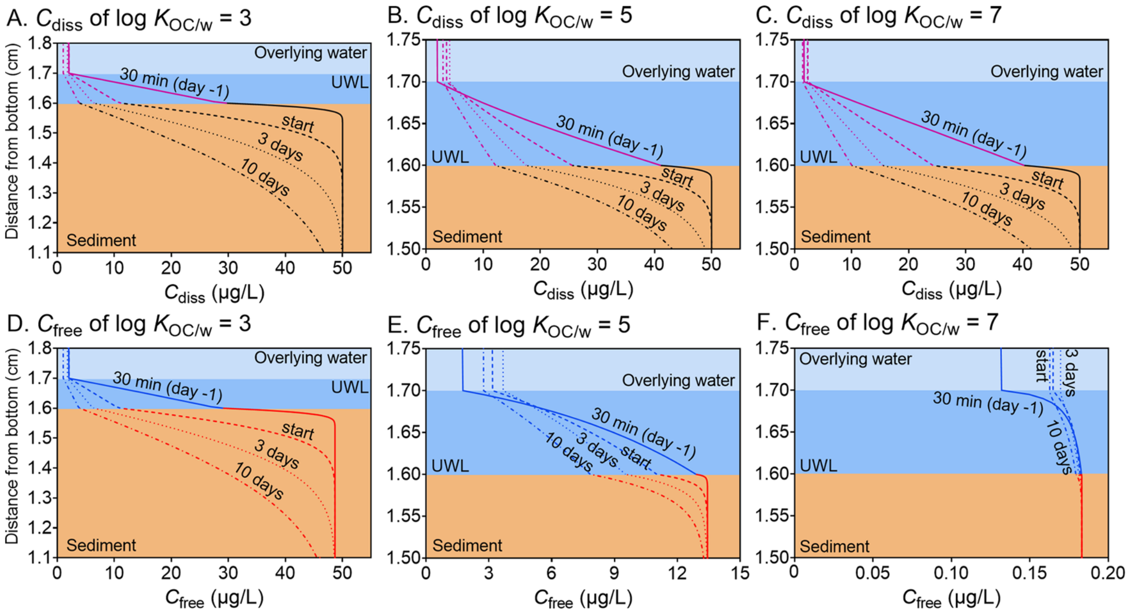

Figure 4. Dependence of the spatial C_{diss} and C_{free} profiles in the sediment, the unstirred water layer, and the overlying water on the log $K_{OC/w}$ of the chemical. Note that for log $K_{OC/w}$ = 3, the upper 5 mm of the sediment is displayed, whereas the upper 1 mm of the sediment is shown for log $K_{OC/w}$ = 5 and 7. $K_{DOC/w}$ was defined as $0.2K_{OC/w}$. D_w and initial $C_{diss,pore}$ were set to 5×10^{-6} cm^2/s and 50 μg/L, respectively. The system parameters correspond to those described in Tables S1 and S2.

can provide accurate predictions for overlying water concentrations.

3.2. Modeling Temporal Concentration Changes. Considering hypothetical chemicals with differing $K_{OC/w}$, the temporal changes of $C_{free,over}$, $C_{diss,over}$, $C_{free,pore}$, and $C_{diss,pore}$ were simulated over the test duration of 10 days using the w/DOC model (Figure 3). All parameters except the chemical's $K_{OC/w}$ were fixed (see Figure 3 caption, Tables S1 and S2).

The model shows that the depth-averaged $C_{diss,pore}$ and $C_{free,pore}$ in the whole sediment are virtually constant during the 10-day toxicity test for log $K_{OC/w} \geq 3$ (Figures 3 and S7), as >90% of the chemical's mass was conserved in the sediment after 10 days. Fixing the sediment concentrations at 100 mg/kg of all log $K_{OC/w}$ tested confirmed that higher affinity for the sediment (i.e., higher log $K_{OC/w}$) generally reduces C_{diss} and C_{free} in both sediment pores and overlying water and hence bioavailability (Figure 3). After the 24 h pre-equilibration period, the water exchange rate was halved (see Section S-3), and $C_{diss,over}$ first increased, reaching a turning point after ~1 day, and then decreased over the 10-day test. The % decrease in $C_{diss,over}$ from the peak was 38–58%. Interestingly, the % decrease in $C_{diss,over}$ was the smallest for log $K_{OC/w}$ of 5. The % decrease as well as the time course of $C_{diss,over}$ for chemicals with log $K_{OC/w}$ 6–7 was rather similar to those for log $K_{OC/w}$ 3–4. This is because the transport of highly hydrophobic chemicals is governed by the DOC transport, which is similar to the transport of relatively hydrophilic chemicals (Figure S2). For any chemical and any time point, we observed $C_{diss,over} < C_{diss,pore}$. At the end of the 10-day test, the $C_{diss,over}$ is expected to be a factor of 48, 19, and 46 lower than $C_{diss,pore}$ for chemicals with a log $K_{OC/w}$ of 3, 5, and 7, respectively; thus, the relationship is not a monotonic function of log $K_{OC/w}$. This is again because the DOC-mediated transport has a substantial influence on highly hydrophobic chemicals, whereas diffusion and sorption of the chemicals themselves determine the behavior of less hydrophobic chemicals.

3.3. Analyzing the Spatial Concentration Profile across the System. In the previous section, we showed

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that the mass of chemicals is largely conserved in the sediment but that the overlying water concentration decreases over time, which might appear counterintuitive. Simulating the spatial C_{diss} profile in the upper 5 and 1 mm of the sediment and in the UWL revealed that C_{diss} considerably decreases at the vicinity of the sediment−water interface rapidly after starting the test (Figure 4A−C). This decrease in concentration reduces the gradient over the UWL and thus the flux from the sediment to the overlying water, which can explain the divergent trends of sediment and overlying water concentrations.

The depletion of the upper sediment concentration is particularly pronounced for chemicals with a lower $\log K_{\mathrm{OC/w}}$ (Figures 4A and S8A). For the chemical with $\log K_{\mathrm{OC/w}}$ of 3, the upper sediment region is rapidly depleted by ∼40% within the first 30 min of the simulation, as a large proportion of the sediment-bound chemicals is transported to the water phase because of a relatively low sorption affinity for the sediment. Furthermore, the dropping of clean water to the overlying water leads to a continuous outflux of chemicals, which keeps the overlying water concentration low. The significant depletion of the upper sediment cannot be compensated for in time by the diffusion of chemicals in the pore water from lower sediment regions as the transport is retarded by sorption to sediment particles. This result agrees with the recent measurements of a vertical chemical gradient in the sediment of mesocosms that was related to retarded chemical mobility due to particle adsorption using spatial modeling.[24] By slow diffusive transport, even relatively hydrophilic chemicals are conserved in the sediment to a larger extent than expected by their K_{d} and the total volume of water exchanged. It is illustrative that for the chemical with $\log K_{\mathrm{OC/w}}$ 3 only 13% loss was predicted by the w/ DOC model, while 49% loss was expected by the two-compartment model. The latter model assumes an (unrealistic) well-mixed sediment compartment and does not capture slow, retarded transport in pore water. The combination of slow sediment pore transport, relatively high desorption to water, and fast water exchange explains the fast increase and subsequent decrease in $C_{\mathrm{diss,over}}$ that was measured experimentally (Figures 2 and S4) and simulated by the diffusion models (Figures 3 and S7). The same mechanisms apply to more hydrophobic chemicals, but the effect is less pronounced. Until the end of the toxicity test, the C_{diss} at the vicinity of the UWL was depleted by 92% ($\log K_{\mathrm{OC/w}}$ 3), 76% ($\log K_{\mathrm{OC/w}}$ 5), and 80% ($\log K_{\mathrm{OC/w}}$ 7), which translates into the decreasing flux from sediment to the overlying water through the UWL and thus decreasing $C_{\mathrm{diss,over}}$ of these chemicals (Figure 3). Interestingly, such a reduction would not be expected for a $\log K_{\mathrm{OC/w}}$ 7 chemical without consideration of cotransport by DOC (∼4% reduction after 10 days in the w/o DOC model, Figures S5, S6, and S9), as DOC-mediated transport substantially increases the total chemical flux from sediment into the overlying water.

Along with the reduction in $C_{\mathrm{diss,over}}$, reduction of $C_{\mathrm{free,over}}$ was also simulated for chemicals with $\log K_{\mathrm{OC/w}} \leq 5$ (Figure 3A,B) because $C_{\mathrm{free,over}} \approx C_{\mathrm{diss,over}}$ for these chemicals. However, for more hydrophobic chemicals with a $\log K_{\mathrm{OC/w}} \geq 6$, $C_{\mathrm{free,over}}$ remained relatively stable till the end of the toxicity test, $\ll C_{\mathrm{diss,over}}$, and similar to $C_{\mathrm{free,pore}}$ (Figures 3C and S7B). This characteristic behavior of $C_{\mathrm{free,over}}$ occurred in the model for the following reasons: The mobility of highly hydrophobic chemicals in the sediment is fully controlled by DOC transport, as shown by $C_{\mathrm{diss,over}}$ of $\log K_{\mathrm{OC/w}} \geq 6$ chemicals following a similar time trend to $[\mathrm{DOC}]_{\mathrm{over}}$ (Figure S2). Thus, the flux of DOC from the sediment to overlying water determines the flux of the chemical and so the value of $C_{\mathrm{diss,over}}$. Temporal decrease of $C_{\mathrm{diss,over}}$ occurs because the sediment-to-overlying water DOC flux decreases over time as the DOC in the upper sediment is depleted as well (Figure S2B). $C_{\mathrm{free,over}}$, in contrast, is controlled by equilibrium partitioning with the DOC-bound species. The bound concentration of chemicals on the DOC weight basis is more or less constant over time and so is $C_{\mathrm{free,over}}$ of very hydrophobic chemicals (Figures 4F and S8D). In a sense, DOC serves as a passive-dosing phase continuously emitted from the sediment to overlying water, keeping the activity (or fugacity) of the chemical in the overlying water similar to that in the sediment.

3.4. Exposure Concentration Gaps. Figure 5 summarizes the predicted gaps between C_{free} and C_{diss} and between concentrations in pore and overlying water. For relatively hydrophilic chemicals ($\log K_{\mathrm{OC/w}} \leq 4$), no difference between C_{free} and C_{diss} in both water zones is expected as the sorption to DOC is negligible. However, the simulations indicated a large concentration gap between pore and overlying water. This gap results from the reduced concentration gradient at the sediment−water interface following depletion of chemicals from the upper sediment and slow chemical diffusion in lower sediment regions (retardation by sorption), as discussed above.

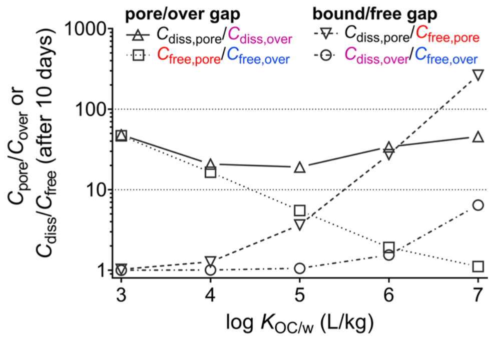

Figure 5. Concentration ratios in space (overlying and pore water) and state (free and dissolved) dependent on the $\log K_{\mathrm{OC/w}}$ ranging from 3−7. $K_{\mathrm{DOC/w}}$ and D_{w} were set to $0.2K_{\mathrm{OC/w}}$ and 5×10^{-6} cm^2/s, respectively. The system parameters correspond to those described in Tables S1 and S2.

With increasing $\log K_{\mathrm{OC/w}}$, the gap between $C_{\mathrm{free,pore}}$ and $C_{\mathrm{free,over}}$ is expected to decrease as the DOC serves as an increasingly effective mobile passive dosing phase, keeping $C_{\mathrm{free,over}}$ close to $C_{\mathrm{free,pore}}$. This trend agrees well with the experimental observations,[23] which show a $C_{\mathrm{free,pore}}/C_{\mathrm{free,over}}$ ratio of 9.5 for phenanthrene ($\log K_{\mathrm{OC/w}} = 4.45$), 4.1 for chlorpyrifos ($\log K_{\mathrm{OC/w}} = 4.99$), 1.6 for pyrene ($\log K_{\mathrm{OC/w}} = 5.19$), 1.5 for benzo[*a*]pyrene ($\log K_{\mathrm{OC/w}} = 6.89$) (Figure S3). In contrast, the model predicts that the ratio of $C_{\mathrm{diss,pore}}$ to $C_{\mathrm{diss,over}}$ remains relatively constant over $\log K_{\mathrm{OC/w}}$ values, which also agrees well with the experimental data (phenanthrene, 11; chlorpyrifos, 12; pyrene, 15; and benzo[*a*]pyrene, 19). For chemicals with a $\log K_{\mathrm{OC/w}} \geq 5$, a gap between $C_{\mathrm{diss,pore}}$ and $C_{\mathrm{free,pore}}$ is predicted due to the high concentration of DOC in the pore water, and this gap linearly increases with $K_{\mathrm{OC/w}}$. The $C_{\mathrm{diss,over}}/C_{\mathrm{free,over}}$ gap is only substantial with $\log K_{\mathrm{OC/w}} > 6$, reflecting the lower DOC concentration in the overlying water.

3.5. Relevance for Bioavailability, Uptake, and Toxicity. Influences of burrowing, swimming, and feeding behavior on the observed toxicity in sediment tests have been debated.[14,15,36] The model results shown in Figure 5 suggest that such influences should highly depend on the sorption properties of chemicals and the difference in DOC concentration between pore and overlying water. For example, if C_{free} controls the toxicity, there is little difference between pore and overlying water for $\log K_{\text{OC}} \geq 6$, and it does not matter whether test organisms burrow into the sediment or swim in the water. Organisms' habitat matters the most for relatively hydrophilic chemicals, e.g., for $\log K_{\text{OC}} = 3$, a $C_{\text{free,pore}}/C_{\text{free,over}}$ gap of 47 is expected. The concentration gradient at the sediment−water interface could be of particular relevance for test organisms that switch from swimming to burrowing influenced by, e.g., the sediment composition[37] and artificial light conditions.[14] Depending on the test organisms' burrowing and swimming activity, the chemical gradient at the sediment−water interface could be reduced by bioturbation as a result of increased mixing of both sediment and stagnant water,[38] which is not considered in the presented models.

The contribution of the bound fraction to the overall uptake of chemicals in sediment toxicity tests has also been a debated issue.[7,8,18,39,40] It remains to be clarified if an increase in bioaccumulation would result from accelerated uptake kinetics into the organism[41] or if uptake of DOC-bound chemicals leads to overall higher organism concentrations compared to water-only exposure. In any case, such an effect is expected to be higher for more hydrophobic chemicals that show significant binding to DOC.[42] Given the gap in DOC concentrations between pore and overlying water (an average factor of 45 at day 10 [23]), the DOC-bound fraction should be more important for endobenthic than epibenthic test organisms. In this case, the additional transport of DOC-bound chemicals needs to be accounted for in the model, whereas for hydrophilic chemicals, the w/o DOC model can also be applied. The difference between $C_{\text{diss,over}}$ and $C_{\text{free,over}}$ is expected not to exceed a factor of 2 for $K_{\text{OC}} \leq 6$ chemicals, but rapidly exceeds a factor of 10 for $K_{\text{OC}} > 7$ chemicals, suggesting that the bound fraction might be an additional uptake route of very hydrophobic chemicals for epibenthic test organisms. Notably, the relevance of DOC-mediated uptake should depend on the DOC source (here: peat moss),[43] the hydrophobicity of the chemical,[41] and the feeding behavior and living locations of the test organisms.[44]

3.6. Implications for the Application of Sediment Toxicity Tests. The model simulations indicated that the chemical exposure in semi-flow-through sediment contact tests can be variable in time ($C_{\text{free,over}}$, $C_{\text{diss,over}}$) and space ($C_{\text{free,over}}/C_{\text{free,pore}}$ and $C_{\text{diss,over}}/C_{\text{diss,pore}}$) and the degree of variability depends strongly on the sorption property of the chemical. As sediment toxicity tests involve test organisms that differ in habitat and feeding activity and are applied to evaluate the toxicity of single chemicals and mixtures with diverse chemical properties, the exposure variability in time and space demonstrated here needs increased consideration in the application of sediment toxicity tests for chemical risk assessment. The determining processes that lead to this variable exposure conditions are the competing kinetic processes of the sediment pore and UWL diffusion, outflux of chemicals due to water exchange, and temporal and spatial variability of DOC concentrations in different water zones. Based on the comparison with experimental data,[23] the interactions of these processes seem to be well depicted by the w/ DOC model presented here. Future experimental derivation of additional system and chemical parameters (Tables S1 and 2) will further increase the accuracy of such transport models and expand their applicability domain to other sediment toxicity tests.

The presented model is useful to describe and predict bioavailable concentrations in various test systems with known sediment composition and water flow rates, enabling a thorough re-evaluation of existing toxicity databases. For instance, differences in effect concentrations between laboratories/protocols or among chemical groups of different hydrophobicities could be normalized using simulated C_{free} or C_{diss}, eventually increasing the comparability between and predictive power of sediment toxicity tests as a whole. The application of the model can also help to optimize the experimental conditions of the tests to achieve stable exposure conditions and/or to close the concentration gap between pore and overlying water. The desired test conditions will depend on the test chemical, test organisms, and the exposure scenario to be tested. Possible adjustments to the test system might involve (1) the composition and physical properties of the artificial sediment (mobility of OC, overall sorption, porosity), (2) the water flow-through method and exchange rate, and (3) supplying precontaminated water for water exchange or application of a passive dosing reservoir in the overlying water. Along with such technical changes, we must debate how well sediment toxicity tests represent the exposure conditions in the environment and/or how neat is the extrapolation of sediment toxicity data to measured C_{free} and C_{diss} in the field. Under field conditions, quasi-steady-state conditions (i.e., constant C_{free} and C_{diss}) and a gap between pore and overlying water can occur especially for legacy persistent organic pollutants following a chemical gradient in the sediment and high water flow velocity, but this gap was also addressed to biodegradation in the water column,[45,46] whereas peak emissions of pesticides from agricultural fields could result in a high temporal concentration in overlying water with a low pore water concentration.[47] Under field conditions, bioaccumulation of polychlorinated biphenyls (PCBs) has been linked to the migratory behavior of fish and invertebrates leading to different exposure in pore water of the sediment with possible additional uptake of highly hydrophobic PCBs by sediment ingestion.[48] Considering these advances in field exposure research, chemical transport modeling data and evaluation of different uptake routes combined with experimental exposure assessment (e.g., by passive sampling) in sediment toxicity tests can be linked to equivalent modeling and measurement techniques in the environment, eventually contributing to bridging the gap between field and laboratory in terms of exposure and toxicity.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.1c03201.

Detailed mathematical description of the w/ DOC model; model geometry and derivation of system, DOC, and chemical parameters; brief description of the materials and methods used in ref 23; additional experimental data compared with model predictions; sensitivity analyses with the w/o DOC model; additional sensitivity analyses with the w/ DOC model; and comparison of the spatial C_{free} profile between w/o and w/ DOC models (PDF)

R code of the w/ DOC model (DOCX)

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Notes

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