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RESEARCH ARTICLE

Experiments in water-macrophyte systems to uncover the dynamics of pesticide mitigation processes in vegetated surface waters/streams

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Abstract Knowledge on the dynamics and the durability of the processes governing the mitigation of pesticide loads by aquatic vegetation in vegetated streams, which are characterized by dynamic discharge regimes and short chemical residence times, is scarce. In a static long-term experiment (48 h), the dissipation of five pesticides from the aqueous phase followed a biphasic pattern in the presence of aquatic macrophytes. A dynamic concentration decrease driven by sorption to the macrophytes ranged from 8.3 to 60.4 % for isoproturon and bifenox, respectively, within the first 2 h of exposure. While the aqueous concentrations of imidacloprid, isoproturon, and tebufenozide remained constant thereafter, the continuous but decelerated concentration decrease of difenoconazole and bifenox in the water-macrophyte systems used here was assumed to be attributed to macrophyte-induced degradation processes. In addition, a semi-static short-term experiment was conducted, where macrophytes were transferred to uncontaminated medium after 2 h of exposure to simulate a transient pesticide peak. In the first part of the experiment, adsorption to macrophytes resulted in partitioning coefficients ($\log K_{D\_Adsorp}$) ranging from 0.2 for imidacloprid to 2.2 for bifenox. One hour after the macrophytes were transferred to the uncontaminated medium, desorption of the compounds from the macrophytes resulted in a new phase equilibrium and K_{D_Desorp} values of 1.46 for difenoconazole and 1.95 for bifenox were determined. A correlation analysis revealed the best match between the compound affinity to adsorb to macrophytes (expressed as K_{D_Adsorp}) and their soil organic carbon-water partitioning coefficient (K_{OC}) compared to their octanol-water partitioning coefficient (K_{OW}) or a mathematically derived partitioning coefficient.

Keywords Pesticides · Risk mitigation · Vegetated streams · Sorption · Aquatic vegetation · Best management practice · UHPLC-MS

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Introduction

The use of pesticides is a common practice in intensive agricultural production processes, and it is beyond discussion that the field application of pesticides, among others, can result in the discharge of pesticides to non-target ecosystems, such as surface waters. Hence, efforts have been made in recent years to diminish the input of pesticides into ecosystems adjacent to agricultural areas. As a result, best management practices (BMP), such as improved application techniques, field buffers, or vegetated treatment systems (VTS), were developed and partially implemented in the field (Stehle et al. 2011; Bereswill et al. 2014). Especially, VTS have been proposed to be highly efficient in the mitigation and retention of pesticide loads. Hence, over the years, the retention efficiency of a variety of constructed wetlands, retention ponds or vegetated streams, and drainage ditches, respectively, and a variety of other VTS have been evaluated (Reichenberger et al. 2007; Gregoire et al. 2008; Stehle et al. 2011). In all of these studies, the retention of pesticides by aquatic macrophytes and partly sediments has been postulated as one of the most important

processes in VTS. Beyond that, the ability of aquatic macrophytes to eliminate pesticides from the aqueous phase has been investigated at the laboratory (Crum et al. 1999; Olette et al. 2008), microcosm (Bouldin et al. 2005), and mesocosm scale (Moore et al. 2009). Furthermore, Passeport et al. (2011) determined high coefficients for pesticide adsorption to wetland plants and forest litter followed by compound-related desorption. In another study, Hand et al. (2001) observed extensive and essentially irreversible adsorption as well as a rapid degradation of lambda-cyhalothrin in two laboratory experiments and an indoor microcosm study. A meta-analysis on the retention of pesticides in VTS (Stehle et al. 2011) revealed macrophyte coverage and the hydraulic retention time (HRT) to be crucial VTS characteristics that determine the retention performance of such systems. In particular, the macrophyte coverage was found to be closely related to the physicochemical properties of the investigated compounds, especially the soil organic carbon-water partitioning coefficient (K_{OC}). According to Stehle et al. (2011), the K_{OC} is a critical factor governing the initial retention of pesticides of these compounds in VTS. Beyond that, Crum et al. (1999) found a better correlation between sorption of six pesticides to aquatic macrophytes and the compound solubility in water instead of the compound's octanol-water partitioning coefficient (K_{OW}). Nonetheless, the retention of three rather hydrophilic fungicides (K_{OW}=245–6607) and two lipophilic biocides (K_{OW}=57,544–125,863) by aquatic macrophytes in vegetated stream mesocosms was found to increase with the compounds K_{OW} (Stang et al. 2013). Although the ability of aquatic macrophytes to interact with pesticides is beyond discussion and several coefficients which are generally available for pesticides have been proposed to predict the fate of these compounds in the aquatic environment, knowledge on the dynamics and the durability of the underlying chemical-macrophyte interaction processes is still very limited.

This holds true especially for vegetated streams that are mainly characterized as flow-through systems with a dynamic discharge regime and comparably short chemical residence times (i.e., transient exposure peaks). A broader understanding of the underlying processes is all the more important, since vegetated streams have been promoted as a pragmatic end-of-pipe strategy for the mitigation of pesticide loads in receiving waters. However, there are only a few studies available that highlighted the suitability of vegetated streams and the influence of aquatic macrophytes on the mitigation of pesticide concentrations in these flowing systems (Schulz et al. 2003; Dabrowski et al. 2006; Elsaesser et al. 2011). These studies were, thus, rather designed to generally assess the suitability of vegetated streams or wetlands for the mitigation of pesticide concentrations, than to gain a deeper understanding on how the dynamics and the persistence of sorption processes to aquatic macrophytes govern the overall retention capability of these systems. After all, there is, to the best of our knowledge, merely one study that not only quantified the sorption processes to aquatic vegetation, but also highlighted the persistence of these processes (Stang et al. 2014). In this study, 8 to 27 % of the applied pesticides were initially retained by macrophytes. However, with the passage of the contaminant peak, the concentration in the macrophyte samples decreased rapidly, while the mass recovery rates in the aqueous phase simultaneously increased. Based on the findings of this mesocosm study, the present laboratory study was designed to gain further knowledge on the interaction between pesticides and aquatic macrophytes in water-macrophyte systems. Hence, the study encompassed two experimental approaches, a static long-term and a semi-static short-term approach, respectively. The static long-term approach aimed at the determination of the general dissipation dynamics of the investigated pesticides from the aqueous phase in the presence of three aquatic macrophyte species. The semi-static short-term approach was conducted to assess the dynamics and the consistency of sorption and desorption processes, respectively, during and subsequent to a simulated peak exposure.

Materials and methods

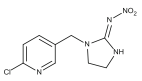
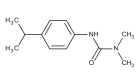
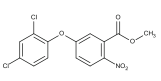
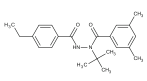
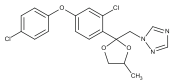
Pesticides

Five commonly used pesticides with a broad range of physicochemical properties (Table 1) were used in the present study. For stock solution preparation, analytical standards (all PESTANAL, Sigma-Aldrich GmbH, Seelze, Germany) of the insecticides imidacloprid (1-(6-chloro-3-pyridylmethyl)-N-nitroimidazolidin-2-ylideneamine) and tebufenozide (N-tert-butyl-N′-(4-ethylbenzoyl)-3,5-dimethylbenzohydrazide), the herbicides isoproturon (3-(4-isopropylphenyl)-1,1-dimethylurea) and bifenox (methyl 5-(2,4-dichlorophenoxy)-2-nitrobenzoate), and the fungicide difenoconazole (3-chloro-4-[(2RS,4RS;2RS,4SR)-4-methyl-2-(1H-1,2,4-triazol-1-ylmethyl)-1,3-dioxolan-2-yl]phenyl 4-chlorophenyl ether) were separately dissolved in methanol (LiChrosolv, Merck KGaA, Darmstadt, Germany) resulting in concentrations of 200 ng/μL. In preparation of the experiments, 1 L of the medium (Michael Smart and Barko 1985) was separately spiked with 500 μL of the respective stock solution to gain a nominal pesticide concentration of 100 μg/L. The pesticide-spiked medium was subsequently stirred for 30 min to ensure homogenous pesticide distribution within the solution.

Macrophytes

Both experimental approaches were performed with three macrophyte species, representative for surface waters in central Europe. The western waterweed (*Elodea nuttallii*) was

Table 1 Physicochemical properties of the investigated pesticides

	Imidacloprid	Isoproturon	Bifenox	Tebufenozide	Difenoconazole
Chemical structure					
Water solubility (mg/L)[a]	610	70.2	0.1	0.83	15
$\log K_{OW}$[a]	0.57	2.5	3.6	4.25	4.36
$\log K_{OC}$[a]	2.35	2.09	3.81	2.76	3.58
$\log K_{D\_math}$[b]	1.39	2.0	3.03	2.42	3.17
Photolytic degradation (DT_{50}; days)[a]	Stable	1,560	265	Stable	Stable
Hydrolytic degradation (DT_{50}; days)[a]	0.2	48	2.2	Stable	Stable

[a] According to the Pesticides Properties Database (PPDB)

[b] Calculated according to the formula by Crum et al. (1999)

taken from the Queich River (49° 13′ 09.53″ N; 7° 53′ 50.76″ E) in the southwest of Germany. The rigid hornwort (*Ceratophyllum demersum*) and the curly-leaf pondweed (*Potamogeton crispus*) were taken from groundwater fed ponds in Derental (51° 41′ 29.44″ N; 9° 25′ 46.24″ E) in the north of Germany. After collection in the field, macrophytes were washed with tap water to remove deposits of sediment or particulate matter. Subsequently, macrophytes were stored in medium at 22 °C and were illuminated according to a light/dark interval of 16/8 h (6600 lx; Biolux L58/965, OSRAM GmbH, Munich, Germany) for at least 1 week prior to use. During collection in the field as well as during storage and the experimental phase, the macrophytes showed normal appearance and were apparently free of algae or periphyton. Chemical analyses that were performed in preparation of the experiments revealed no previous contamination with the investigated pesticides.

Experimental setup

In general, all experiments were conducted in water-macrophyte systems that consisted of glass containers with a volumetric capacity of 2 L. In preparation of the experiments, the macrophytes were added to the glass jars that contained 1 L of pesticide-spiked nutrient medium instantaneously before the glass jars were finally placed on a horizontal shaker (Bühler VKS 75 B control shaker, Edmund Bühler GmbH, Hechingen, Germany). The horizontal shaker was constantly operated at 55 rpm to simulate a constant water movement and thus to provide a slight circulation of the pesticide-spiked medium around the macrophytes, as it may occur in slow-flowing streams. The experiments were conducted under standardized conditions (pH = 8.1 ± 0.5) in a temperature-controlled (22.5 ± 1 °C) and darkened room. The glass jars were illuminated with artificial daylight (6600 lx; Biolux L18/965, OSRAM GmbH, Munich, Germany) to provide the basis for the maintenance of photosynthetic activity to the macrophytes. While the illumination pursued a light/dark interval of 16/8 h during the static long-term experiments, glass jars were continuously illuminated during the semi-static short-term experiments lasting 6 h in total.

For the static long-term experiments, three replicates of glass jars containing 4, 8, and 16 g (fresh weight) of *E. nuttallii*, *C. demersum*, and *P. crispus*, respectively, were exposed to the pesticide-spiked medium and placed on the horizontal shaker for 48 h. Additionally, three glass jars remained free of macrophytes and served as control treatments to assess potential loss of the applied pesticides by other than macrophyte-induced dissipation or degradation processes. Throughout the experimental phase, eight aqueous samples (1 mL) were taken from each glass jar at 0, 1, 2, 4, 8, 12, 24, and 48 h (t_0,…,t_{48}) after the start of the experiment. At the end of the experimental phase, the medium was decanted from the glass jars, before macrophytes were removed and immediately stored at −20 °C in aluminum bowls, once remaining medium was carefully drained from the macrophytes.

The semi-static short-term experiment was designed in order to simulate a peak exposure event and thus comprised two experimental phases. During the initial sorption period, nine treatments containing 16 g (fresh weight) of *E. nuttallii*, *C. demersum*, and *P. crispus*, respectively, were exposed to the pesticide-spiked medium for 2 h. After this period of time, aqueous samples (t_{A2}; 1 mL) were taken from each treatment before the medium was decanted. The macrophytes were removed from glass jars, and the remaining medium was carefully drained. The transfer of the macrophytes to glass jars that contained 1 L of uncontaminated medium and the repositioning on the horizontal shaker represented the start of the

desorption period. To assess the desorption dynamics of the pesticides from the macrophytes, three of the total nine glass jars used per setup were removed from the horizontal shaker after 1 (t_{D1}), 2 (t_{D2}), and 4 h (t_{D4}). The medium was decanted into amber glass bottles to preserve the medium for further processing. In addition, the macrophytes were immediately stored at −20 °C in aluminum bowls after the drainage of remaining medium.

Chemical analyses

Aqueous samples from the static long-term experiment and the initial sorption period of the semi-static short-term experiment were immediately stored in amber glass HPLC vials at −20 °C until chemical analyses. Aqueous samples that were collected during the desorption period of the semi-static short-term experiments, however, were promptly extracted from the samples using solid-phase extraction (SPE) as described in Stang et al. (2014). Briefly, samples (1 L) were transferred to dropping funnels and subsequently percolated through the C18-SPE cartridges (Chromabond C18/6 mL/1000 mg, Macherey-Nagel, Düren, Germany; flow rate 20 mL/min) previously conditioned with methanol (3×5 mL; LiChrosolv, Merck KGaA, Darmstadt, Germany) and deionized water (3×5 mL). The eluates (3×5 mL of methanol) were finally evaporated until dryness, reconstituted in methanol (1 mL), and stored in amber glass vials at −20 °C until chemical analyses. For the validation of the SPE procedure, three replicate samples consisting of 1 L medium were spiked with the respective pesticide and processed as described above, resulting in recovery rates ranging from 84.6±14.3 % for bifenox to 106.9±4.4 % for isoproturon (Table S1).

Pesticide residues in macrophyte samples from both experimental approaches were extracted by accelerated solvent extraction (ASE; ASE 350, Dionex GmbH, Idstein, Germany). For macrophyte extraction, a maximum of 1 g (dry weight) of the lyophilized samples was weighed into 34 mL extraction cells which were finally padded with cindered sea sand (Carl Roth GmbH, Karlsruhe, Germany). The extraction procedure comprised an equilibration period (5 min) and four static extraction cycles (10 min each) at 80 °C with acetonitrile (LiChrosolv, Merck KGaA, Darmstadt, Germany) and acetone (SupraSolve, Merck KGaA, Darmstadt, Germany) with a ratio by volume of 50/50. Extracts were collected in amber glass vials (60 mL) and entirely evaporated under a slight stream of nitrogen, before being reconstituted in 1 mL of methanol. To eliminate potential matrix effects, samples were diluted (1/1000; *v*/*v*) with methanol prior to chemical analysis. For method validation, 1 g of lyophilized blank macrophyte samples (n=3) was spiked with 1 mL of a solution that contained the investigated pesticide dissolved in methanol at a concentration of 100 μg/mL. After the methanol was entirely evaporated, samples were processed as described above to determine recovery rates and the repeatability of the entire extraction procedure (Table S1).

Chemical analyses were performed with an ultra-high-performance chromatographic system coupled to a mass spectrometer (UHPLC-MS; Exactive, Thermo Fisher Scientific, Dreieich, Germany) according to the method described in Stang et al. (2014; Table S2). The investigated pesticides were identified as the $[M+H]^+$ adducts as well as, in the case of bifenox, the $[M+NH_4]^+$ adduct, respectively (Table S3). The quantification of pesticide concentrations in all samples was performed by the use of an external calibration (1–100 ng/mL). Limits of quantification (LOQ) were determined according to the requirements of DIN 32645 (Table S3). The semi-quantitative analysis of bifenox acid in aqueous samples was performed under the same chromatographic conditions, whereas the MS was operated in the negative ESI mode for the identification of the $[M-H]^-$ adduct. Bifenox acid was identified as the ion with the exact mass of 325.9617 *m*/*z* and a retention time of 4.8 min (Fig. S2). The identity of the ion was confirmed by means of an analytical reference standard (Dr. Ehrenstorfer GmbH, Augsburg, Germany).

Data analyses

In order to identify potential degradation of the investigated compounds during the experimental phase, mass balances, expressed as recovery rates, were compiled. The recovery rates (REC_{static}) for the static long-term approach were assessed according to Eq. 1, where M_0 is the initially applied amount of the respective pesticide, M_{48} is the corresponding fraction that remained in the aqueous phase at the end of the experimental phase, and M_{Macro} is the fraction that was found in macrophytes.

$$\mathrm{REC}_{\mathrm{static}}(\%) = \left(\frac{M_{48} + M_{\mathrm{Macro}}}{M_0}\right) \times 100 \quad (1)$$

Experimentally derived partitioning coefficients were calculated to describe adsorption ($\log K_{D\_Adsorp}$) as well as desorption ($\log K_{D\_Desorp}$) processes, respectively, during the semi-static short-term exposure scenario. In Eqs. 2 and 3, C_{Macro} (μg/kg ww) is the pesticide concentration in macrophytes related to the biomass based on wet weight, C_{Desorp} (μg/L) is the pesticide concentration in the aqueous phase after the desorption period, and $C_{Aqueous}$ (μg/L) is the concentration that remained in the aqueous phase after the adsorption period.

$$\log K_{\mathrm{D\_Adsorp}}(\mathrm{L/kg}) = \log\left(\frac{C_{\mathrm{Macro}} + C_{\mathrm{Desorp}}}{C_{\mathrm{Aqueous}}}\right) \quad (2)$$

$$\log K_{\mathrm{D\_Desorp}}(\mathrm{L/kg}) = \log\left(\frac{C_{\mathrm{Macro}}}{C_{\mathrm{Desorp}}}\right) \quad (3)$$

Correlation analyses for the experimentally derived $\log K_{D\_Adsorp}$ as a function of the $\log K_{OW}$, the $\log K_{OC}$, and the mathematically derived $\log K_{D\_math}$ (Crum et al. 1999), respectively, of the investigated compounds were performed on the basis of the Pearson correlation coefficient using SPSS 21.0 software (IBM, Chicago, IL).

Results and discussion

Static long-term scenario

Generally, the degree of pesticide dissipation in the macrophyte treatments was found to be determined by two factors: the pesticide itself and the macrophyte biomass. The pesticide concentration in all control treatments remained stable (Fig. S1) during the entire experimental phase, indicating that the influence of abiotic degradation processes, such as hydrolysis or photolysis, can be considered negligible. However, in the majority of the macrophyte treatments, irrespective of the macrophyte species present and the final degree of pesticide dissipation, the decrease of the investigated pesticides in the aqueous phase followed a similar pattern. Within the first 2 to 4 h of exposure, a compound-specific dissipation dynamic was observed that resulted in an initial concentration equilibrium between the aqueous phase and the macrophytes. Subsequently, the pesticide concentrations in the aqueous phase remained either constant or the dissipation dynamics decelerated noticeably (Fig. S1). Compared to the other investigated compounds, the decrease of the imidacloprid concentrations in all treatments was less pronounced and was, thus, hardly quantifiable during the entire experimental phase. The isoproturon concentrations in the treatments containing 4, 8, and 16 g of the respective macrophyte species decreased on average (mean±SE) by 2.0±2.6, 6.0±2.7, and 8.3±2.9 %, respectively, within the first 2 h of exposure and remained more or less stable (2.6±4.1, 7.8±4.1, and 10.0±3.8 %) until the end of the experimental phase (Fig. 1). Also, the dissipation rates of tebufenozide that were observed after 2 h of exposure (6.5±4.0, 3.6±3.6, and 5.6±6.7 %) remained rather constant until the end of the experimental phase (3.7±3.5, 5.9 ±4.6, and 9.8±6.3 %). Furthermore, the recovery rates (REC_{static}) of imidacloprid, isoproturon, and tebufenozide ranged from 93.6 to 106.9 % in all treatments, and the amount of residues that were found in the macrophytes largely corresponded with the observed dissipation of the respective pesticides in the aqueous phase (Fig. 2). For instance, in the treatments with the highest biomass of the three macrophytes, the concentration of tebufenozide in the aqueous phase decreased on average by 9.8±6.3 % after 48 h. Simultaneously, the average concentration in the macrophytes increased and accounted for 4.7±2.3 % of the initially applied amount of tebufenozide. It is therefore considered that the dissipation dynamics of these compounds followed a first-order kinetic, since the decrease of the pesticide concentration in the aqueous phase can be attributed to sorption to the macrophytes. However, in the difenoconazole and the bifenox treatments, the dissipation of the compounds was found to be determined by an additional process. The initial difenoconazole concentrations in the treatments containing 4, 8, and 16 g of macrophytes decreased by 9.9±5.6, 16.8± 5.1, and 37.8±5.9 % (Fig. 1) within 2 h and resulted in biomass-related dissipation rates of 24.3±2.8, 38.6±11.7, and 57.4±8.6 % after 48 h, respectively (Fig. 1). The dissipation dynamics that were observed for bifenox were generally higher than those determined for difenoconazole and differed considerably among the three macrophyte species (Fig. S1). In the treatments containing *C. demersum* and *P. crispus*, the dissipation pattern was similar to the other compounds, even though resulting in higher biomass-related dissipation rates that ranged from 51.2±1.0 to 76.1±3.2 % and from 70.1± 1.0 to 91.2±4.0 %, respectively. Furthermore, in the treatments containing *E. nuttallii*, a continuous decline of bifenox concentrations was observed. The bifenox concentration in

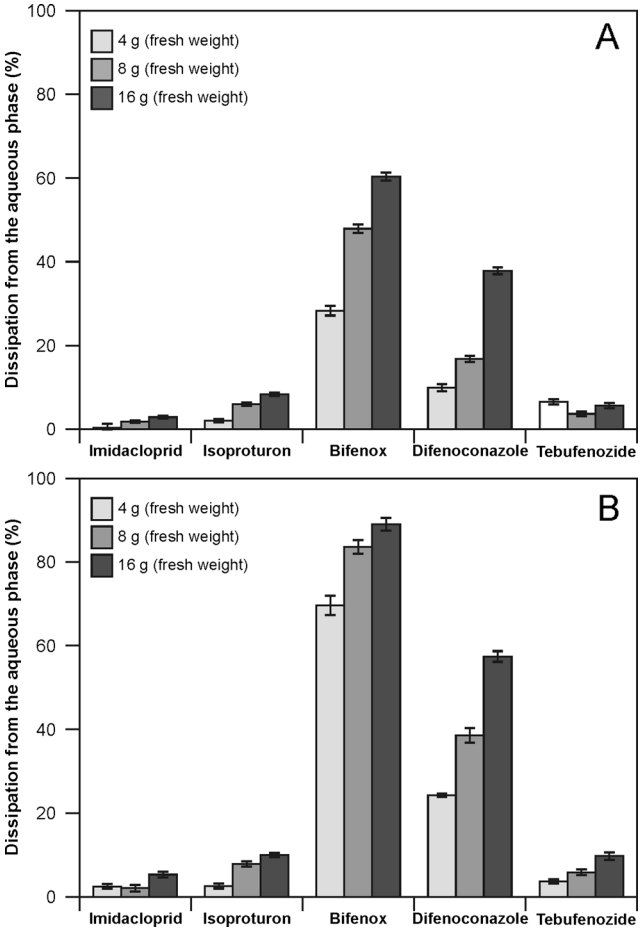


Fig. 1 Average dissipation (mean±SE) of the investigated pesticides from the aqueous phase in the presence of different biomasses of *E. nuttallii*, *C. demersum*, and *P. crispus* after 2 (**a**) and 48 h (**b**)

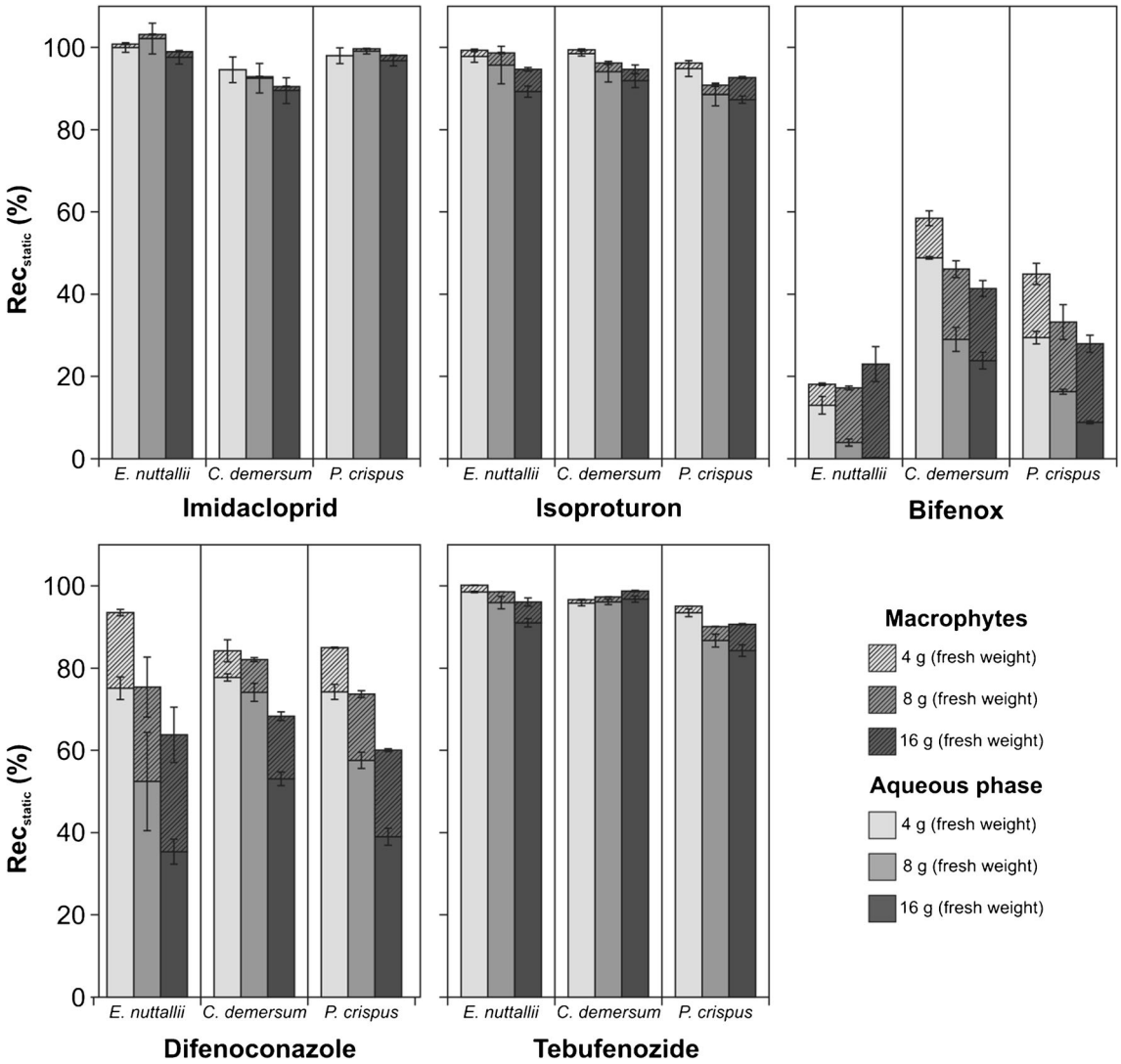


Fig. 2 Recovery rates (Rec_{static}; mean±SD) of the investigated pesticides and distribution of the remaining amount of the parent compound between the aqueous phase and the macrophytes

the treatments that contained 4 and 8 g of *E. nuttallii* decreased by 87.0±2.5 and 96.1±1.0 %, respectively, after 48 h of exposure. During the same period of time, the bifenox concentration in the treatments with the highest biomass (16 g) decreased even below the LOQ. In addition, the chemical analysis of aqueous and macrophyte samples from the difenoconazole as well as from the bifenox treatments, respectively, revealed results fundamentally different from the other investigated compounds. Indeed, there was a biomass-related concentration decrease in the aqueous phase in all macrophyte treatments, but the amount of difenoconazole and bifenox that was recovered in the aqueous phase and in the macrophytes at the end of the experimental phase did not correspond to the initially applied amount of both compounds (Fig. 2). In the difenoconazole treatments with the highest biomass, for instance, only 62.1 % (*P. crispus*) to 70.0 % (*C. demersum*) of the initially applied amount of the compound was recovered (Fig. 2). Similar observations were made in the bifenox treatments, where the recovery rates (REC_{static}) in the treatments with the highest biomass merely ranged from 23.1 % in the *E. nuttallii* to 43.4 % in the *C. demersum* treatments, respectively (Fig. 2). According to the observations described above, it appears that the dissipation of the difenoconazole and bifenox in the water-macrophyte systems used here is mainly dominated by two macrophyte-induced processes: sorption to macrophytes and the subsequent and continuous degradation of the parent compound. For bifenox, this assumption is in line with the rapid degradation of the compound in water-sediment systems for which a DT_{50} of 0.11 days was reported (European Food Safety Authority (EFSA) 2007) and was confirmed, since the formation of bifenox acid was detected in all macrophyte treatments (Fig. S3). Beyond that, the signal intensity of the ion that was identified as bifenox acid increased with time in aqueous samples and was, in addition, linked to

the macrophytes biomass (Fig. S3). Bifenox acid is formed in a variety of environmental matrices (EFSA 2013) as a result of hydroxylation, a process that was also described in a study by Dosnon-Olette et al. (2011), in which the authors linked the increase of the cytochrome P450 activity with the detoxification of the fungicide dimetomorph via hydroxylation in the presence of *Elodea canadensis*. For difenoconazole, no degradation products could be identified due to analytical limitations and it could thus not be clarified whether the low recovery rates (REC_{static}) in the water-macrophyte systems were attributed to macrophyte-induced degradation of the compound or if difenoconazole was bound to the macrophytes in a non-extractable manner. However, the decelerated but continuous decrease of the difenoconazole concentrations that was observed in the macrophyte treatments (Fig. S1) may be regarded as an indication for the degradation of the compound. Consequently, a second-order kinetic attributed to the initial sorption and the subsequent degradation of bifenox and difenoconazole can be assumed. Similar observations were also made by Garcinuno et al. (2006), who reported mass recoveries of 57, 53, and 55 % of carbaryl, linuron, and permethrin, respectively, and stated that the compounds were degraded and/or bound in an irreversible manner to *Lupinus angustifolius* in a hydroponic system. Beyond that, Schulz et al. (2003a) concluded that besides sorption to living plant biomass that accounted for 10.5 % of the initially retained azinphos-methyl mass, a variety of additional degradation processes were of importance for the loss of the compound in a vegetated flow-through wetland in South Africa.

Semi-static short-term exposure scenario

The concentration decrease until the end of the exposure period of 2 h (t_{A2}) was similar to the observations that were made in the same period of time in the static long-term scenario. Whereas the average concentration decrease of imidacloprid (not quantifiable), isoproturon (7.0±6.4 %), and tebufenozide (4.6±3.7 %) was less pronounced, the difenoconazole and the bifenox concentrations in the aqueous phase decreased significantly, resulting in an average rate of decrease ranging from 38.7±8.0 to 69.4±7.0 %, respectively. Simultaneously, the concentration of the investigated compounds in the macrophytes increased proportionally. However, after the macrophytes were transferred to the uncontaminated medium (t_{A2}), the concentration of the investigated pesticides in the aqueous phase increased rapidly accompanied by a closely coupled decrease of the pesticide concentration in the macrophytes (Fig. 3). For instance, the average concentration of isoproturon in the aqueous phase at t_{D1} corresponded to 6.9 ±1.2 % of the initially applied amount of the pesticide and thus to the concentration decrease measured at t_{A2}. Similar observations were made for imidacloprid and tebufenozide, of which 2.6±0.2 and 7.9±4.9 %, respectively, of the initially applied amounts of the compounds were recovered in the aqueous phase at t_{D1}, while the concentrations in the macrophyte samples simultaneously decreased below the LOQ. These observations illustrate that a new phase equilibrium between the macrophytes and the aqueous phase was already established after this period of time. The transfer of the macrophytes from the difenoconazole and the bifenox treatments, respectively, to the uncontaminated medium resulted in a different water/macrophyte distribution of the compounds. Indeed, the concentration in the aqueous phase increased also rapidly within the first hour of the desorption period, but there was also a considerable amount of both pesticides that remained in the macrophytes (Fig. 3). At the end of the adsorption period (t_{A2}), a distribution ratio of 2.1±0.5 between the aqueous phase and the macrophytes was assessed for difenoconazole, which resulted in an experimentally derived partitioning coefficient ($\log K_{D\_Adsorp}$) of 1.45±0.10 (Table S4). After the macrophytes were transferred to uncontaminated medium, a similar average water/macrophyte ratio of 2.2±0.6 as well as a similar $\log K_{D\_Desorp}$ of 1.46±0.11 was determined already at t_{D1} and remained stable until the end of the desorption period. In the bifenox treatments, the transfer of the compound from the macrophytes into the aqueous phase occurred just as fast as in the difenoconazole treatments, even though the distribution patterns between both matrices differed markedly. In the treatments containing *E. nuttallii*, a water/macrophyte distribution ratio of 0.4±0.1 and a $\log K_{D\_Adsorp}$ of 2.20±0.08 at the end of the sorption period (t_{A2}) were determined (Table S4). As already found during the static long-term experiment, a considerable decrease of bifenox was observed in both matrices indicating a rapid degradation of the parent compound. Hence, the direct comparison of the compounds' distribution between the aqueous phase and the macrophytes during the sorption and desorption period, respectively, is hardly possible. However, the observations that were made in the bifenox treatments that contained *C. demersum* and *P. crispus* allow for drawing comparative conclusions regarding the distribution of the compound between both phases. In these treatments, the pesticide showed a stronger tendency to adsorb to the macrophytes instead of remaining in the aqueous phase. Hence, an average water/macrophyte ratio of 0.7±0.1 as well as an average $\log K_{D\_Adsorp}$ of 2.13±0.06 was assessed at the end of the sorption period (t_{A2}). Although the observations from the sorption period underline that bifenox is the compound with the highest affinity to adsorb to the macrophytes, the concentration in the aqueous phase increased also rapidly after the macrophytes were transferred to the uncontaminated medium, resulting in a water/macrophyte ratio of 0.8±0.2 and a $\log K_{D\_Desorp}$ of 1.92± 0.08 at t_{D1}. Thus, the results indicate that adsorption/desorption processes in the water-macrophyte systems followed basic equilibrium equations, as they are already described for adsorption/desorption processes in soil.

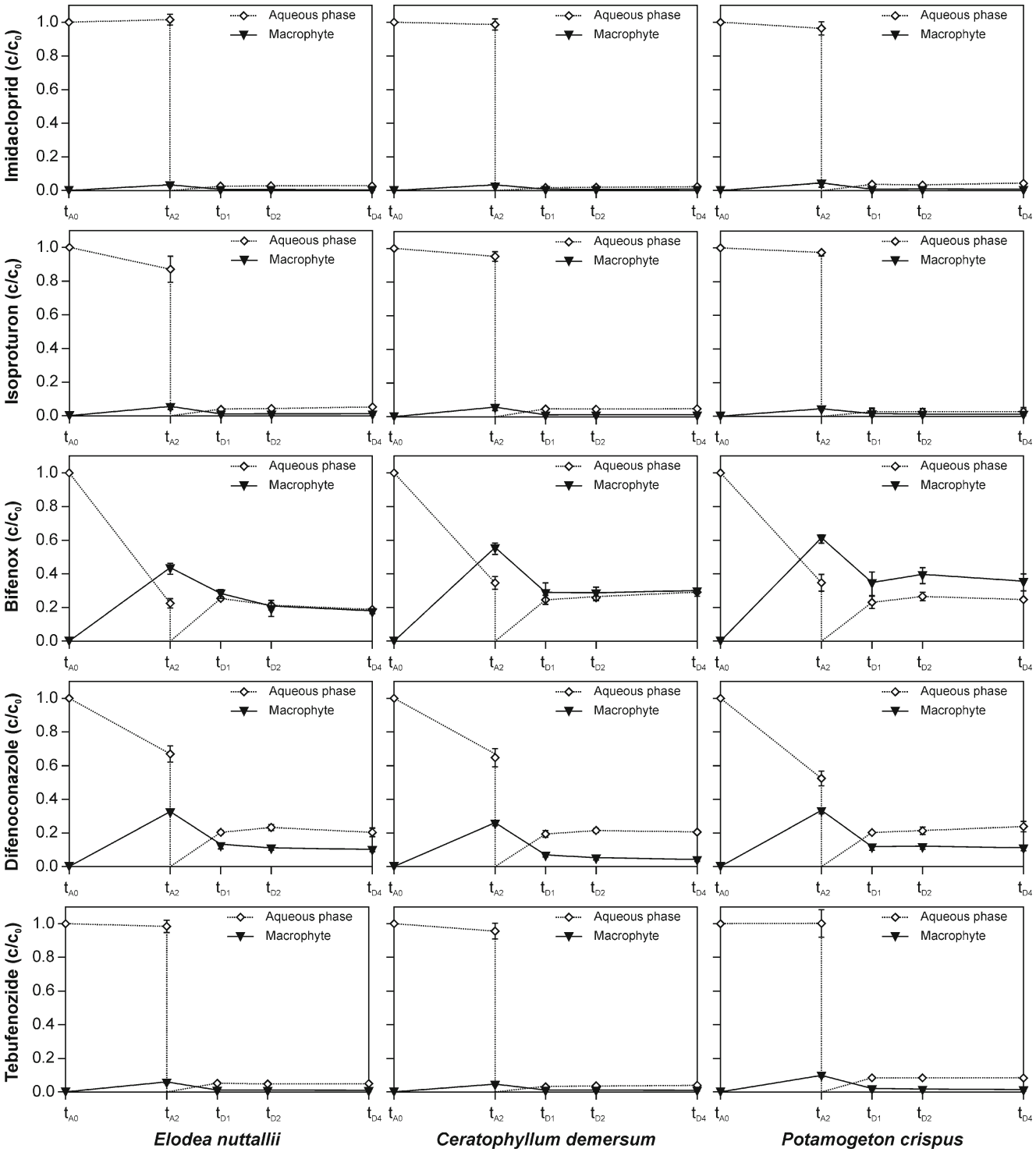


Fig. 3 Temporal gradient of the pesticide concentration (mean±SD) in the aqueous phase and in macrophytes. *Dotted lines* display the concentration in the aqueous phase, and *continuous lines* display the concentration in macrophytes; t_{A0} = start of the experiment, t_{A2} = end of the sorption period after 2 h and transfer of macrophytes into uncontaminated medium, $t_{D1,\ D2,\ D4}$ = time (D1=1 h, D2=2 h, D4= 4 h) after the transfer of the macrophytes to uncontaminated medium

With the currently presented results in mind and considering the conditions in the field, for instance, in running surface waters where an edge-of-field runoff would lead to a pesticide peak that comes along with a dynamic concentration increase and decrease in the aqueous phase, respectively, the findings of the present study provide insights in the processes that determine the macrophyte-induced mitigation of pesticide concentrations in such systems. The experiments provide

knowledge on the dynamics that determine the temporal frame and the persistence of sorption and desorption processes during a short-term pesticide exposure. The experiments revealed, on the one hand, that sorption is a dynamic and rapid process that is implemented, once the concentration in the aqueous phase increases and thus supports the findings of Hand et al. (2001) who also observed rapid adsorption of lambda-cyhalothrin to aquatic plants. On the other hand, the observations confirm that sorption to aquatic macrophytes constitutes a reversible process where a concentration decrease in the aqueous phase induces desorption to obtain an equilibrium between both phases. Hence, the present study supports the findings of a study in vegetated stream mesocosms (Stang et al. 2014), where the concentration of experimentally applied pesticides in macrophyte samples increased also rapidly and continuously with the rising of the pesticide concentration in the aqueous phase, which led to an initial mass retention of the applied pesticides ranging from 7.9 to 27.0 %. In addition, the pesticide concentration in the macrophytes decreased also rapidly after the concentration maximum of the contaminant peak was reached and the pesticide concentration in the aqueous phase started to decline, resulting in pesticide concentrations below the LOQ within 6 h and a well-balanced recovery rate at the mesocosm outlets.

The potential impact of aquatic macrophytes on the fate and the distribution of pesticides in the aquatic environment is an undisputed fact, since a variety of authors have described the beneficial contribution of aquatic macrophytes on the retention of pesticides in surface waters or vegetated wetlands (Vymazal and Březinová 2015). However, it is also generally accepted that the compound affinity to adsorb to macrophytes and, thus, the degree of elimination from the aqueous phase are primarily governed by compound-specific properties. Hence, a variety of coefficients were proposed or examined concerning the predictability of a compound affinity to interact with aquatic macrophytes. Based on the findings of a batch equilibrium study with six pesticides, Crum et al. (1999) derived a mathematical formula that described the sorption coefficient (here log K_{D_math}) as a function of the compound solubility in water. In turn, a study by Stehle et al. (2011) identified the compounds K_{OC} as one of two pesticide-specific properties that determines the best retention of the investigated pesticides in VTS. Besides this, mass retention of three fungicides and two biocides as a function of the compound lipophility was observed in a study in vegetated stream mesocosms (Stang et al. 2013). Indeed, the suitability of the proposed coefficients to describe a compounds' tendency to adsorb to macrophytes is certainly not unexpected, especially since a relationship between solubility in water, lipophility, and the soil adsorption coefficient is generally assumed. Also, in the present study, the correlation analyses on the basis of the pesticides logK_{D_Adsorp}, derived from the findings of the semi-static short-term exposure scenario, as a function of the physicochemical substance properties logK_{OW}, logK_{OC}, and logK_{D_math} revealed that sorption of the investigated pesticides to the macrophytes was significantly correlated with all of the considered coefficients, whereas the degree of correlation varied markedly (Fig. 4). The lowest correlation of the logK_{D_Adsorp} was found for the logK_{OW} (R^2=0.352; ρ=0.01; n=135), followed by the mathematically derived logK_{D_math} with a R^2=0.574; ρ=0.01; n=135. The analyses revealed that both coefficients tended either to overestimate or to underestimate the sorption to macrophytes, especially in the upper ranges of values. For instance, for the rather lipophilic compound tebufenozide (logK_{OW}= 4.25), a low logK_{D_Adsorp} of 0.72 was determined, while the less lipophilic bifenox (logK_{OW}=3.6) showed an obviously stronger tendency to adsorb to the macrophytes (logK_{D_Adsorp}=2.15). However, the compounds logK_{OC} was found to have the best predictive power (R^2=0.842; ρ=0.01; n=135) of the consulted coefficients to describe the compound's affinity to adsorb to macrophytes. This appears plausible when considering the function of the particular coefficients

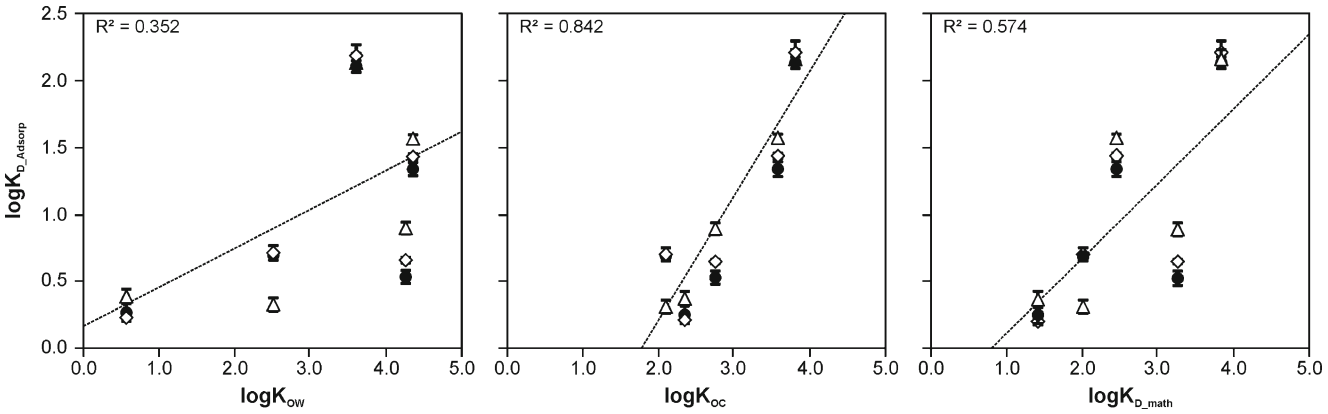


Fig. 4 Correlation of the experimentally derived logK_{D_Adsorp} (n=135) of the investigated compounds at the end of the adsorption period in treatments containing *E. nuttallii* (*open diamonds*), *C. demersum* (*black circles*), and *P. crispus* (*open triangles*) with different physicochemical properties of the investigated pesticides (logK_{OW}, logK_{OC}, and logK_{D_math}); for a better presentation, each *diamond*, *circle*, or *triangle* displays the logK_{D_Adsorp} as the mean±SD (n=9) per pesticide

and how they are derived. While the logK_{OW} displays the compound solubility in fat, the logK_{D_math} is determined by the compound solubility in water. However, sorption to organic matter is, beyond others, governed by a variety of molecular as well as structural properties of a compound (Schwarzenbach et al. 2005). Hence, the sole consideration of a single property of a substance regarding the sorption to macrophytes may be misleading. In contrast, the logK_{OC} is derived as a measure for the sorption of a compound to organic matter and, thus, its mobility in the environment (Schwarzenbach et al. 2005). Hence, the results of the present study indicate that a compounds logK_{OC} is the most reliable coefficient to estimate the sorption of a pesticide to aquatic macrophytes and thus support the findings of Stehle et al. (2011). Summing up, the results of the present study are considered valuable to improve the general understanding of the interaction between aquatic macrophytes and pesticides, especially with regard to enhance the targeted use of aquatic macrophytes within the scope of BMP. In addition, the data presented above may be utilized to refine aquatic exposure models that are commonly used to assess the fate of pesticides in the environment.

Conclusions

The present study was performed to gain knowledge on the dynamics that govern the interaction between aquatic macrophytes and pesticides in the aqueous environment. The results of the present study demonstrate that sorption and desorption of pesticides to and from aquatic macrophytes, respectively, are dynamic processes that are governed by principle physicochemical properties of the compounds. Nevertheless, it can be concluded that aquatic macrophytes can represent a temporary sink for pesticides and thus can help to mitigate pesticide loads in surface waters.

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