Diffusion of the Synthetic Pyrethroid Permethrin into Bed-Sediments

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Bed-sediments are a sink for many micro-organic contaminants in aquatic environments. The impact of toxic contaminants on benthic fauna often depends on their spatial distribution, and the fate of the parent compounds and their metabolites. The distribution of a synthetic pyrethroid, permethrin, a compound known to be toxic to aquatic invertebrates, was studied using river bed-sediments in lotic flume channels. trans/cis-Permethrin diagnostic ratios were used to quantify the photoisomerization of the trans isomer in water. Rates were affected by the presence of sediment particles and colloids when compared to distilled water alone. Two experiments in dark/light conditions with replicate channels were undertaken using natural sediment, previously contaminated with permethrin, to examine the effect of the growth of an algal biofilm at the sediment–water interface on diffuse fluxes of permethrin into the sediment. After 42 days, the bulk water was removed, allowing a fine sectioning of the sediment bed (i.e., every mm down to 5 mm and then 5–10 mm, then every 10 mm down to 50 mm). Permethrin was detected in all cases down to a depth of 5–10 mm, in agreement with estimates by the Millington and Quirk model, and measurements of concentrations in pore water produced distribution coefficients from the results after 42 days of exposure (12). In this case, the residence time of permethrin in the sediment was calculated from the ratio of trans/cis isomers on the assumption of the generally acknowledged lower persistence of the trans isomer (8, 9).

Introduction

Despite a long-term necessity for alternative insecticides, pyrethroids remain the option of choice as compared to the use of persistent organochlorines (1). The synthetic pyrethroid insecticide permethrin, a List II classified compound under the Dangerous Substance Directive (74/464/EC), failed 42.6% of monitored English and Welsh surface freshwaters for its set Environmental Quality Standard (EQS) value of 0.1 μg L⁻¹ in 1997 (2). Despite a low toxicity to mammals, its high toxicity to aquatic life (3), combined with the endocrine activity of some of its environmental metabolites (4) and its toxicity toward algae and cyanobacteria (5), demonstrated the significance of studying the behavior and fate of permethrin in freshwaters. Because permethrin manufacturing leads to the production of racemic isomer mixtures, it remains crucial to investigate the environmental fate of not only the “active” substance, in this case the cis isomer, but of both isomers of permethrin, because the trans isomer may significantly contribute to the overall ecotoxicological impact of release into the environment (6).

Permethrin is intensively used in the Northeast of England for moth-proofing in the textile industry, resulting in its detection in the Rivers Aire and Calder in the Humber catchment during a sampling campaign in 1995–1996 (7). While concentrations varied from 0.01 to 0.37 μg L⁻¹ in the whole-water samples, its hydrophobicity and affinity to sediment particles were demonstrated by concentrations measured in bed-sediments generally higher than 1000 and 200 μg kg⁻¹ dry weight of sediment for the cis and trans isomers, respectively (7). In this case, the residence time of permethrin in the sediment was calculated from the ratio of trans/cis isomers on the assumption of the generally acknowledged lower persistence of the trans isomer (8, 9).

Fine bed-sediment depositories found in low-flow environments are an important sink for hydrophobic micro-organic contaminants (MOCs), such as permethrin, after their introduction into freshwaters. Numerous studies relate the (bio)degradation of permethrin in soils generally (8, 9) or by specific microbial communities (10). Because few studies have focused on the sorption/degradation (batch sorption isotherm measurements and water-sediment column experiments) of permethrin (11, 12), its uptake/bioconcentration in periphyton or invertebrates (13), or movement in rivers by analyzing results from field studies, an understanding of its behavior in a riverine environment acknowledged to be contaminated with permethrin is essential. This work investigates the diffusive transport of cis- and trans-permethrin in bed-sediment from the River Calder, using experimental flumes to mimic lotic freshwaters. The flow over the sediment was chosen to be low enough to avoid suspension of sediment and to permit only diffusive transport, with minimal advective flow at the sediment–water interface (SWI). The movement of MOCs exclusively through diffusion in pore waters (PWS) is influenced by the following: (i) sorption to sediment particles/colloids and their components, for example, natural organic matter (OM) and clay; (ii) sorption to, and metabolism at the SWI by algal and bacterial biofilm (13); (iii) degradation through biotic/abiotic processes (12, 14); and (iv) bioturbation by bottom-dwelling macroorganisms, for example, oligochaetes worms, through physical mixing. These processes may be incorporated in models to predict the distribution, persistence, and movement of MOCs.

In the present study, vertical depth–distribution profiles of cis/trans-permethrin in a 50 mm-deep bed of sediment are given, both in the whole sediment and in pore waters. Crucially, the sediment-bed sectioning with a fine depth-resolution (ca. 1 mm) at the sediment–water interface allows the detailed characterization of processes occurring. Distribution coefficients from the results after 42 days of exposure.
were determined for each sediment section. The sediment surface was sampled at different time intervals to investigate changes in permethrin concentration with time and biofilm development.

Objectives of this work were as follows: (i) to study the fate of the compound in the absence of sediment by analyzing trans/cis-permethrin isomer diagnostic ratios in bulk solution; and (ii) to perform experiments involving a sediment-bed in dark/natural light conditions to examine the effect of an algal biofilm on permethrin diffusion into bed-sediment.

Materials and Methodology

**Chemicals.** cis-Permethrin (99.8% purity) was supplied by The Laboratory of the Government Chemist (Teddington, Middlesex, U.K.), while the trans isomer (99.8% purity) was obtained from the laboratory of Dr. Ehrenstorfer (D-86199 Augsburg, Germany). Decachlorobiphenyl (DCBP, 99.8% purity) was used as internal standard during the analysis of permethrin and was supplied by Chem Service/Greyhound (Augsburg, Germany). Decachlorobiphenyl (DCBP, 99.8% purity) was used as internal standard during the analysis of permethrin and was supplied by Chem Service/Greyhound (Birkenhead, U.K.). Pesticide-grade acetone, methanol, and ethyl acetate. AR-grade anhydrous sodium sulfate, and potassium hydrogen carbonate were all purchased from BDH (Poole, U.K.). Milli-Q water was provided by an Elix water purification system gradient A10 (Millipore). 200 mg L\(^{-1}\) stock solutions of cis/trans-permethrin in ethyl acetate were prepared for the production of working standards for the analysis and for spiking solutions for flume experiments.

**River Sediment.** Because a major interest resides in the study of a system identified as being in contact with permethrin (14), surface bed-sediment was collected from the River Calder (Humber catchment) in the Northeast of England at Methley Bridge (NGR SE409258) in May 2000. Sediments from a depth <5 cm were gathered from the riverbed using a stainless steel scoop. Sediments were subsequently sieved on-site (stainless steel. 2 mm mesh) and brought back in 10-L plastic cylinders to the laboratory where the overlying water was continuously aerated. The sediments were thoroughly mixed before being introduced into two replicate flumes.

**Experimental Flume Channels.** A diagram of the flume channels may be found in Allan et al. (15). Flume channels were initially developed to study nutrient dynamics in streams (16) and were later used for investigations on chemical fluxes at the SWI in the presence of natural diatom biofilms (17). The 2 m-long, 10 cm-wide acrylic channels are designed to bring into contact a 50 mm-deep bed of sediment with an aerated overlying solution with control of the water velocity. The water is recirculated using a magnetically coupled centrifugal pump, with the flow measured with a transducer and controlled by a butterfly valve. The preparation of a flat bed of sediment and the use of low flow rates (water velocity of 10 cm s\(^{-1}\) and flow rate of 5 L s\(^{-1}\)) avoided sediment resuspension and permitted the study of transport exclusively through diffusion in pore waters. The flumes were housed in a fluvarium with a glass roof allowing light to reach the channels. The channels were immersed in a tank with flowing water from the River Frome that passes through the fluvarium.

**Experiments without Sediment.** The channels were used in two experiments without a sediment bed. Approximately 24 L of 10 mmol L\(^{-1}\) KHCO\(_3\) (same ionic strength as river water) was recirculated, with aeration of the bulk solution using glass frits. Dissolved oxygen (DO), pH, electrical conductivity, and temperature were measured at different times of the day during the 15 day-experiments. The pesticide solution was evaporated to near dryness under nitrogen flow and reconstituted in acetone to obtain 2 mL spiking solutions containing ca. 1000 \(\mu g\) of each isomer of permethrin for all spiking solutions, except for the first experiment where the mass of trans permethrin was 1200 \(\mu g\). At the start of the experiment, the bulk solution of each channel was spiked and samples were collected for analysis. The water volume was maintained constant by addition of deionized water. During the two experiments, channel 1 was kept in the light, while channel 2 was kept in the dark. The bulk solution in the second experiment was previously in contact with river sediment from the river Calder for a 6 week-period. Details of the experimental conditions for temperature, conductivity, pH, and dissolved oxygen may be found in previous work (15).  

**Experiments with a Sediment-Bed in Light/Dark Conditions.** Two experiments of duration of 6 weeks were conducted. In the first, the channels were in the dark, while the second experiment was in light conditions permitting the growth of a photosynthetic biofilm. A flat sediment-bed was layered in the channels, 20 L of KHCO\(_3\) (10 mmol L\(^{-1}\)) was added, and the aerated solution was recirculated at 10 cm s\(^{-1}\). The sediments were left for 6 days before spiking with a pesticide mixture containing 1 mg of each isomer of permethrin in 2 mL of acetone. The bulk solutions were sampled as described above. Populations of *oligochaete* worms were left to develop naturally. Surficial sediments (ca. 1 mm depth) were collected using a spatula with a knife-edge, and development of the surface biofilm was monitored weekly during the experiment under light conditions. The penetration of dissolved oxygen into the sediment was measured using microelectrodes as described previously (17).  

At the end of the experiments, after a cautious removal of the overlying solution, the sediment-bed was longitudinally sectioned using a precalibrated slicing tool, at 1 mm intervals down to 5 mm depth, then 5 mm to 10 mm depth, and every 10 mm down to 50 mm depth. The tool had been designed to fit the width of the channels and to slide on the edges; for experiments in light conditions, the algal biofilm was sampled separately. Sediments were subsequently subsampled for pesticide analysis and characterization. The porosity, organic matter content, chlorophyll *a*, extrapolymeric substances secreted by microorganisms to attach to surfaces, and surface area were determined for each sediment sample, and the whole-sample and clay mineralogy were determined for the whole sediment. 73% (w/w) of the total mineral content was quartz, and clays were all under 5%. The sediment also included calcite, albite, microcline, kaolinite, and hematite. After centrifugation, pore water was also analyzed for dissolved silicon. Methods and equipment used for these analyses are described in detail elsewhere (15).  

**Extraction and Analysis of Permethrin.** The extraction of permethrin from water and sediment samples was performed using methods described in detail in Allan et al. (15). In brief, overlying and pore-water samples were extracted by solid-phase extraction with an ISOLUTE 6 mL silica-bonded C\(_{18}\) (CE) SPE cartridge. The cartridge was initially conditioned with 6 mL of methanol for 5 min, and then replaced by 10 mL of milli-Q water, before processing 300 mL of sample. The sample bottle was rinsed with ethyl acetate and permethrin eluted from the column using ethyl acetate. Extracts were dried and reduced under a gentle flow of high-grade nitrogen to 2 mL.

Samples of sediment sections were centrifuged with a MSE high-speed 18 centrifuge for 60 min at 6000 rpm. To minimize adsorption of permethrin on hardware surfaces, solvent-rinsed stainless steel tubes were used. Interstitial waters were subsequently extracted as described above. Sediment samples were freeze-dried prior to supercritical fluid extraction with a Dionex SFE-703 system. Resulting ethyl acetate extracts were subsequently reduced under nitrogen to 1–2 mL. All extracts were further dried prior to analysis. One-milliliter samples in ethyl acetate were spiked with an internal standard using 10 \(\mu L\) of DCBP (106 \(\mu g\) mL\(^{-1}\)) prior to analysis by GC/MS. The analysis was performed using a Perkin-Elmer Autosystem XL GC coupled to a Turbomass.
mass spectrometer. Column and carrier gas specifications, injector, and oven temperature may be found in Allan et al. (15). The detection was performed in positive ionization (+EI at +70 eV), and single-ion recording was used for the detection after main and confirmation ions were selected in full scan (M/2 e [50–500]). Main and confirmation ions were 163 and 183 for cis- and trans-permethrin, and 178 and 214 for DCBP. Recoveries for the SPE procedure were 97% (±6%) and 77% (±4%), and for SFE of 81% (±15%) and 80% (±4%) for the cis and trans isomers of permethrin, respectively (standard deviations in brackets).

Results and Discussion

Vertical Concentration Profiles and Temporal Changes in Overlying Solution. Temporal variation in concentrations of cis- and trans-permethrin in bulk solution of both experiments generally showed maximum concentrations of 20 $\mu$g L$^{-1}$ (Figure 1) at the first sampling event (20 min) which then dropped rapidly, because of sorption to the sediment-bed and acrylic edges of the channels (18). As the vapor pressure of permethrin is very low, ca. $1.3 \times 10^{-6}$ to $1 \times 10^{-5}$ Pa (19), the combination of mixing and rapid sorption after spiking prevented the expected nominal concentration (50 $\mu$g L$^{-1}$) from being attained.

Concentrations of both isomers at the end of the experiments reached values close to 1 $\mu$g L$^{-1}$ in dark conditions (Figures 1a and 2a) and 0.1 $\mu$g L$^{-1}$ in light conditions (Figures 1d and 2d), respectively, suggesting that this 10-fold difference was caused by the biofilm growth in the channels providing additional surfaces for sorption.

The measured concentrations in the sediment bed were consistently higher for cis-permethrin as compared to trans-permethrin. In all cases, whole-sediment concentration for both isomers were found highest for the top and showed a sharp decrease with depth, to values ~10 $\mu$g kg$^{-1}$ (dry wt) deeper in the sediment, generally revealing a diffusive penetration of permethrin to 5–10 mm deep in the sediment bed after 6 weeks. Total concentrations of permethrin determined by sampling the bulk sediment prior to its introduction into the channels varied between 13 and 15 $\mu$g kg$^{-1}$ for the cis isomer, and 1 and 3 $\mu$g kg$^{-1}$ for the trans isomer. Maximum cis-permethrin concentrations were 1512 and 1108 $\mu$g kg$^{-1}$ (dry wt) for channels 1 and 2 under dark conditions (Figure 1b) and 1624 and 1604 $\mu$g kg$^{-1}$ (dry wt) for channels 1 and 2 under light conditions (Figure 1e).

Maximum concentrations of trans-permethrin were 962 and 691 $\mu$g kg$^{-1}$, and 734 and 805 $\mu$g kg$^{-1}$ (dry wt) for the top layer of channels 1 and 2 under dark and light conditions, respectively (Figure 1b and e). Permethrin was detected in pore waters down to a depth of 30 mm. cis-Permethrin also exhibited higher pore-water concentrations than the trans isomer. Profiles for both isomers in the experiment in the dark gave highest concentration at 4–5 mm below the surface (Figure 1c and f). Highest pore-water concentrations observed for the experiment under light conditions were found just below the surface (Figure 2c and f). The presence of the biofilm may have reduced interactions between bulk and pore waters. A linear regression across pore-water concentration gradients just below the sediment surface, assuming a diffuse boundary layer of ∼0.5 mm, allowed the calculation of hypothetical final bulk solution concentrations in the range 0.06–0.15 and 0.3–2.5 $\mu$g L$^{-1}$ for both isomers in dark and light, respectively. In dark condition, bulk concentrations were found higher than those calculated with the regression (Figures 1a and 2a), while in the light, hypothetical values overestimated actual final bulk solution concentrations (Figure 1d and e). Maximum pore-water concentrations generally varied around the value of 1 $\mu$g L$^{-1}$. It is likely that the increasing concentrations measured for the 10–20 mm-deep section are the result of the extraction of sediment particles simultaneously to pore water because of the low porosity of the deeper sections of sediment.

Regardless of decreasing bulk-water concentrations, permethrin concentrations in the whole sediment at the surface

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**FIGURE 1.** Temporal changes in overlying solution concentration (a and d), and resulting whole sediment (b and e) and pore water (c and f) concentration—depth profiles for cis-permethrin in dark (a, b, and c) and light (d, e, and f) conditions for channels 1 (○) and 2 (□).

**FIGURE 2.** Temporal changes in overlying solution concentration (a and d), and resulting whole sediment (b and e) and pore water (c and f) concentration—depth profiles for trans-permethrin in dark (a, b, and c) and light (d, e, and f) conditions for channels 1 (○) and 2 (□).
remained high. Although the pore-water profiles indicate a transfer of permethrin from the sediment, this was not shown by the sediment profile. Slow sorption/desorption or irreversible sorption phenomenon involving organic matter and/or the biofilm may be strongly expected in this system (20).

Despite high concentrations of cis- and trans-permethrin in the sediment near the surface, pore-water concentrations remained low, illustrating the hydrophobicity of permethrin. This is further demonstrated by permethrin diffusing to only approximately 5–10 mm deep in the sediment in 42 days, while in the same experimental approach, simazine and lindane were shown to diffuse to 30–50 mm deep in the sediment (15).

Sharom and Solomon (11) investigated the diffusion of permethrin into lake sediment using column experiments. Permethrin concentrations were determined in the sediment after slicing it into two 1 cm-layers. Despite the high organic matter content of that lake sediment (43% w/w), over 40% of the total radiolabeled permethrin apparently remained in solution 4 days after spiking. It may have been the result of dissolved organic matter initially present in the sediment, because the water and sediment phases were thoroughly mixed before settling of the sediment. After 8 days, permethrin was detected in the second centimeter-slice of the sediment layer, which is rapid when compared to results of the present study. In the present work, a low water-velocity certainly produced a diffuse boundary layer that may have resulted in mass transfer resistance reducing the overall fluxes of chemicals into the sediment bed. However, because Sharom and Solomon’s work was undertaken without mixing of the bulk solution (i.e., larger distance to travel by diffusion), further reduction of permethrin diffusion may be expected, which does not corroborate our findings. In another effort to model organic contaminant transport into lake sediment, diffusion of Arochlor 1242 was investigated in laboratory experiments (21). The range of log $K_{OC}$ values for PCB congeners constituting Arochlor 1242 is similar to values compiled from the literature for permethrin (19). Therefore, the diffusion of Arochlor 1242 to a depth of less than 10 mm in 43 days is in good agreement with results showed here. Studies on the diffusion of carbendazim in sediment by Koelmans and co-workers (22) revealed a behavior similar to those of simazine and lindane, in agreement with their respective hydrophobicity. In the modeling of concentration profiles of carbendazim, Koelmans used organic matter-normalized Freundlich coefficients to describe the sorption of the fungicide. Organic-matter-dependent sorption was absolutely crucial because, as seen in the present work, after settling of the sediment bed, the organic matter content of the top layer was significantly higher than for deeper sediment and needed to be accounted for. Compaction of the sediment bed led to porosity profiles similar to those measured in the present work. The strong affinity of permethrin to soil/sediment particles is a characteristic shared by many pyrethroid insecticides. In soil leaching experiments with deltamethrin, 80 pore volumes did not achieve more than 3–8% leaching of the insecticide (23). Despite advective fluxes, over 90% of deltamethrin remained in the top 20 mm of soil columns.

**Isomer Ratios in Overlying Water, Pore Water, and Sediment.** Investigation into temporal changes of the ratio of concentrations of trans/cis-permethrin may reveal differences in degradation rates between the two isomers (11) and provide information about retention times of permethrin in sediments and water (14):

$$r_{t/c} = \frac{C_{t}}{C_{c}} = \exp[(k_{cis} - k_{trans})t]$$

(1)

where $r_{t/c}$ is the ratio of permethrin at time $t$ (24), $C_{t}$ and $C_{c}$ are initial concentration of both isomers at time $t = 0$, and $k_{cis}$ and $k_{trans}$ are degradation rate constants for the cis and trans isomers, respectively. However, in experiments in light conditions, the photoisomerization of the trans into the cis isomer results in the following equation:

$$r_{t/c} = \frac{C_{t}}{C_{c}} = \exp[(k_{cis} - k_{trans} - 2k_{photo})t]$$

(2)

where $k_{photo}$ represents the first-order photoisomerization rate constant (s$^{-1}$). Temporal variations in the trans/cis concentration ratio in water were modeled with first-order kinetics, and, by the difference between eqs 1 and 2, photoisomerization rates were obtained. Temporal changes in the ratios of the isomer concentrations in deionized water, river water, and for the overlying solution from the set of experiments with a bed of sediment demonstrated a larger difference in degradation rates in the channel kept in light as compared to the one in dark conditions. In the case of the experiment with sediment, photoisomerization rates were calculated from the differences in degradation rates for averaged results in the dark and averaged results from the experiment in light conditions. Photoisomerization rates obtained using river water ($8.20 \times 10^{-8}$ s$^{-1}$, half-life of 98 days) and for the experiment with a sediment-bed ($7.83 \times 10^{-8}$ s$^{-1}$; half-life of 102 days) were consistently lower than using deionized water ($9.02 \times 10^{-8}$ s$^{-1}$, half-life of 89 days). The ratio of isomers in the surface sediment/biofilm samples showed the least difference in degradation rates between the two isomers. This suggests that sorption to sediment or algae cells during experiments with a bed of sediment, or to colloids and dissolved organic matter using river water, reduces the availability of the trans isomer for photoisomerization, but also the overall availability of permethrin to microorganisms capable of metabolizing it (11).

Trans/cis isomer concentration ratios were also investigated in the top four sediment sections and biofilm. At the end of the experiment under dark conditions, the average pore water and whole-sediment concentration ratios for the top 4 mm of sediment were 0.76 ($\pm 0.08$) and 0.68 ($\pm 0.10$), respectively. For the experiment in the light, pore water and whole sediment ratios were 0.57 ($\pm 0.03$) and 0.49 ($\pm 0.06$), respectively. While no significant difference between whole-sediment and pore water ratios was observed (t-test, $P > 0.05$), significantly lower ratios were observed in the experiment under light conditions both for the whole sediment and in pore waters as compared to ratios for the experiment in the dark (t-test, $P < 0.01$). The average trans/cis ratio in the biofilm at the end of the experiment in the light was 0.41 ($\pm 0.01$). In all cases, the trans isomer was observed to disappear more rapidly than the cis isomer, and losses were highest in light conditions. As average temperatures were similar for both experiments (15), it may be unlikely that losses were due to temperature-induced higher microbial metabolism (8). This accelerated degradation of trans-permethrin in the light suggests that processes linked to the increase in biological activity in surficial sediments under light conditions affect the fate of trans-permethrin in sediments.

**Experimentally Determined Distribution Coefficients, $K_{d}$’s.** The measurement of pore-water concentrations as well as total sediment concentrations allowed the calculation of distribution coefficients, $K_{d}$’s, for each of the sections down to 30 mm below the surface. The quantification of the organic matter content also allowed the calculation of organic matter-normalized distribution coefficients ($K_{OM}$). Distribution coefficients for both isomers are the highest for the top layer, with values in the range of 2000–3700 L kg$^{-1}$ in the experiment in the dark (channels 1 and 2) and 730–5800 L kg$^{-1}$ for the
experiment in the light (channels 1 and 2). Significantly lower $K_d$ values observed for both isomers in channel 1 in the light were the result of the relatively higher pore-water concentrations (Figures 1f and 2f). Distribution coefficients decreased very rapidly with depth. Calculated values for both experiments are not significant.

**TABLE 1. Examples of Distribution ($K_d$) and Organic Matter-Normalized Distribution Coefficients ($K_{OM}$) Determined at the End of the Experiments for Each Sediment Layer for Channel 2 (Depth is in mm)**

<table>
<thead>
<tr>
<th>Sediment Sections (mm)</th>
<th>cis-permethrin</th>
<th>trans-permethrin</th>
</tr>
</thead>
<tbody>
<tr>
<td>dark</td>
<td>light</td>
<td>dark</td>
</tr>
<tr>
<td>0–1</td>
<td>2631$^a$</td>
<td>35 007$^b$</td>
</tr>
<tr>
<td>1–2</td>
<td>1471</td>
<td>25 845</td>
</tr>
<tr>
<td>2–3</td>
<td>309</td>
<td>66 449</td>
</tr>
<tr>
<td>3–4</td>
<td>46</td>
<td>1069</td>
</tr>
<tr>
<td>4–5</td>
<td>49</td>
<td>1106</td>
</tr>
<tr>
<td>5–10</td>
<td>15</td>
<td>1279</td>
</tr>
<tr>
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<td>24</td>
<td>493</td>
</tr>
<tr>
<td>20–30</td>
<td>64</td>
<td>1496</td>
</tr>
</tbody>
</table>

$^a$ Distribution coefficients $K_d$. $^b$ Organic matter normalized-distribution coefficients $K_{OM}$. $^c$ Differences in $K_d$ between light and dark conditions for both channels are not significant.

**FIGURE 3. Profiles of porosity (% v/v), organic matter (% w/w), surface area (m$^2$ g$^{-1}$), and chlorophyll a (µg g$^{-1}$) in the sediment-bed under dark conditions in channels 1 (●) and 2 (□), respectively, and light conditions in channels 1 (▲) and 2 (●) (VOL. 39, NO. 2, 2005 / ENVIRONMENTAL SCIENCE & TECHNOLOGY).**

It is believed to be the result of compaction of the sediment bed, supported by surface area profiles (Figure 3c) and porosity gradients. The reparation of fine sediment particles, with high surface area and greater organic matter coating (27), resulted in higher porosity, also induced a higher organic matter content at the surface. We have seen that organic matter, surface area, and porosity profiles were induced by compactions. Thus, permethrin dissolved in bulk solution will sorb preferentially to smaller particles present in higher numbers at the sediment surface. This may augment the bioavailability of permethrin to benthic organisms (28), for example, certain oligochaete worms which have been shown to feed selectively on fine particulate material with a high organic matter content (29). In this paper, researchers demonstrated that the bioconcentration of benzo(a)pyrene (BaP) and polychlorobiphenyls (PCB) differed for *Lumbriculus variegatus*, an oligochaete and chironomid larvae (29). The oligochaete was found to accumulate BaP with the highest efficiency from selective feeding on sediment, while the accumulation of PCB by chironomids was greatest from the algae. In any cases, trophic transfer of permethrin in the river food web may be strongly expected despite the high sorption capacity of permethrin.

While no significant differences in OM were observed between dark and light conditions, profiles of chlorophyll a illustrate the presence of an autotrophic biofilm. Even in dark conditions, a slight increase in chlorophyll a was detected (Figure 3d). The presence of this biofilm may have provided additional organic surface/membranes for sorption. Despite trends of specific surface area profiles showing an increase toward the surface, the value for the top layer in both experiments is slightly lower, possibly explained by the presence of filamentous algal material or extraplasmic substances.

The comparison of $K_d$ values calculated for each of the isomers did not reveal major differences, although values for the trans isomer tend to be slightly lower than those for the cis isomer. However, it is hard without quantification of metabolites and accurate mass balances to distinguish whether this difference is the result of sorption or degradation.

Differences in distribution coefficients that might have been expected between the experiments in light or dark conditions were not observed. The separate sampling of the biofilm at the end of the experiment in light conditions may have prevented the detection of higher $K_d$'s. Equally, colloids and dissolved organic matter were not accounted for in pore water and may have a substantial effect on observed $K_d$'s. Therefore, calculated $K_d$'s in Table 1 may not reflect the true distribution coefficients between pore water and sediment particles (30). Valsaraj and co-workers (31) observed DOC diffusion out of the sediment, and the creation of DOC...
concentration gradients not correlated to TOC profiles in the sediment. This DOC gradient may explain the shape of pore-water concentration profiles observed here, particularly for the results in the dark. In experiments by Lin and co-workers (32) investigating diffusive fluxes of 2,2′,4,4′-tetrachlorobiphenyl in pore waters of low ionic strength, sediment aeration resulted in a decrease in the aromaticity of the dissolved organic matter (DOM) and also in DOM concentration in pore waters. In the present work, dissolved oxygen was shown to penetrate between 2 and 4 mm deep in the sediment bed.

The range of $K_d$’s found here was used as input in the Millington and Quirk model ($M$–$Q$) to determine whether the observed depths of diffusion of permethrin were in agreement with sediment partitioning data and other studies. This equation often used to predict solute diffusivity in soil (33) was employed to estimate the effective depth of diffusion, $z$, of permethrin into the bed-sediment:

$$z = \sqrt{\frac{4D_w \epsilon}{\epsilon + \rho_s K_d}}$$  \hspace{1cm} (3)

where $D_w$ is the molecular diffusivity of permethrin in water (m$^2$ s$^{-1}$), $\epsilon$ is the sediment porosity, $\epsilon + \rho_s K_d$ accounts for sediment tortuosity, $\rho_s$ is the sediment density (kg L$^{-1}$), and $K_d$ is the distribution coefficient of permethrin between the sediment and water. With a diffusion coefficient of $3.38 \times 10^{-10}$ m$^2$ s$^{-1}$ obtained using the Wilke–Chang equation (15), estimates were calculated for porosities varying between 0.4 and 0.8 (see Figure 3a), $K_d$’s between 50 and 5500 L kg$^{-1}$, and a sediment density of 2.5 kg L$^{-1}$. With an upper $K_d$ limit of 5500 L kg$^{-1}$, permethrin was estimated to diffuse to a depth of 0.4–0.5 mm, while with a $K_d$ of 50 L kg$^{-1}$, the depth of diffusion was calculated between 3.9 and 5.4 mm (Table 2). Therefore, observed values are in good agreement with estimates given by the $M$–$Q$ model. However, values calculated are only estimates, and their use may be limited as permethrin concentration in the overlying solution was not constant and partition coefficients may vary with time. Applying this methodology to data from another Sharom and Solomon (11), for example, a $K_d$ of 389 L kg$^{-1}$, revealed a depth of diffusion of only 1.8–2.0 mm as compared to the observed >10 mm observed diffusion. A comparison to less hydrophobic pesticides, lindane, simazine, and carbendazim, from other studies is also provided in Table 2 (15, 22).

**Temporal Changes in Surface Sediment/Biofilm Concentrations.** Changes occurring at the sediment surface were monitored throughout the experiments in light and dark conditions (Figure 4). Under dark conditions, a slight oligochaete worm activity (evidenced by recently deposited faecal pellets on less than 10% of the surface area) was observed, but no biofilm growth was detected. Conversely, 2 weeks into the experiment in the light, just less than 40% of the surface was heterogeneously covered by diatoms with the presence of few filamentous algae. Four weeks after the start of the experiment, half of the sediment surface was covered by diatoms and under 20% of the surface presented filamentous algae. Diatoms and filamentous algae represented approximately 80% of the total surface of the sediment at the end of the experiment, while worm activity was observed to decrease from 10% to 15% to less than 3% during the 6-week experiment. Microscopic observation (×40) revealed the presence of large numbers of *Synechococcus* sp., *Nitzschia* sp., and *Navicula* sp. diatoms. In lower numbers, green algae included *Closterium* sp., *Sceneudesmus*, or *Cocconeis* sp. Filamentous algae were mainly *Microspora* sp. and blue-green algae. Dissolved silicon (34) and oxygen profiles in sediment pore water (not shown here) as well as chlorophyll a profiles (Figure 3d) clearly supported the presence of the biofilm. The top 1 mm of the sediment bed sampled during the experiment in the light was analyzed for permethrin. Results presented in Table 3 generally show an increase in concentrations of each isomer of permethrin with time in the top section of sediment in channel 1. A similar trend, although not as clear, is also observed in channel 2. Concentrations of trans-permethrin were generally half of those of the cis isomer. Because permethrin is highly hydrophobic, it does not bind only to sediment but also to the acrylic edges of the channels, creating a three-way interaction between the sides of the channels, the bulk water, and the sediment surface. As the concentration in the bulk water decreased, compounds desorbed from the edges and subsequently sorbed to the sediment bed. The affinity of permethrin to the sediment surface might also have been amplified by the growth of the algal and bacterial biofilm at the surface. This is supported by concentrations of permethrin in the filamentous algae (sampled separately at the end of the experiment) of 3379 and 2523 µg kg$^{-1}$ DW of the cis isomer and 1370 and 1035 µg kg$^{-1}$ DW of the trans isomer in channels 1 and 2.

<table>
<thead>
<tr>
<th>log $K_{ow}$</th>
<th>$K_d$ (L kg$^{-1}$)</th>
<th>time (days)</th>
<th>porosity</th>
<th>predicted*</th>
<th>observed*</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>permethrin</td>
<td>6.1</td>
<td>50–5500</td>
<td>42</td>
<td>0.5–0.8</td>
<td>0.4–5.4</td>
<td>5–10</td>
</tr>
<tr>
<td></td>
<td>389</td>
<td>28</td>
<td></td>
<td>~0.95</td>
<td>1.8–2.0</td>
<td>&gt;10</td>
</tr>
<tr>
<td>lindane</td>
<td>3.7</td>
<td>1–2600</td>
<td>42</td>
<td>0.5–0.8</td>
<td>1.5–2.1</td>
<td>&gt;10</td>
</tr>
<tr>
<td></td>
<td>343</td>
<td>28</td>
<td></td>
<td>0.5–0.8</td>
<td>0.7–3.8</td>
<td>30–50</td>
</tr>
<tr>
<td>simazine</td>
<td>2.1</td>
<td>1–100</td>
<td>42</td>
<td>0.5–0.8</td>
<td>3.4–40.2</td>
<td>30–50</td>
</tr>
<tr>
<td>carbendazim</td>
<td>2.2</td>
<td>1–3</td>
<td>60</td>
<td>0.2–0.8</td>
<td>5.4–65.3</td>
<td>&gt;60</td>
</tr>
</tbody>
</table>

*Depth of penetration calculated with the Millington and Quirk model. *Experimentally determined depth of penetration.


**TABLE 3. Temporal Changes in Permethrin Concentrations in the Top 1-mm Section of Sediment/Biofilm and Observed Sediment Top Layer/Overlying Water Kd’s during the Experiment in Light Conditions**

<table>
<thead>
<tr>
<th>Time after Spiking (days)</th>
<th>cis-permethrin (µg kg⁻¹ DW)</th>
<th>trans-permethrin (µg kg⁻¹ DW)</th>
<th>Channel 1</th>
<th>Channel 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>concentration</td>
<td>observed Kd e (L kg⁻¹)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>c</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>679 ± 102</td>
<td>378 ± 16</td>
<td>5660</td>
<td>14 240</td>
</tr>
<tr>
<td>17</td>
<td>728 ± 110</td>
<td>391 ± 16</td>
<td>10 400</td>
<td>16 200</td>
</tr>
<tr>
<td>24</td>
<td>1222 ± 229</td>
<td>653 ± 27</td>
<td>16 910</td>
<td>24 640</td>
</tr>
<tr>
<td>31</td>
<td>1542 ± 232</td>
<td>702 ± 29</td>
<td>35 580</td>
<td>61 040</td>
</tr>
<tr>
<td>42 e</td>
<td>1624 ± 244</td>
<td>734 ± 30</td>
<td>42 16 240</td>
<td>34 790</td>
</tr>
<tr>
<td>42 e</td>
<td>3379 ± 507</td>
<td>1370 ± 555</td>
<td>42 14 747</td>
<td>606.0</td>
</tr>
</tbody>
</table>

* Top section of sediment/overlying water distribution coefficients. * Chlorophyll a content. * Organic matter content obtained by ignition at 550 °C. * Algal biofilm concentrations at the end of the experiment in light conditions.

respectively (Table 3). These values were higher than those determined in the top layer of sediment after 42 days. Previous work had shown the significance of periphyton as a sink for permethrin, with both slow degradation and a tendency for slow desorption (13) and bioconcentration factors of 100. The trans isomer was also observed to disappear more rapidly than the cis isomer. Observed partition coefficients calculated in Table 3 are in the same range (10 ± 800) × 10¹ L kg⁻¹ as those determined for different organic contaminants (with log Kow's similar to those of permethrin) for a bacterial biofilm grown with natural river water (35) in a roto-torque reactor.

In addition, Table 3 gives partition coefficients at the various time intervals between the bulk water and the top layer of sediment. These coefficients show an increase, due in part to decreasing bulk solution concentrations. Despite these decreasing concentrations, permethrin was not shown to desorb from the sediment particles. Sorption isotherms are often determined between sediment and water, but influences by the bacterial/algal growth are frequently neglected. However, our results emphasize the importance of accounting for the effects of biofilms.

It is often difficult to distinguish between sorption and degradation phenomena, particularly when investigating a natural environment for an extended period of time. Fifty percent and 44% of cis-permethrin in channels 1 and 2, respectively, and 40% of trans permethrin in each channel, were recovered at the end of the experiment in the dark. Mass balances at the end of the experiment in the light resulted in the recovery of 42% and 54% of the cis isomer and 29% and 28% of the trans-permethrin isomer in channels 1 and 2, respectively. Mass balances calculated for the trans isomer are significantly different (t-test, P < 0.01) whether the experiment was run in the light or not. This result is consistent with photoisomerization rates and trans/cis isomer ratios in sediment, pore water, and biofilm determined above. These mass balances, however, show that half of permethrin is usually degraded in these experiments over the 42-day period.

In summary, diffusive transfer of permethrin into bed-sediment was shown to be a slow process, with permethrin generally detected at maximum depths between 5 and 10 mm below the sediment surface after 42 days. Photoisomerization rates in bulk solution, deduced from changes in trans/cis isomer ratios, were observed to decline in the order: deionized water > river water > experiments with a sediment-bed. This indicates that the presence of surfaces for sorption, for example, dissolved organic matter, algal biofilm, or sediment particles, reduces the availability of trans permethrin. Analysis of trans/cis isomer ratios in bed-sediments revealed significantly greater losses of trans-permethrin in the experiment involving a biofilm. Irreversible sorption to organic matter, the presence of a diffuse boundary layer at the sediment–water interface inducing mass transfer resistance, partitioning into the biofilm, or the presence of pore-water colloids are some explanations that may be brought forward to justify the none-releas of permethrin from the sediment bed when the overlying water concentrations decreased. This issue, however, requires further investigation. It has been shown that the presence of an algal biofilm influences fluxes of contaminants across the interface and their spatial distribution.

Higher concentrations in pore water at the surface of the sediment as compared to the bulk water represent a danger to benthic organisms. This work has shown that specific association of permethrin, and more generally hydrophobic micro-organic contaminants, with fine sediment particulates that are compacted at the surface has the potential to enhance the availability of permethrin to the selective feeding behavior of certain benthic organisms. In addition, the high affinity to the algal biofilm suggests that permethrin may remain available for food-web bioconcentration. While it is believed that sorption to coarse sediments may reduce the availability of hydrophobic contaminants to benthic invertebrates, this work shows that sorption to specific compartments of the sediment bed, for example, fine particles, algal cell, and bacterial biofilm, may enhance its bioavailability to macro-invertebrates or pelagic organisms.

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**Literature Cited**


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