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Uptake, Translocation, and Elimination in Sediment-Rooted Macrophytes: A Model-Supported Analysis of Whole Sediment Test Data

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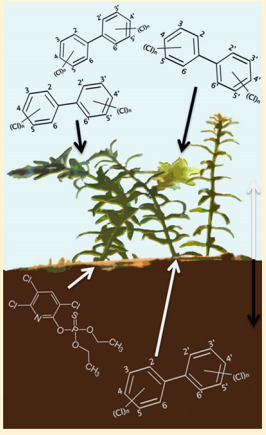
Supporting Information

ABSTRACT: Understanding bioaccumulation in sediment-rooted macrophytes is crucial for the development of sediment toxicity tests using macrophytes. Here, we explore bioaccumulation in sediment-rooted macrophytes by tracking and modeling chemical flows of chlorpyrifos, linuron, and six PCBs in water−sediment−macrophyte systems. Chemical fluxes across the interfaces between pore water, overlying water, shoots, and roots were modeled using a novel multicompartment model. The modeling yielded the first mass-transfer parameter set reported for bioaccumulation by sediment-rooted macrophytes, with satisfactory narrow confidence limits for more than half of the estimated parameters. Exposure via the water column led to rapid uptake by *Elodea canadensis* and *Myriophyllum spicatum* shoots, followed by transport to the roots within 1−3 days, after which tissue concentrations gradually declined. Translocation played an important role in the exchange between shoots and roots. Exposure via spiked sediment led to gradual uptake by the roots, but subsequent transport to the shoots and overlying water remained limited for the chemicals studied. These contrasting patterns show that exposure is sensitive to test set up, chemical properties, and species traits. Although field-concentrations in water and sediment will differ from those in the tests, the model parameters can be assumed applicable for modeling exposure to macrophytes in the field.



INTRODUCTION

Macrophytes play a key role in the ecological functioning of aquatic ecosystems[1] and form an important pathway for redistribution of organic chemicals among plant material, water column,[2] and the food web and, therefore, should be considered in environmental risk assessment. Historically, most ecotoxicological plant research concerned terrestrial and emergent plants and focused on agricultural crops or phytoremediation. Submerged macrophytes, however, cannot be compared with terrestrial and emergent plants as they lack transport processes driven by transpiration.[3] For submerged macrophytes, research has been limited to uptake and elimination kinetics from the overlying water (e.g., refs 4−10), lacking the presence of a sediment phase. Absence of sediment in toxicity tests for sediment-rooted macrophytes is not ecologically realistic. Recently, the importance of developing whole sediment toxicity tests for sediment-rooted macrophytes has been recognized.[11,12] For instance, the Aquatic Macrophyte Risk Assessment for Pesticides (AMRAP) workshop identified a lack of knowledge regarding the relative importance of sediment exposure for uptake of toxicants by rooted macrophytes.[12] To date, uptake of organic chemicals in sediment-inclusive test systems has been described only for *Hydrilla verticillata* with three insecticides,[13] for *Myriophyllum spicatum* with one herbicide,[14] and *Myriophyllum elatinoides* for a metabolite of pyrethroids.[15] The last two studies also considered elimination to the water column.

Aquatic macrophytes may accumulate, translocate, and eliminate organic chemicals by roots, shoots, or both (Table S1, Supporting Information), thereby enhancing or decreasing chemical bioavailability in a complex manner.[2,16,17] The importance of exposure from sediment, water, or air depends on macrophyte traits such as growth form, e.g., free floating, emerged, or submerged. In prospective risk assessment, *Lemna* is the standard freshwater test species. *Lemna* is, however, a free-floating, nonsediment-rooted macrophyte that might not represent other growth forms like sediment-rooted macrophytes, especially if the chemical test concerns sediment-bound chemicals.[12,18] For sediment-bound chemicals, tests with sediment-rooted macrophyte species, such as the dicot *M. spicatum*, are recommended to account for different exposure routes.[12] As monocot or dicot species might differ in their uptake and elimination traits and sensitivity, it is recommended to use both types (e.g., *M. spicatum* and *Elodea canadensis*) in the risk assessment.[12] In addition to macrophyte traits, chemical

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Table 1. Chemical Characteristics

chemical	log K_{OW} [a]	solubility at 25 °C [c] (mol/L)	K_{OC} [f] (L/kg)	$K_{P,SED}$ [h] (m^3/kg)	K_{POM} [i] (L/kg)
Linuron	3.00 [b]	2.56×10^{-4} [d,e]	406 [g]	8.12×10^{-3}	269 [j]
Chlorpyrifos	4.66 [b]	2.99×10^{-6} [d,e]	8151 [d]	1.63×10^{-1}	12782 [j]
PCB 2	4.60	2.54×10^{-5}	15136	3.03×10^{-1}	45352
PCB 3	4.60	7.13×10^{-6}	15136	3.03×10^{-1}	45352
PCB 28	5.58	6.12×10^{-7}	143582	2.87×10^{0}	268835
PCB 29	5.58	3.50×10^{-7}	143582	2.87×10^{0}	268835
PCB 149	6.66	1.18×10^{-8}	1737801	3.48×10^{1}	1932235
PCB 155	6.50	7.45×10^{-9}	1202264	2.40×10^{1}	1443777

[a]van Noort et al.[50] [b]Tomlin.[51] [c]Paasivitra and Sinkkonen.[52] [d]The pesticide properties database.[37] [e]Solubility was measured at 20 °C. [f]Seth et al.[33] [g]Burešová et al.[14] [h]$K_{P,SED}$ was as calculated with K_{OC} values and an organic carbon fraction of 0.02. [i]Hawthorne et al.[53] [j]Endo et al.[54]

properties influence uptake, translocation, accumulation, and elimination of organic compounds.[7,19−21] This implies that studies on chemical bioavailability and exposure should account for a range of chemical properties.

Bioaccumulation models are very useful to generalize bioaccumulation data. However, we are not aware of modeling studies with sediment-rooted macrophytes that consider chemical exchange across all relevant compartments such as pore water, overlying water, sediment, macrophyte shoots, and roots while also accounting for translocation.

The aim of the present study was to assess the relative importance and characteristic time scales of uptake, translocation, and elimination pathways of organic chemicals in sediment-rooted, submerged aquatic macrophytes, in order to assist the development of whole sediment toxicity tests in the context of prospective risk assessment. The second aim was to assess the parameters that describe bioaccumulation in macrophytes, which also is relevant for modeling these processes in the field.

To achieve these aims, laboratory experiments were performed in which concentrations in sediment, overlying water, shoots, and roots were measured as a function of time for two freshwater sediment-rooted macrophytes; *E. canadensis* and *M. spicatum*, representing different macrophyte anatomy and physiology. Test chemicals included six polychlorinated biphenyls (PCBs) and the insecticide chlorpyrifos (CPF). Our previously published data on the herbicide linuron (LIN)[14] were included in the modeling. The experimental design included spiking of six PCBs in three couples that were practically identical based on hydrophobicity. Per couple, one PCB was spiked in the overlying water phase and the other PCB in the sediment phase. CPF was also spiked in the sediment phase. Experimental data were used to parametrize a multicompartment sediment bioaccumulation model that describes the chemical flows in the test systems.

MATERIALS AND METHODS

Chemicals and Materials. Experimental test chemicals were PCB couples 2 and 3, 28 and 29, 149 and 155, and CPF. LIN data were obtained from our previous study.[14] Further details are provided as Supporting Information.

Sediment and Test Medium. Sediment was prepared following OECD 218,[22] with a small modification described in ISO 16191.[23] Peat (5%), calcium carbonate powder (2%), and an aqueous nutrient medium of 0.36 and 0.30 g N/L were mixed to obtain a homogeneous slurry. The slurry was spiked with PCBs and CPF and thoroughly mixed with quartz sand (75%) and kaolin clay (18%). Barko and Smart medium[24] was used as the overlying water phase. Further details and sediment characteristics are provided as Supporting Information (Table S2).

Spiking Procedure. Overlying water was spiked with PCBs 2, 28, and 149, whereas the sediment was spiked with almost identical PCBs 3, 29, 155, and CPF (see Table 1 for chemical characteristics). PCB pairs (2 and 3; 28 and 29; 149 and155) were selected on the basis of their very similar K_{ow} values (Table 1), whereas the pairs represented a range of log K_{ow} between 4.63 and 6.67. Furthermore, log K_{ow} of CPF matches with PCBs 2 and 3. This setup allows for a direct comparison of chemical flows from water versus sediment as source compartments in the test systems. CPF was chosen to see potential differences between a pesticide and PCBs, e.g., with respect to uptake, degradation, and metabolism.

Spiking of Sediment. Sediment was spiked with PCBs 3, 29, 155, and CPF in acetone to reach target concentrations of 20 μg/kg dry weight (DW) for these PCBs and 40 μg/kg for the more degradable CPF. After spiking, pre-equilibration was 4 weeks for PCBs and 2 weeks for CPF. Polyoxymethylene (POM) passive samplers[25] were added to the sediment in order to acquire in situ pore water concentrations at the start of exposure.

Spiking of Overlying Water. Under gentle stirring, the overlying water of each test system was spiked with a solution of PCB 2, 28, and 149 in acetone in three portions of 25 μL to reach target concentrations of 10000 μg/m^3 for PCB 2 and 28 and 1000 μg/m^3 for PCB 149. These initial concentrations were at least 75% below the aqueous solubility of the compounds. Further details on spiking are provided as Supporting Information.

Macrophytes. *Myriophyllum spicatum* (Linnaeus 1753) (Eurasian water milfoil, dicotyledonous) and *Elodea canadensis* (Michx) (water pest, monocotyledonous) (Table S3, Supporting Information), were collected from uncontaminated ditches at the experimental station at The Sinderhoeve in Renkum, The Netherlands. A random selection of pregrown healthy macrophytes of similar size was used for the experiment. A subsample of 10 individuals per species was used for chemical analyses of background concentrations. Ten individuals were used for the determination of lipid content,[26] which was expressed as a percentage based on wet weight. Lengths of main and side shoots, number of side shoots and roots, wet and dry weight of roots and shoots, and concentrations in shoots and roots were determined at the start and at the end of the experiment (further method details provided as Supporting Information).

Macrophyte Bioaccumulation Test. The experiment followed the test protocol accepted by OECD for *Myriophyllum spicatum*[27] with modifications regarding sediment layering and spiking (see the Supporting Information for details). The 28-day test was conducted in a climate room at 18 °C under white fluorescent light with an average (standard deviation (SD)) light intensity of 156 (16) μE m^{-2} s^{-1} and a photoperiod of 16 h light/

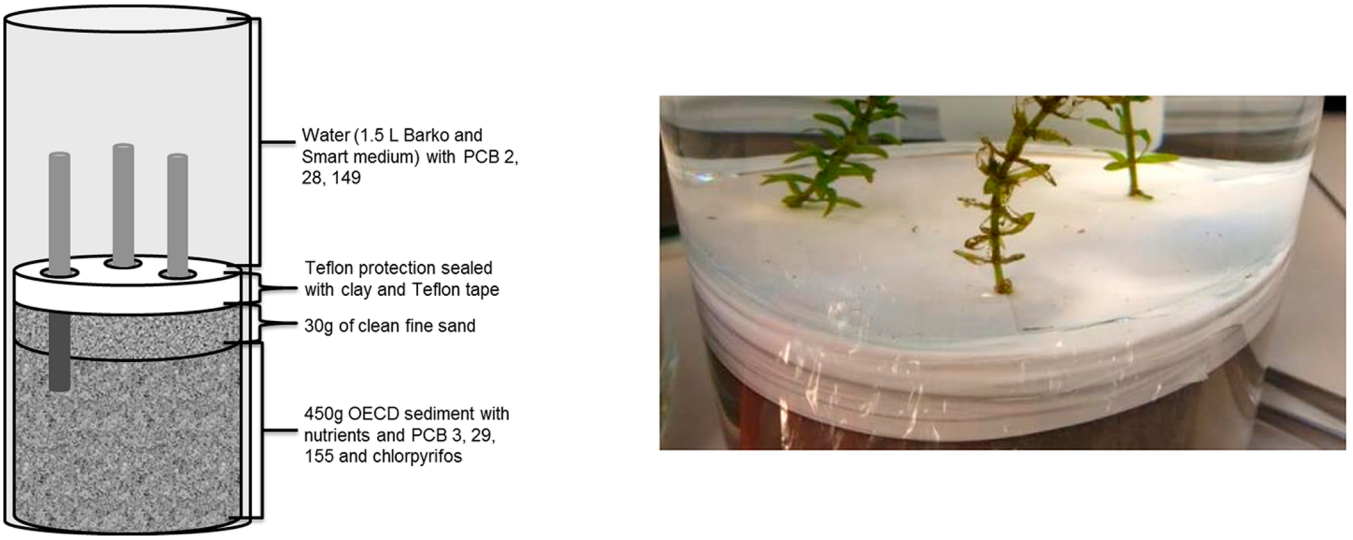

Figure 1. Test set up showing the Teflon impermeable layer to prevent direct sediment−water exchange.

8 h dark. Tested treatments were (A) a "capped" system, i.e., with a polytetrafluoroethylene (Teflon) impermeable layer at the sediment−water interface modified from Hinman and Klaine[13] and with the macrophyte stem penetrating the Teflon layer, and (B) an "open" system, i.e., without impermeable layer (Figure 1 and Figure S2, Supporting Information). The Teflon cap in treatment A separated the sediment from the overlying water to specifically detect translocation by the macrophytes. Treatment B represented conditions in a standard toxicity test set up and accounted for all naturally occurring pathways. Nonspiked control treatments were (n = 3) capped without acetone, open without acetone, open with acetone (to detect acetone spike effects), and Teflon layer cap penetrated by a stainless steel rod instead of the macrophytes stems to check on leakage through the barrier (details provided as Supporting Information). After 1, 3, 7, 14, and 28 d, three pots per treatment were sacrificed for chemical analysis. Chlorophyll, dissolved oxygen (DO) concentrations, pH, and temperature were recorded weekly (see the Supporting Information for details).

Extraction and Analyses. For details on extraction, detection, and quality assurance, the reader is referred to the Supporting Information (Tables S4−S6). In short, overlying water samples were hexane extracted, macrophyte samples were acetone extracted, and sediment samples were extracted with accelerated solvent extraction (ASE). POM samplers were Soxhlet extracted. Extracts were analyzed on a gas chromatograph with a μ-electron capture detector. Data were corrected for blanks. Analytical recoveries for macrophyte samples ranged between 75.6% and 101.8%, and for sediment between 77.3% and 96.6%.

Data Analyses. Root and shoot relative growth and chemical concentrations were calculated on the basis of DW. Relative growth rate data were checked for normality with Q−Q plots and for equality of variances with Levene's test and tested with an ANOVA with a significant level α = 0.05 using IBM SPSS Statistics version 19.

Sediment−water partition coefficients ($K_{P,SED}$) were calculated as the ratio of DW-based concentration in sediment (C_{SED}) and POM-based concentration in pore water (C_{PW}), after preequilibration. Macrophyte−water partition coefficients (m^3/kg) after 28 days of bioaccumulation were calculated for shoots (K_S = C_S/C_{OW}) and roots (K_R = C_R/C_{PW}) based on concentration in shoots (C_S), roots (C_R), overlying water (C_{OW}), and pore water (C_{PW}), and biota sediment accumulation factors (BSAF; −) were calculated as BSAF = C_R/C_{SED}.

Modeling Chemical Flows in Sediment Systems with Rooted Macrophytes. *Model Definition.* Following first-order mass balance modeling concepts,[28,29] a model was developed that accounts for mass transfer across overlying water, shoot, root, and sediment interfaces and translocation (Figure 2 and

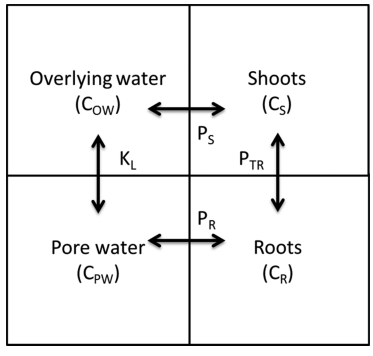

Figure 2. Schematic model description for uptake, translocation, and elimination in a sediment, water, and submerged macrophyte system with C_{OW}, the concentration in overlying water, C_S, the concentration in shoots, C_R, the concentration in roots, C_{PW}, the concentration in pore water, K_L, the benthic boundary layer mass transfer coefficient, P_S, the shoot chemical permeability coefficient, P_{TR}, the translocation mass transfer coefficient, and P_R, the root chemical permeability coefficient.

Table S7, Supporting Information). The concentration in overlying water (C_{OW}; μg/m^3) as a function of time (t) can be described by transport between overlying water and pore water, between overlying water and shoots, and by a lumped first-order loss (volatilization, degradation, photolysis) rate constant (k_{LOSS}; d^{-1})

$$\frac{dC_{OW}}{dt} = \frac{K_L A_{SED}}{V_{OW}}(C_{PW} - C_{OW}) + \frac{P_S A_{S,T}}{V_{OW}}\left(\frac{C_S}{K_S} - C_{OW}\right) - k_{LOSS}C_{OW} \quad (1)$$

with K_L (m/d) as the benthic boundary layer (BBL) mass transfer coefficient, A_{SED} (m^2) the sediment−water interface surface, V_{OW} (m^3) the volume of overlying water, P_S (m/d) the

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shoot chemical permeability coefficient, $A_{S,t}$ (m^2) the shoot surface in overlying water, C_{pw} ($\mu g/m^3$) the concentration in pore water, C_S ($\mu g/kg$) the concentration in shoots, and K_S (m^3/kg) the shoot−water partition coefficient. Time-dependent parameters carry subscript '*t*' and are calculated with auxiliary functions (see below).

The concentration in pore water can be described by transport between overlying water and pore water and pore water and roots

$$\frac{dC_{PW}}{dt} = \frac{K_L A_{SED}}{V_{PW}}(C_{OW} - C_{PW}) + \frac{P_R A_{R,t}}{V_{PW}}\left(\frac{C_R}{K_R} - C_{PW}\right) \quad (2)$$

with P_R (m/d) root chemical permeability coefficient, $A_{R,t}$ (m^2) root surface, V_{PW} (m^3) *apparent* pore water volume,[28−30] and K_R (m^3/kg) root−water partition coefficient. The apparent pore water volume is defined as

$$V_{PW} = V'_{PW} + K_{P,SED} M_{SEd} \quad (3)$$

with V'_{PW} (m^3) sediment interstitial pore water volume, $K_{P,SED}$ (m^3/kg) sediment−water partition coefficient (Table 1), and M_{SED} (kg DW) sediment mass.

The concentration in shoots can be described by transport between overlying water and shoots and transport between shoots and roots (translocation)

$$\frac{dC_S}{dt} = \frac{P_S A_{S,t}}{M_{S,t}}\left(C_{OW} - \frac{C_S}{K_S}\right) + \frac{P_{TR} A_{TR,t}}{M_{S,t}}\left(\frac{C_R}{K_R} - \frac{C_S}{K_S}\right) \quad (4)$$

with P_{TR} (m/d) translocation mass transfer coefficient, $A_{TR,t}$ (m^2) time-dependent stem cross-sectional area, and $M_{S,t}$ (kg DW) mass of shoots.

The concentration in roots (C_R; $\mu g/kg$) can be described by transport between pore water and roots and transport between shoots and roots:

$$\frac{dC_R}{dt} = \frac{P_R A_{R,t}}{M_{R,t}}\left(C_{PW} - \frac{C_R}{K_R}\right) + \frac{P_{TR} A_{TR}}{M_{R,t}}\left(\frac{C_S}{K_S} - \frac{C_R}{K_R}\right) \quad (5)$$

The time-dependent masses $M_{R,t}$ and $M_{S,t}$ were modeled assuming first-order growth with rate constants (d^{-1}) for root ($k_{G,R}$) or shoot ($k_{G,S}$), calculated from measured data. Growth made a relevant contribution to modeling uptake as neglecting it resulted in different modeled concentrations, e.g., about 30% in macrophytes for PCB 28 (pilot simulations not shown). Surface areas $A_{R,t}$ and $A_{S,t}$ were calculated as the product of these masses ($M_{R,t}$ and $M_{S,t}$) and the specific surface areas 25 m^2/kg for *E. canadensis* and 40 m^2/kg for *M. spicatum*.[31] Stem cross-sectional area (A_{TR}) was calculated from measured stem biomass and length over time, assuming a cylindrical shape and constant density of the stem. Equations for these calculations are provided as Supporting Information.

Parameter Estimation. The above model equations were implemented in Mathematica 8.0 (Wolfram Research). Parameters for PCBs and CPF were estimated accounting for experiment-specific boundary conditions. Additional optimizations were done with data from the open and capped systems combined. For LIN, data from five exposure concentrations[14] were combined. As many parameters as possible were set at independently measured or estimated values (e.g., K_S and K_R). If a value was not available for a PCB, the value of the partner PCB within the chemically identical congener pair was used. This assumes that PCBs with (practically) identical log K_{ow} have identical K_S or K_R within error limits. This assumption is supported by earlier evidence for bioconcentration of hydrophobic organic chemicals to macrophytes being driven by hydrophobic partitioning into lipids.[32] For LIN, a value for K_S was calculated from earlier data.[14] The LIN K_R value was estimated using a significant regression between log K_R and log K_{OC}[33] ($\log K_R = (0.892 \pm 0.118) \log K_{OC} - (0.372 \pm 0.239)$ ($R^2 = 0.80$) (Figure 3), constructed with K_R values for CPF, PCB 3, 29, and 155 measured for *E. canadensis* and *M. spicatum*. For

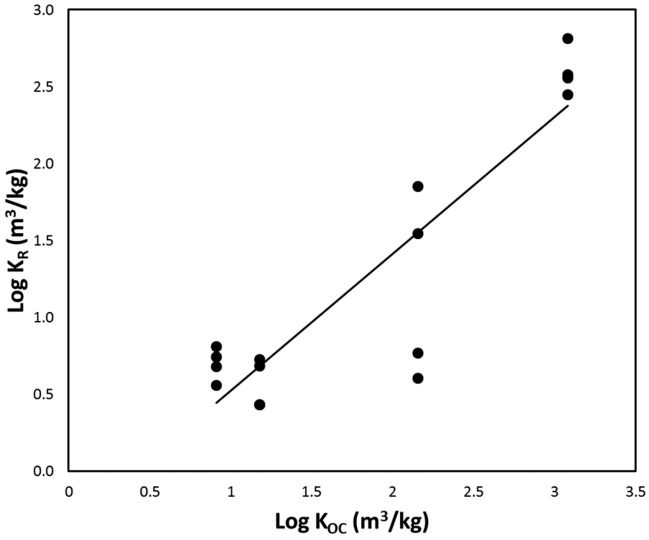

Figure 3. Relation between the root−water partition coefficient (K_R; m^3/kg) and organic carbon−water partition coefficient (K_{OC}; m^3/kg). Regression line: $\log K_R = (0.892 \pm 0.118) \log K_{OC} - (0.372 \pm 0.239)$ (R^2=0.80).

PCBs and CPF in capped systems, K_L was set to 0 because mass transfer across the cap was negligible. For open systems, K_L was set to the established literature value of 0.025 m/d, which was assessed in similar systems.[30] The previously published LIN systems[14] used a sand bed as a layer of limited permeability. The mass-transfer coefficient in this layer was estimated to be 2.38×10^{-4} m/d based on an in-bed and BBL dual mass transfer resistance model, which is detailed in the Supporting Information (Table S8). Because LIN mass transfer across the sand bed was very limited, uncertainty in this parameter was of marginal importance. Initial pore water and overlying water concentrations were based on measured concentrations. Remaining parameters were optimized, i.e., shoot and root permeability coefficients (P_S and P_R) and translocation mass transfer coefficient (P_{TR}). For volatile PCBs 2 and 3, also the loss rate constant (k_{LOSS}) was optimized. Model input parameters are summarized in Table S9 (Supporting Information). Equations 2−5 were solved with the Mathematica function NDSolve. Goodness-of-fit of the model was calculated using Pearson's Chi^2 statistic. Confidence intervals of 90% (α = 0.90) for the parameters were calculated using the likelihood-profiling method as described previously.[34] Confidence limits wider than 2 orders of magnitude were not reported. For further details, the reader is referred to the Supporting Information.

RESULTS AND DISCUSSION

General Evaluation and Features of the Test. *Macrophyte Performance.* During the test, a good water quality was attained with an average (SD) water temperature of 21.5 (1.7) °C, pH 9.14 (0.86), 13.01 (3.44) mg/L dissolved oxygen, and conductivity 396 (98) μS/m for all treatments (Table S10, Supporting Information). For the control treatments, coefficients of variation for measured total length and weight were below 35% and in most cases below 25% at day 28 (Table S11, Supporting Information), which meets the validity requirements for macrophyte tests.[27,35] Macrophytes grew better in open systems then in capped systems, although for *M. spicatum* differences were small and within the range of experimental variation and published values.[36] In open systems, measured macrophyte endpoints total length and biomass met the requirement of a doubling within a period of 14 days.[27] For *E. canadensis*, measured (ANOVA $p = 0.003$ for specific growth rate for total length) and modeled specific growth rates were higher in open systems compared to capped systems (Table S12, Supporting Information). Main stem growth for *E. canadensis* was less than the growth in total length, which can be explained by its growth strategy that is to invest more in side shoots. Moreover, development of water roots might have hampered root development in the capped systems, where roots could not penetrate into the sediment. For *M. spicatum*, the specific growth rates were similar between capped and open systems.

Average (SD) lipid content was 2.1 (0.54)% for *E. canadensis* and 0.2 (0.09)% for *M. spicatum* at the start of the experiment. The value for *M. spicatum* is very similar to the 0.2 (0.02)% reported by Gobas et al.[7]

Efficiency of the Impermeable Layer. In the capped control treatment, none of the PCBs spiked in the overlying water layer were found in the sediment after 28 days. For PCBs and CPF spiked in the sediment layer, average concentrations in overlying water were below detection limit. Based on these data, we conclude that the Teflon cap was practically impermeable during the test.

Spiking Losses and Mass Balance. Concentrations in overlying water measured 20 min after spiking ranged between 27% (PCB 2) and 62% (PCB 28) of nominal concentrations. Concentrations in sediment measured after 28d pre-equilibration ranged from 66% (PCB 3) to 95% (PCB 155) of nominal concentrations at $t = 0$ (Table S6, Supporting Information). Thus, in both compartments the more volatile PCBs deviated more from the nominal concentration, suggesting volatilization losses for these PCBs, as expected. Total mass for chemicals spiked in overlying water decreased rapidly and was between 24% and 0% of initial mass after 28 d. Total mass for chemicals spiked in sediment was stable for the first 14 d, after which the mass started to decrease slightly. CPF losses were highest, which is in accordance with the shorter half-life of CPF, observed earlier in sediment water systems.[37] Other than volatilization, loss of chemicals might also be due to chemical or biological degradation e.g. metabolism by macrophytes or microorganisms. Not much is known, however, about sequestering and transformation of hydrophobic chemicals in macrophytes. These processes are often assumed to be of minor importance compared to loss of chemicals in the sediment−water compartments, e.g., due to macrophyte-induced pH changes or to dissolved organic carbon (DOC) exudates absorbing the chemicals.[7,32,38] Moreover, chemical uptake by the Teflon layer (<0.4%) and algae (<0.1%) showed a negligible contribution in the mass balance (calculations not shown). It must be noted that conservation of mass was not aimed for in these systems that were designed to mimic actual open systems as used in toxicity tests with macrophytes. For details on measured concentrations, see Tables S13−S18 and for details on mass balances, see Tables S19−S22 (Supporting Information).

Bioconcentration Factors. Measured K_S and K_R values (Table S23, Supporting Information) were in general higher for PCBs with a higher hydrophobicity. This pattern for root partitioning was in agreement with literature.[19,39,40] Shoot partitioning, however, differs from the typical patterns for terrestrial and emerged plants[5,39−41] and the theory stating that uptake and translocation diminishes with increasing *K*ow.[42] For more hydrophobic PCBs, K_R values were much higher than K_S, reflecting differences in shoot and root tissue composition. BSAFs range between 0.6 and 2.9 for *E. canadensis* (Table S23, Supporting Information) after lipid and OM normalization, which agrees well to values between 1.35 and 3.05 reported for *Elodea nuttallii* after 4 months of equilibration,[2] and which is also close to the range of 1−2 suggested by equilibrium partitioning theory.[43]

Chemical Flows in Sediment−Water Macrophyte Test Systems. In general, similar exposure patterns over time were observed for *E. canadensis* and *M. spicatum* in capped and open systems for both water and sediment spiked chemicals (Figure 4 and Figure S2, Supporting Information). Below, we discuss water and sediment spiked chemicals separately.

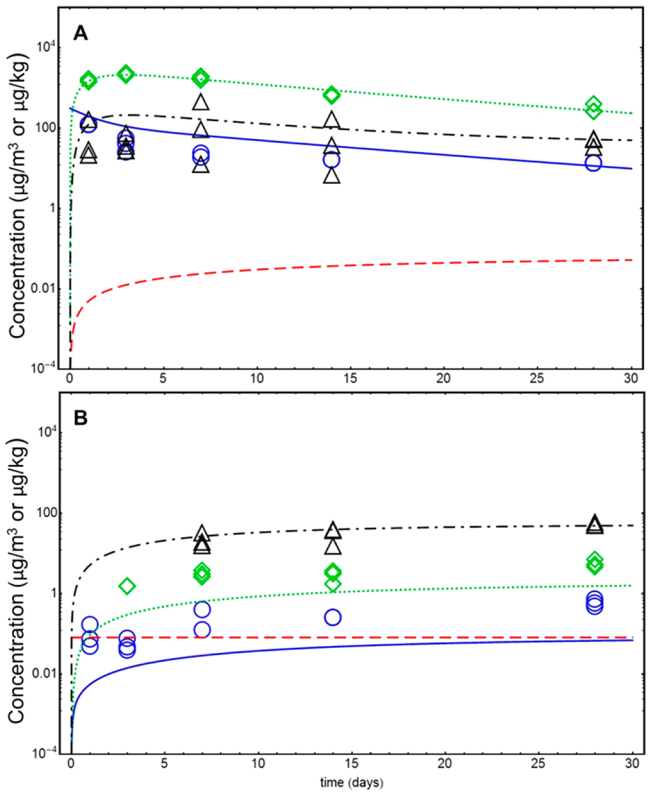

Figure 4. Measured (symbols) and modeled (curves) concentrations in overlying water (blue circles, ○, solid line; μg/m³), pore water (red dashed line; μg/m³), shoots (green diamonds, ◇, dotted line; μg/kg), and roots (black triangles, Δ, dash dot line; μg/kg) for water-spiked PCB 149 (A) and sediment-spiked PCB 155 (B) for *Elodea canadensis* in open systems.

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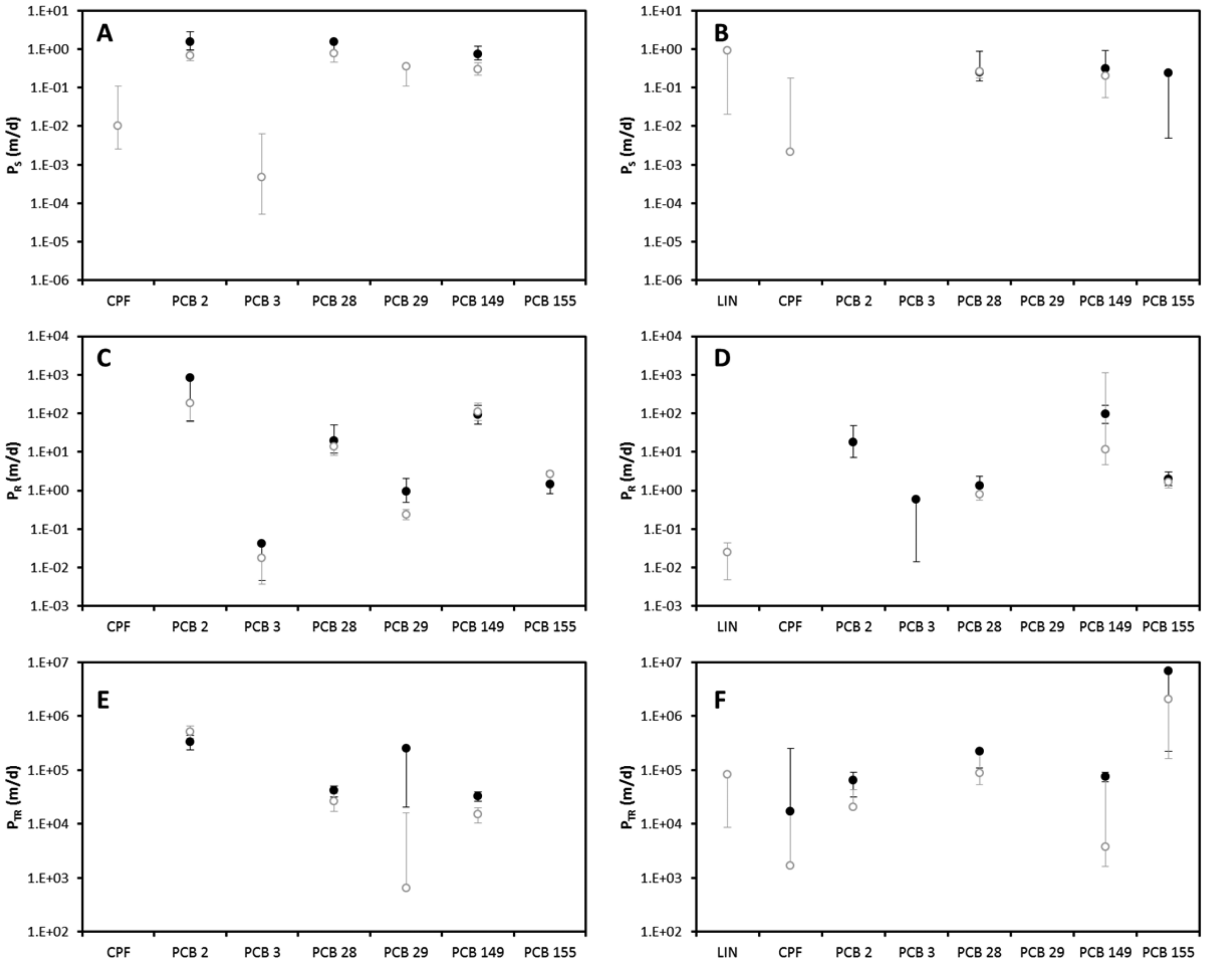

Figure 5. Optimized model parameters and 90% confidence limits for shoot chemical permeability coefficient (P_S m/d) (A, B), root chemical permeability coefficient (P_R; m/d) (C, D), and translocation mass transfer coefficient (P_{TR}; m/d) (E, F) for capped system (black circles, ●) and open systems (gray open circles, ○), *Elodea canadensis* (A, C, E), and *Myriophyllum spicatum* (B, D, F). LIN, CPF, PCB 3, PCB 29, and PCB 155 are sediment spiked. PCB 2, PCB 28, and PCB 149 are water spiked. Parameter values are only included if a 90% confidence limit could be assessed in at least one direction.

Water-Spiked PCBs. In the first 3 days, concentrations of PCBs 2, 28, and 149 in overlying water decreased rapidly whereas concentration in shoots and roots rapidly increased (Figure 4A and Figure S2 and Tables S13, S14, S17, and S18, Supporting Information). After a maximum was reached, concentrations in water, shoots, and roots gradually decreased, a decrease that was less for more hydrophobic PCBs. Concentrations in overlying water decreased more rapidly during the first day in capped systems than in open systems. Although we cannot provide a conclusive explanation, this might be caused by higher DOC concentrations being present in open systems, leading to a higher concentrations of DOC-associated PCBs in the water layer. No steady state was reached within 28 days, although water and shoot concentrations had a constant ratio after 7−14 days, confirming that equilibrium had been reached.

Sediment-Spiked PCBs, CPF, and LIN. Concentrations of PCBs 3, 29, 155, and CPF in sediment decreased slightly, whereas the concentration in the roots increased rapidly during the first days and then increased slowly during the remaining days of exposure (Figure 4B and Figure S2 and Tables S15 and S18, Supporting Information). Chemicals in shoots were detected mainly in open systems compared to only a few cases in capped systems. Concentrations in overlying water were a factor of 10−100× higher for open systems than in capped systems. CPF concentrations in overlying water were 10−100× higher than PCB concentrations, and PCB 3 concentrations were slightly higher than PCB 29 and 155 concentrations (Figure 4B and Figure S2). Both observations can be explained by the lower hydrophobicity and higher solubility of CPF and PCB 3. For capped systems, chemical concentrations in overlying water increased earlier in time than in shoots, or even when no chemicals were detected in the shoots at all. This could be caused by some incidental leakage through the impermeable layer, although the control showed that the layer worked well. Another explanation could be that translocation was initially high and decreased over time while elimination to overlying water occurred very fast, decreasing concentrations in shoots below the limit of detection. In previous experiments in our lab where OECD sediment was spiked with LIN, similar patterns were observed:[14] an initial rapid increase of LIN in roots and shoots of *M. spicatum* during the first week, after which an equilibrium was reached. Steady state was reached only in open systems on day 28, where the overlying water concentrations appeared to approach pore water concentrations.

Modeling Flows between Water, Macrophytes, And Sediment. The multicompartment model provided good fits to the observed data for most chemicals (Figure 4 and Figure S2). More nondetects occurred in sediment-spiked systems than in

water spiked systems, which affected the number of data available for parameter estimation and therefore affected the precision of parameter values and confidence limits (Figure 5 and Table S24, Supporting Information). For PCB 3, the number of meaningful confidence limits was lowest, which is explained from the low number of data. Although chemical concentrations in roots were unavailable for LIN, parameter estimates were quite accurate because multiple experimental data sets were combined in the optimization.

To our knowledge, the modeling yielded the first mass transfer parameter set reported for bioaccumulation in macrophytes in sediment-water systems (Figure 5 and Table S24, Supporting Information). For more than half of the estimated parameters, satisfactory narrow confidence limits were found (Figure 5), which allow for further interpretation. Overall, the chemical permeability coefficients seem to vary across macrophyte species and chemicals (Figure 5 and Table S24, Supporting Information), yet seem to be similar for capped and open systems. This confirms that the process descriptions (eqs 1−5) and parametrizations are valid in both capped and open systems and that parameter estimation can also be done with combined capped and open system data (Table S25, Supporting Information). The latter combined estimations yielded similar parameter values and ranges as the separate sets, albeit that the number of estimated confidence limits was slightly higher, at the cost of losing experiment-specific (i.e., capped vs open systems) information. Therefore, the separate parameter sets are discussed here.

Shoot chemical permeability coefficients (P_S) were fairly similar across species and chemicals (Figure 5), implying that the resistance of cell walls in the shoots does not substantially change with hydrophobicity.[19] The root chemical permeability coefficients (P_R) were in general higher than shoot chemical permeability coefficients, which imply that root permeation is easier than shoot permeation (Figure 5). P_R values for water-spiked chemicals were higher than the sediment spiked chemicals especially for *E. canadensis*. It can be hypothesized that this overall slower permeation of chemicals from the sediment phase can be explained from a fraction of total chemical concentration being bound to DOC, which therefore is less bioavailable. P_R value for LIN was lower compared to the other chemicals, possibly due to the lower log K_{OW} that might cause LIN to be transported more easily by the water stream into the roots.

Translocation might occur from roots to shoots when the chemical passes the endodermis[41] and enters the xylem and from shoots to roots when the chemical passes the cuticle and enters the phloem. Translocation coefficients (P_{TR}) were much higher than P_S and P_R (Table S24, Supporting Information). Note, however, that the translocation values were calculated relative to stem cross sectional area, which was very small, yielding a much smaller difference when fluxes are compared (discussed below). Furthermore, we hypothesize that the higher values might reflect the result of water flows in the stem including some DOC facilitated transport of hydrophobic test chemicals.[29,44] It is expected that transport trough the phloem and xylem depends on solubility and hydrophobicity, thus both a soluble and a hydrophobic chemical might have a high translocation potential by either water or DOC. For *M. spicatum,* this trend of increasing translocation coefficients with increasing logK_{OW} was observed whereas for *E. canadensis* a slightly decreasing trend was observed. CPF is expected to quickly cross biomembranes but then might sorb to lipid membranes of the inner root tissue,[45] while translocation of CPF to shoot biomass is low.[41] Our results for CPF did not show different P_{TR} values compared to those for PCBs with similar logK_{OW}. Also P_{TR} for LIN was similar to other chemicals (Figure 5). In capped sediment spiked systems, concentrations in shoots did not align with model predictions as most values were below detection limits except for the first few days for *M. spicatum*. High translocation values might account for the overestimation.

Relative Importance of Transport Pathways in Whole-Sediment Test Systems with Sediment-Rooted Macrophytes. Knowledge on the chemical transport and exposure pathways is important for the development and interpretation of sediment-rooted macrophyte tests such as proposed by the OECD.[27] Therefore, chemical transport fluxes (μg/d) were calculated across the interfaces between the four compartments: sediment, overlying water, shoots, and roots (eqs S13−S16) using the parameters from Table S24, Supporting Information.

In general, initial fluxes are high and directed toward the compartments with lower fugacity as the system strives for equilibrium (Figure 6 and Figures S3 and S4, Supporting Information). After this initial phase, fluxes decrease and might even change direction, for instance like for water to shoot exchange of PCB 149 in the water spiked systems (Figure S3, panels 26−29, Supporting Information). In the capped systems, macrophytes can take up, translocate, and eliminate organic chemicals both from overlying water to pore water and vice versa via roots and shoots (Figures S3 and S4, Supporting Information). This confirms that macrophytes can act as a chemical pump and thus can contribute to the redistribution of chemicals in aquatic ecosystems as was proposed earlier by Roessink et al.[2] However, the relative importance of this pathway depends on the role of direct BBL transfer, which can only be

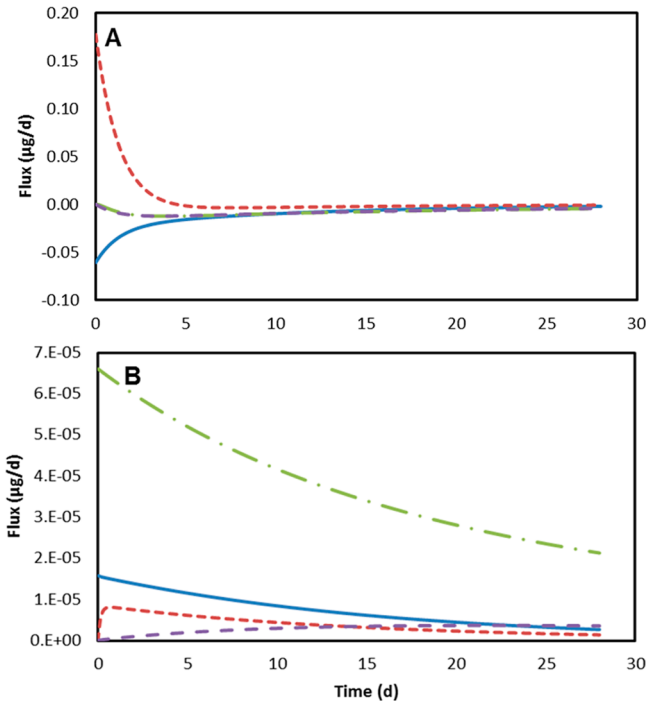

Figure 6. Chemical fluxes (μg/d) from pore water to overlying water (blue solid line), from overlying water to shoots (red dotted line), from pore water to roots (green dash dot line), and from roots to shoots (purple dash line) for water-spiked PCB 149 (A) and sediment-spiked PCB 155 (B) for *Elodea canadensis* in open systems. Note the differences in scale on the *y*-axes.

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assessed by analyzing the open systems. Therefore, below, we mainly discuss the open systems, as these are most relevant for test development and field situations.

Water-Spiked PCBs in Open Systems. Water-spiked systems seem to approach a state with low fluxes faster than sediment spiked systems (Figure 6A and Figure S3, Supporting Information). The major pathway was from overlying water to shoots, then from shoots to roots and then from roots to pore water. For PCB 2, translocation was more important than direct transport from overlying water to pore water (Figure S3, panels 10−13, Supporting Information). With increasing hydrophobicity, the flux from overlying water to pore water became more important. For PCB 149 (Figure 6A), the flux across the BBL dominated the translocation flux at start and became less important over time.

Sediment-Spiked PCBs, CPF, and LIN in Open Systems. Patterns for sediment-spiked chemicals were less clear than for water-spiked chemicals, probably due to the lower confidence of the parameters. For LIN, the increased concentrations in the shoots were explained from translocation by the roots as concentrations of LIN in overlying water were 1000 times lower than those in pore water.[14] The fluxes calculated for LIN (Figure S3, panels 1−5, Supporting Information) support this interpretation. At the start, both pathways from pore water to overlying water and from pore water to roots played an important role. Later, the contribution of the flux from pore water to overlying water decreased while at the same time translocation fluxes from roots to shoots increased followed by a flux of LIN from shoots to overlying water. For CPF and *E. canadensis* (Figure S3, panels 6 and 7, Supporting Information), there was an initial flux from overlying water to pore water, which after 9 days switched from pore water to overlying water due to the initial CPF concentration in overlying water. Uptake in the macrophyte was from pore water to roots and overlying water to shoots. Translocation and elimination did not occur. For CPF for *M. spicatum* and PCB 3 (Figure S3, panels 8, 9, and 14−17, Supporting Information), the flux from pore water to overlying water was higher than the translocation flux for *E. canadensis* whereas for *M. spicatum* these two fluxes were similar. In all cases, except for PCB 3 accumulating in *M. spicatum*, the flux was directed from overlying water to shoots. For PCB 29 accumulating in *E. canadensis*, the BBL flux dominated over the translocation flux (Figure S3, panel 23, Supporting Information) and uptake was by shoots from overlying water and by roots from pore water. For *M. spicatum*, chemical fluxes were difficult to interpret although it appeared that the BBL and the translocation fluxes were similar. For PCB 155 accumulating in *E. canadensis*, the BBL flux dominated the translocation flux at start while later the dominance switched whereas for *M. spicatum* translocation dominated the BBL flux during the entire 28 d test period. In general, the BBL flux dominated translocation for *E. canadensis* whereas the opposite was observed for *M. spicatum*. This might explained by the higher water flow in *M. spicatum* compared to *E. canadensis* (Table S3, Supporting Information). The presently modeled fluxes indicated that translocation from roots to shoots occurred. Previous reports on exposure from sediment spiked systems showed translocation for atrazine ($\log K_{ow} = 2.7$), and to some extent for lindane ($\log K_{ow} = 5.2$) and chlordane ($\log K_{ow} = 5.6$) in *H. verticillata*,[13] for 3-phenoxybenzoic acid ($\log K_{ow} = 3.91$) in *M. elatinoides*,[15] for linuron ($\log K_{ow} = 3.0$) in *M. spicatum*,[14] and for polycyclic aromatic hydrocarbons ($\log K_{ow} = 3.4−6.2$) in *Zostera marina*.[46] PCBs, however, were not measured in shoots of *Z. marina* apart from low concentrations after 32 weeks, indicating that no translocation occurred. Terrestrial plants and emerged macrophytes show more translocation for PCBs (e.g.[47,48]), probably because of transport induced by evaporation. Suppression of translocation, however, might occur as an active process in submerged macrophytes, as has been shown for *Myriophyllum aquaticum* and 2,4 D.[49]

In summary, for flux and concentration temporal patterns of water spiked chemicals in open systems the major pathway was from overlying water to shoots to roots and then to pore water. With increasing hydrophobicity, the direct overlying water to pore water exchange became more important. For sediment spiked chemicals in open systems, the major pathway was parallel transport from pore water to roots and to overlying water, followed by translocation from roots to shoots. Depending on the chemical, shoots could take up from or release to overlying water. For *E. canadensis*, BBL transfer was more important than translocation for all sediment spiked chemicals whereas for *M. spicatum* translocation was more important expect for CPF.

IMPLICATIONS

This work showed that an exposure period of 28 days might not be sufficient for sediment spiked toxicity tests with sediment-rooted macrophytes as the uptake from sediment and translocation to shoots is a slow chemical- and species-specific process, and equilibrium is only reached after 28 days. For macrophyte toxicity tests with a spiked water layer, 28 days are sufficient as chemicals were more rapidly translocated from shoot to root than the other way around. In both cases, however, the chemical transport processes are highly dynamic and assessing exposure in the test would require sufficiently frequent sampling of macrophyte biomass for chemical analysis.

This work further showed that chemical flows in macrophyte−sediment−water test systems can be understood using first-order mass balance modeling concepts. Using this type of parametrized models, optimum test duration and conditions can be designed a priori as part of a prospective risk assessment framework. In addition, actual exposure in a test can be assessed using the modeled concentration profiles. Furthermore, the model parameters can be applied for modeling hydrophobic organic chemical fate under natural conditions in the field, especially for stagnant systems, where the relative importance of root to shoot transfer compared to sediment to water to shoot transfer also depends on the macrophyte density. The model can be applied to other species when accounting for differences in parameter values and required process formulations (e.g., exposure routes). When linking chemical exposure to effects, this model can be used as input for population effect models, which could serve as a tool in environmental risk assessment.

ASSOCIATED CONTENT

Supporting Information

Additional information including Figure S1, material and methods including Tables S2−S9 and Figure S1, and results including Tables S9−S25 and Figures S2− S4. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Wetzel, R. G. *Limnology: Lake and River Ecosystems*; Monograph, 3rd ed.; Academic Press: New York, 2001.

(2) Roessink, I.; Moermond, C. T. A.; Gillissen, F.; Koelmans, A. A. Impacts of manipulated regime shifts in shallow lake model ecosystems on the fate of hydrophobic organic compounds. *Water Res.* **2010**, *44* (20), 6153−6163.

(3) Pedersen, O.; Sand-Jensen, K. Water transport in submerged macrophytes. *Aquat. Bot.* **1993**, *44* (4), 385−406.

(4) Crum, S. J. H.; van Kammen-Polman, A. M. M.; Leistra, M. Sorption of nine pesticides to three aquatic macrophytes. *Arch. Environ. Contam. Toxicol.* **1999**, *37* (3), 310−316.

(5) de Carvalho, R. F.; Bromilow, R. H.; Greenwood, R. Uptake and translocation of non-ionised pesticides in the emergent aquatic plant parrot feather *Myriophyllum aquaticum*. *Pest Manage. Sci.* **2007**, *63* (8), 798−802.

(6) Gao, J.; Garrison, A. W.; Hoehamer, C.; Mazur, C. S.; Wolfe, N. L. Uptake and phytotransformation of organophosphorus pesticides by axenically cultivated aquatic plants. *J. Agric. Food Chem.* **2000**, *48* (12), 6114−6120.

(7) Gobas, F.; McNeil, E. J.; Lovettdoust, L.; Haffner, G. D. Bioconcentration of chlorinated aromatic hydrocarbons in aquatic macrophytes. *Environ. Sci. Technol.* **1991**, *25* (5), 924−929.

(8) Turgut, C. Uptake and modeling of pesticides by roots and shoots of parrotfeather (*Myriophyllum aquaticum*). *Environ. Sci. Pollut. Res.* **2005**, *12* (6), 342−346.

(9) Turgut, C.; Fomin, A. The ability of *Myriophyllum aquaticum* (Vell.) verdcourt in the uptake and the translocation of pesticides via roots with a view to using the plants in sediment toxicity testing. *J. Appl. Bot.-Angew. Bot.* **2002**, *76* (1−2), 62−65.

(10) Wolf, S. D.; Wooten, S. E.; Lassiter, R. R. Predicting chemical accumulation in shoots of aquatic plants. *Environ. Toxicol. Chem.* **1991**, *10* (5), 665−680.

(11) Diepens, N. J.; Arts, G. H. P.; Brock, T. C. M.; Smidt, H.; Van Den Brink, P. J.; Van Den Heuvel-Greve, M. J.; Koelmans, A. A. Sediment toxicity testing of organic chemicals in the context of prospective risk assessment: A review. *Crit. Rev. Environ. Sci. Technol.* **2014**, *44* (3), 255−302.

(12) Maltby, L.; Arnold, D.; Arts, G. H. P.; Davies, J.; Heimbach, F.; Pickl, C.; Poulsen, V. *Aquatic Macrophyte Risk Assessment for Pesticides*; SETAC Press & CRC Press, Taylor and Francis Group: Boca Raton, 2010; p 135.

(13) Hinman, M. L.; Klaine, S. J. Uptake and translocation of selected organic pesticides by the rooted aquatic plant *Hydrilla verticillata* Royle. *Environ. Sci. Technol.* **1992**, *26* (3), 609−613.

(14) Burešová, H.; Crum, S. J. H.; Belgers, J. D. M.; Adriaanse, P. I.; Arts, G. H. P. Effects of linuron on a rooted aquatic macrophyte in sediment-dosed test systems. *Environ. Pollut.* **2013**, *175* (0), 117−124.

(15) Ando, D.; Fujisawa, T.; Katagi, T. Uptake, translocation, and metabolism of 3-phenoxybenzoic acid in the submerged rooted macrophyte water milfoil (*Myriophyllum elatinoides*). *J. Pestic. Sci.* **2012**, *37* (4), 342−346.

(16) Lytle, J. S.; Lytle, T. F. Use of plants for toxicity assessment of estuarine ecosystems. *Environ. Toxicol. Chem.* **2001**, *20* (1), 68−83.

(17) Peters, E. C.; Gassman, N. J.; Firman, J. C.; Richmond, R. H.; Power, E. A. Ecotoxicology of tropical marine ecosystems. *Environ. Toxicol. Chem.* **1997**, *16* (1), 12−40.

(18) Vervliet-Scheebaum, M.; Knauer, K.; Maund, S. J.; Grade, R.; Wagner, E. Evaluating the necessity of additional aquatic plant testing by comparing the sensitivities of different species. *Hydrobiologia* **2006**, *570*, 231−236.

(19) Trapp, S. Modelling uptake into roots and subsequent translocation of neutral and ionisable organic compounds. *Pest Manage. Sci.* **2000**, *56* (9), 767−778.

(20) Li, Q.; Chen, B. Organic pollutant clustered in the plant cuticular membranes: visualizing the distribution of phenanthrene in leaf cuticle using two-photon confocal scanning laser microscopy. *Environ. Sci. Technol.* **2014**, *48* (9), 4774−4781.

(21) Limmer, M. A.; Burken, J. G. Plant translocation of organic compounds: molecular and physicochemical predictors. *Environ. Sci. Technol. Lett.* **2014**, *1* (2), 156−161.

(22) OECD. *Test No. 218: Sediment-water Chironomid toxicity using spiked sediment*; OECD Publishing: Paris, 2004.

(23) ISO *ISO/DIS 16191: Water quality - Determination of the toxic effect of sediment and soil on the growth behaviour of Myriophyllum aquaticum*; International Organization for Standardization: Geneva, 2010.

(24) Smart, M. R.; Barko, J. W. Laboratory culture of submersed freshwater macrophytes on natural sediments. *Aquat. Bot.* **1985**, *21* (3), 251−263.

(25) Jonker, M. T. O.; Koelmans, A. A. Polyoxymethylene solid phase extraction as a partitioning method for hydrophobic organic chemicals in sediment and soot. *Environ. Sci. Technol.* **2001**, *35* (18), 3742−3748.

(26) Bligh, E. G.; Dyer, W. J. A rapid method of total lipid extraction and purification. *Can. J. Biochem. Physiol.* **1959**, *37* (8), 911−917.

(27) OECD Accepted OECD test guideline for water-sediment *Myriophyllum spicatum* toxicity test (Myrio 2-Phase), April 2014. http://www.oecd.org/env/ehs/testing/section2effectsonbioticsystems.htm.

(28) Koelmans, A. A.; Jonker, M. T. O. Effects of black carbon on bioturbation-induced benthic fluxes of polychlorinated biphenyls. *Chemosphere* **2011**, *84* (8), 1150−1157.

(29) Kupryianchyk, D.; Noori, A.; Rakowska, M. I.; Grotenhuis, J. T. C.; Koelmans, A. A. Bioturbation and dissolved organic matter enhance contaminant fluxes from sediment treated with powdered and granular activated carbon. *Environ. Sci. Technol.* **2013**, *47* (10), 5092−5100.

(30) Koelmans, A. A.; Poot, A.; Lange, H. J. D.; Velzeboer, I.; Harmsen, J.; Noort, P. C. M. v. Estimation of in Situ sediment-to-water fluxes of polycyclic aromatic hydrocarbons, polychlorobiphenyls and polybrominated diphenylethers. *Environ. Sci. Technol.* **2010**, *44* (8), 3014−3020.

(31) Boenisch, G.; Kattge, J. http://www.try-db.org (accessed March 13, 2014).

(32) Vanier, C.; Planas, D.; Sylvestre, M. Equilibrium partition theory applied to PCBs in macrophytes. *Environ. Sci. Technol.* **2001**, *35* (24), 4830−4833.

(33) Seth, R.; Mackay, D.; Muncke, J. Estimating the organic carbon partition coefficient and its variability for hydrophobic chemicals. *Environ. Sci. Technol.* **1999**, *33* (14), 2390−2394.

(34) Moerbeek, M.; Piersma, A. H.; Slob, W. A comparison of three methods for calculating confidence intervals for the benchmark dose. *Risk Anal.* **2004**, *24* (1), 31−40.

(35) AMEG. *Myriophyllum toxicity test: Results of a ringtest using M. aquaticum and M. spicatum grown in a sediment-water-system*; Aquatic Macrophyte Ecotoxicology Group: SETAC, Germany, 2012; p 131.

(36) Arts, G. H. P.; Belgers, J. D. M.; Hoekzema, C. H.; Thissen, J. T. N. M. Sensitivity of submersed freshwater macrophytes and endpoints in laboratory toxicity tests. *Environ. Pollut.* **2008**, *153* (1), 199−206.

(37) University of Hertfordshire The Pesticide Properties DataBase (PPDB) developed by the Agriculture & Environment Research Unit (AERU).

(38) Gobas, F. A. P. C. A model for predicting the bioaccumulation of hydrophobic organic chemicals in aquatic food-webs: application to Lake Ontario. *Ecol. Modelling* **1993**, *69* (1−2), 1−17.

(39) Briggs, G. G.; Bromilow, R. H.; Evans, A. A. Relationships between lipophilicity and root uptake and translocation of non-ionised chemicals by barley. *Pestic. Sci.* **1982**, *13* (5), 495−504.
(40) Burken, J. G.; Schnoor, J. L. Predictive relationships for uptake of organic contaminants by hybrid poplar trees. *Environ. Sci. Technol.* **1998**, *32* (21), 3379−3385.
(41) Trapp, S.; Matthies, M.; McFarlane, C. Model for uptake of xenobiotics into plants: Validation with bromacil experiments. *Environ. Toxicol. Chem.* **1994**, *13* (3), 413−422.
(42) Dettenmaier, E. M.; Doucette, W. J.; Bugbee, B. Chemical hydrophobicity and uptake by plant roots. *Environ. Sci. Technol.* **2008**, *43* (2), 324−329.
(43) Weisbrod, A. V.; Woodburn, K. B.; Koelmans, A. A.; Parkerton, T. F.; McElroy, A. E.; Borgå, K. Evaluation of bioaccumulation using in vivo laboratory and field studies. *Integr. Environ. Assess. Manag.* **2009**, *5* (4), 598−623.
(44) ter Laak, T. L.; van Eijkeren, J. C. H.; Busser, F. J. M.; van Leeuwen, H. P.; Hermens, J. L. M. Facilitated transport of polychlorinated biphenyls and polybrominated diphenyl ethers by dissolved organic matter. *Environ. Sci. Technol.* **2009**, *43* (5), 1379−1385.
(45) Clarkson, D. T. Root Structure and Sites of Ion Uptake; In *Plant Roots the Hidden Half*; Waisel, Y., Eshel, A., Kafkafi, U., Eds.; Marcel-Dekker, Inc.: New York, 1991; 415.
(46) Huesemann, M. H.; Hausmann, T. S.; Fortman, T. J.; Thom, R. M.; Cullinan, V. In situ phytoremediation of PAH- and PCB-contaminated marine sediments with eelgrass (*Zostera marina*). *Ecol. Eng.* **2009**, *35* (10), 1395−1404.
(47) Chu, W. K.; Wong, M. H.; Zhang, J. Accumulation, distribution and transformation of DDT and PCBs by Phragmites australis and Oryza sativa L.: I. Whole plant study. *Environ. Geochem. Health* **2006**, *28* (1−2), 159−168.
(48) Zeeb, B. A.; Amphlett, J. S.; Rutter, A.; Reimer, K. J. Potential for phytoremediation of polychlorinated biphenyl-(PCB)-contaminated soil. *Int. J. Phytoremed.* **2006**, *8* (3), 199−221.
(49) Sutton, D. L.; Bingham, S. W. Uptake and translocation of 2,4-D-1-^{14}C in Parrotfeather. *Weed Sci.* **1970**, *18* (2), 193−196.
(50) van Noort, P. C. M.; Haftka, J. J. H.; Parsons, J. R. Updated abraham solvation parameters for polychlorinated biphenyls. *Environ. Sci. Technol.* **2010**, *44* (18), 7037−7042.
(51) Tomlin, C. D. S. *The pesticide manual a world compendium*, 13th ed.; BCPC: Hampshire, U.K., 2003.
(52) Paasivirta, J.; Sinkkonen, S. I. Environmentally relevant properties of all 209 polychlorinated biphenyl congeners for modeling their fate in different natural and climatic conditions. *J. Chem. Eng. Data* **2009**, *54* (4), 1189−1213.
(53) Hawthorne, S. B.; Miller, D. J.; Grabanski, C. B. Measuring low picogram per liter concentrations of freely dissolved polychlorinated biphenyls in sediment pore water using passive sampling with polyoxymethylene. *Anal. Chem.* **2009**, *81* (22), 9472−9480.
(54) Endo, S.; Hale, S. E.; Goss, K. U.; Arp, H. P. H. Equilibrium partition coefficients of diverse polar and nonpolar organic compounds to polyoxymethylene (POM) passive sampling devices. *Environ. Sci. Technol.* **2011**, *45* (23), 10124−10132.