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Distribution of pyrethroid insecticides in secondary wastewater effluent

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Abstract

Although the freely dissolved form of hydrophobic organic chemicals may best predict aquatic toxicity, differentiating between dissolved and particle bound forms is challenging at environmentally relevant concentrations for compounds with low toxicity thresholds such as pyrethroid insecticides. We investigated the distribution of pyrethroids among three forms: freely dissolved, complexed with dissolved organic carbon (DOC), and sorbed to suspended particulate matter, during a yearlong study at a secondary wastewater treatment plant. Effluent was fractionated by laboratory centrifugation to determine if sorption was driven by particle size.

Linear distribution coefficients were estimated for pyrethroid sorption to suspended particulate matter (K_{id}) and dissolved organic carbon (K_{idoc}) at environmentally relevant pyrethroid concentrations. Resulting K_{id} values were higher than those reported for other environmental solids, and variation between sampling events correlated well with available particle surface area. Fractionation results suggest that no more than 40% of the pyrethroid remaining in secondary effluent could be removed by extending settling periods. Less than 6%of the total pyrethroid load in wastewater effluent was present in the dissolved form across all sampling events and chemicals.

Keywords

Pesticides; Pyrethroids; Adsorption; Bioavailability; Municipal effluents

INTRODUCTION

Pyrethroids are insecticides widely used in urban environments by consumers and professional pesticide applicators. These compounds have low water solubility (~ug/L) and are hydrophobic, with log K_{ow} values ranging from 4 to 7 [1]. Pyrethroids have a strong affinity for the organic phase but have been shown to wash off application sites, associated with dissolved organic carbon (DOC) [2] or sediment [3]. Once transported to urban creeks, toxicity to aquatic life [4–6] has been observed in the water column and bed sediments. Off-target transport into urban waterways [7], presence in household dust [8] and drain disposal [9] have led to the presence of pyrethroids in municipal wastewater and sludge in Europe

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SUPPLEMENTAL DATA

Supporting information and figures are included in a supplemental data file.

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[10–13] and the United States [5, 9]. While removal efficiencies between 84% [9]–99% [12] have been reported for permethrin from water depending on the influent concentrations, the amount remaining in the effluent may still be of concern to aquatic life. For example, in the United Kingdom, Turner et al. concluded that discharges from a local treatment plant may not be within the permitted limits (Environmental Quality Standard of 10 ng/L) if the plant has limited dilution [10].

In California, the Central Valley Regional Water Quality Control Board has developed acute and chronic water quality criteria recommendations for 5 pyrethroids in the Sacramento River and San Joaquin River basins [14]. The standards are in the low/sub parts per trillion range and previous research indicated that municipal wastewater treatment plants may be significant sources of pyrethroids to the San Francisco Bay, at least under dry flow conditions [5]. The Sacramento Regional Wastewater Treatment Plant (SRWTP) discharges effluent into the Sacramento River and could be affected if a total maximum daily load (TMDL) standard is adopted.

Research indicates that pyrethroid toxicity to aquatic organisms can be mitigated by the presence of dissolved organic carbon (DOC) and/or suspended particulate matter (SP) [15–17]. The Criteria Reports note the distinction between the freely dissolved concentration and whole water concentration as well. For example, the permethrin report states “It is recommended that the freely dissolved permethrin concentration is measured for criteria compliance because this appears to be the best predictor of the bioavailable fraction” [14].

Polybrominateddiphenylether (PBDEs) congeners, halogenated hydrophobic compounds, have been shown to be discharged in effluent sorbed to SP [18], and it appears that pyrethroids behave similarly. A study with four different treatment techniques in Spain found that pyrethroids were mainly associated with the SP in wastewater samples [19]. A study by Budd et al. illustrated that maximum removal of pyrethroids in constructed wetlands for the treatment of agricultural tailwater depended on the size and composition of the particles removed [20]. Previously reported pyrethroid effluent concentrations in California have been whole water values, with no distinction made between amounts bound to different phases (SP, DOC) in the effluent.

The distribution of chemicals among the sorbed, complexed or freely dissolved forms can be described in many cases using linear distribution coefficients, K_{id} and K_{idoc}. Values of distribution coefficients reported for pyrethroids have mainly been estimated from those for sediments or natural organic matter. Sorption studies have been conducted with sludge and other hydrophobic contaminants such as PBDEs, polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). PBDEs sorption was shown to increase through the treatment process with a higher K_{id} value in effluent than in influent [18]. The study of PCB and PAH sorption to different types of sludges showed that sludge physical and chemical properties were more important than micropollutant characteristics [21]. SRWTP discharged effluent contains a low suspended solids concentration (<10 mg/L), but fine particles could provide ample surface area for sorption. SP and DOC generated by a wastewater treatment process will have different properties (particle size distributions, organic content and character) that affect the sorption/complexation of pyrethroids. Our study characterizes the sorption of pyrethroids to SP and DOC in a secondary effluent produced from an activated sludge system.

Specifically, our first objective was to investigate whether pyrethroid sorption onto SP exhibited any size preference to provide information about potential efficacy of physical treatment methods. Second, we wanted to quantify the distribution of a subset of the most frequently detected pyrethroids among the aqueous, SP, and DOC forms. Through the

course of our discussion we have operationally defined DOC as organic matter that passes through a 0.45 um filter and freely dissolved pyrethroid as interacting only with water not SP or DOC. Distribution coefficients allow us to estimate the freely dissolved pyrethroid concentrations in the discharged effluent for comparison with the chronic proposed water quality standards, which are in the sub-parts per trillion range. Application of these values to other water systems is also discussed.

EXPERIMENTAL METHODS

Chemicals

Standards of bifenthrin (CAS# 82657-04-3), λ-cyhalothrin (CAS# 91465-08-6), β-cyfluthrin (CAS# 68359-37-5), esfenvalerate (CAS# 66230-04-4), permethrin (CAS# 52645-53-1), cypermethrin (CAS# 52315-07-8), and deltamethrin (CAS# 64121-95-5) were purchased separately as 100 ug/mL solutions from ChemService. The internal standard 4-4′ dibromooctofluorobiphenyl (DBOFB) was purchased as a 250 ug/mL solution from Supelco. The labeled surrogates cis-permethrin (phenoxy-13C6) and trans-permethrin (dimethyl D6) were purchased as 100 ug/mL solutions from Chemservice and EQ Laboratories, Inc., respectively. Solvents used were hexane (pesticide grade), dichloromethane (DCM) (Optima), and acetonitrile (HPLC grade) and were purchased from Fisher Scientific.

Sampling

The SRWTP is a secondary treatment system that employs a pure oxygen activated sludge process. After biological treatment, solids are settled out and the water is chlorinated and dechlorinated and discharged into the Sacramento River. This plant treats an average of approximately 150 million gallons per day during dry weather. Six sampling events were performed at the treatment plant over the course of a year. Three sampling events were pre-scheduled dry weather events. Three were storm events scheduled 24–48 h in advance based upon predicted rainfall of greater than 2.5 cm in a 24 h period.

All glassware used in sampling and extraction was pre-baked at 450°C for four h. Sampling was performed at the plant outfall on the Sacramento River. Dechlorinated final effluent (DFE) was removed from discharge lines with a peristaltic pump and plastic tubing. Subsequently, DFE was fed through Teflon tubing to a 20 L glass jar with a spigot which drained effluent into a flow through centrifuge (FTC). The FTC was operated at setting 11 (11,000 *g*). The total volume centrifuged varied depending on effluent flow rate and estimated total suspended solid (TSS) concentration and was selected with the goal of collecting 1g of suspended particulates. FTC supernatant was discarded with the exception of two subsamples which were collected in two pre-baked amber 4-L glass bottles.

Pyrethroid loss to sampling equipment is always a concern particularly when plastic or Teflon is employed. A report by the USGS indicates that loss is minimal if the water is constantly moving as it contacts plastic or Teflon surfaces [22] as it was in our setup. Prior to the introduction of DFE, MilliQ water (Millipore) was pumped through the entire system and collected at the outlet of the FTC as a field blank. Grab samples of DFE were collected prior to the FTC. Two liters were collected in pre-baked amber glass 1-L bottles to be extracted for measurement of whole water pyrethroid concentrations. Five liters were collected in pre-baked 200 mL glass centrifuge tubes for particle fractionation by laboratory centrifugation. Direct collection into tubes minimized potential pyrethroid glassware loss and any biasing of particle size by transfer during pouring or pipetting.

For the partitioning study, DFE was passed through the FTC. All samples were transported on ice to the lab where they were stored at 4°C for no longer than 3 days before processing.

The FTC was transported intact and upon arrival at the lab it was disassembled, particles were collected and stored in 1-L amber glass bottles at 4°C.

Particle fractionation and pyrethroid analysis

Particle fractionation of the collected DFE sample was achieved by laboratory centrifugation. Assuming a mid-point density of 1.8 g/mL, sample was divided and centrifuged at 30 *g* for removal of particles with a diameter greater than 2.6 μm and 1720 *g* to remove all particles larger than 0.8 μm. The top portion of supernatant was removed from the centrifuge tube by a wide bore glass pipette and combined with other tubes. The final volume of each centrifuged fraction was divided into four replicates and processed concurrently with four samples of uncentrifuged DFE. In the first event, only two replicates were processed. Pyrethroid extraction was based upon a previously published method [23] with the following modifications: 500 mL samples were spiked with trans-permethrin (dimethyl D6) as a recovery surrogate and extracted three times with DCM. In the first event, cis-permethrin (phenoxy-13C6) was used as a surrogate. The organic extracts were passed through 2 cm of pre-baked sodium sulfate and solvent exchanged to hexane and evaporated to 0.5 mL. Sample clean-up consisted of passing extracts through two stacked solid phase extraction cartridges, the top a Supelclean™ ENVI-Carb II™/PSA (300 mg/600 mg, Sigma Aldrich) and the bottom a LC-Alumina-A (2 g, Sigma Aldrich). Cartridges were pre-conditioned with 10 mL acetonitrile, 10 mL DCM, and 10 mL hexane. Extracts were loaded on the top column and eluted with 7 mL 3:7 DCM:hexane, the top cartridge was removed and the second elution of 7 mL of DCM was passed through. Cleaned extracts were evaporated to 0.4 mL hexane under a stream of nitrogen. DBOFB was added as an internal standard (IS).

Pyrethroid determination was performed using a HP-6890 gas chromatograph (GC) (Agilent Technologies) coupled to a HP-5973N quadrupole mass spectrometer (MS) detector operated in negative chemical ionization (NCI) mode with methane as the reagent gas. The GC column was a 30 m × 0.25 mm × 0.25 um DB-5MS-DG capillary column. Helium was used as the carrier gas with a constant flow of 1 mL/min. Three μL of sample was injected in splitless mode. The injector temperature was 280 °C and the purge time was 1.50 min after injection. The oven temperature program was as follows: initial temperature 100°C, hold 1 min, ramp to 200°C at 15 °C/min, ramp to 290°C at 4°C/min, and ramp to 300°C at 10°C/min and hold for 4 min with a total run time of 35 min. The transfer line, source and quadrupole temperatures were 300°C, 150°C, and 106°C respectively. Pyrethroids were analyzed in selected ion monitoring (SIM) mode. Table 1 shows the monitored ions. Permethrin analysis in the first event was done with the same system, column and method, but ionization was switched to electron impact (70 eV). The source and the quadrupole temperatures were 230°C and 150°C respectively.

The identification of the seven pyrethroids of interest was based upon the comparison of their retention time, ions, and ion ratios with pyrethroid standards. Quantification was done with a calibration curve normalized to the IS response. All calibration curves had a R^2 >0.99.

The particle size distribution (PSD) was measured for both the whole DFE and centrifuged fractions by LiQuilaz (Particle Measuring Systems, Inc.). Total suspended solids and volatile suspended solids (VSS) concentrations were measured for the whole DFE as per standard methods [24].

Quality control

The instrumental limit of detection (LOD) was determined by multiplying the standard deviation of seven replicate injections by 3.14. The reporting limit for the present study was determined by the lowest standard in the calibration curve, which was always above the LOD. Table 2 shows the LODs.

A field blank of deionized water (Milli-Q) water was passed through the pump and centrifuge system to check for contamination in the sampling set-up. A method blank of deionized water (Milli-Q) was analyzed to ensure contamination did not occur during sampling extraction and analysis. If contamination was observed the results for that particular pyrethroid were not used. A lab spike and a lab spike duplicate were extracted with every sampling event with the exception of the first event. Spike recoveries ranged from 46% to 131% varying between event and chemical. Surrogate recoveries for the first event were an average of 39%, the remaining five events ranged from 61% to 120% with an average of 87%. Reported values were not corrected for surrogate recovery.

Statistical difference (α=0.05) between the treatment means was determined by Tukey's test with SAS 9.3 software.

Pyrethroid distribution coefficients

The distribution coefficient (K_{id}) between the suspended wastewater particulate (SP) matter and the four most frequently detected pyrethroids was determined by a standard isotherm technique. The SP collected from the FTC was recombined with FTC supernatant to produce a total suspended solids concentration of ~ 15 mg/L. The solution was characterized by TSS and PSD measurements. A portion of the solution was divided into 2 replicates, extracted and analyzed as described in the particle fractionation section to determine the whole water pyrethroid concentration. The remaining particle solution was divided into 36 mL aliquots and placed in pre-baked centrifuge tubes. Bifenthrin, λ-cyhalothrin, and cypermethrin were added together in 20 ng, 40 ng, 80 ng, and 160 ng increments. With the exception of bifenthrin all resulting aqueous concentrations were below the reported solubilities for these chemicals. Bifenthrin's reported solubility is 14 ng/L[1], however, the resulting isotherm indicated that solubility was not exceeded (see Results Section). The highest spike did not exceed 0.3% solvent v/v. Permethrin was added separately because it required larger pyrethroid additions due to its higher limit of detection. It was added in 80 ng, 120 ng, 160 ng, and 198 ng increments, all below its reported solubility. A rate experiment showed that the time between pyrethroid addition and the attainment of sorptive equilibrium was short (< 90 min) (Supplemental Data, Figure S1)). After addition, the samples were wrapped in aluminum foil to avoid exposure to the light and were tumbled at 20 rpm overnight (~16 h). The samples were centrifuged for 30 min at 2400 *g* to remove the SP. A 30 mL aliquot was transferred to a 40 mL amber glass vial without disturbing the settled solids.

Solid phase microextraction (SPME) is currently the primary method for measurement of a hydrophobic contaminant's freely dissolved concentration. Generally, the reported method LOD is in the low part per trillion range [25]. Pyrethroid extraction and analysis was done by SPME following the method described in Bondarenko et al. [26]. The 30 mL sample was placed on a Cimarec stir plate (Thermo Scientific); a glass stir bar was added and the sample was mixed at 1200 rpm. A 24 gauge SPME fiber holder (Supelco) with a 7 μm polydimethylsiloxane (PDMS) fiber (Supelco) was positioned 2 cm below the sample surface. Time to equilibrium between the SPME fiber and the aqueous pyrethroid is quite long, > 150 min as shown by a fiber uptake rate experiment (Supplemental Data, Figure S2)). Non-equilibrium sampling was performed with a 20 min sampling time. At 20 min, only 1% of the standard containing 600 pg was observed to be removed by the extraction,

indicating that the equilibrium between the phases would not be significantly disturbed by mass extraction. All conditions such as sampling time, sampling depth, mixing speed, inlet desorption depth, etc. were closely matched between samples and standards. After extraction, the fiber was desorbed in the GC inlet. The same GC-NCI-MS method and column were used as previously described. The method was modified for manual SPME injections. The inlet was operated in pulsed splitless mode with an initial temperature of 260 °C. The fiber was desorbed/cleaned in the inlet for 5 min after sampling. The pulse pressure was 50 psi, with a pulse time of 3 min. The purge time was 1.50 min. The initial oven temperature was 160 °C, held for 1 min, ramped at 10 °C/min to 300 °C, and held for 6 min producing a total runtime of 21 min. The day of the SPME extraction, 5 standards were prepared in 30 mL of deionized (Milli-Q) water by adding pyrethroid in acetone (did not exceed 0.4% v/v solvent). Standards were analyzed after the samples. Standard curves were highly linear (R^2>0.99). The SPME LOD was determined by extracting and desorbing 7 replicates of a lower standard concentration. The standard deviation of the replicates was multiplied by 3.14 to obtain the LODs (Table 2).

To evaluate pyrethroid glassware losses, the sample vials were solvent extracted after SPME sampling. The sample was discarded, vials and caps were air dried in a dark container overnight, and vials were rinsed three times with 3 mL aliquots of 3:7 DCM:hexane; rinses were combined and evaporated to a final volume of 0.4 mL. Two clean vials were spiked with the target pyrethroids and allowed to dry to evaluate method recovery. Pyrethroids were quantitated as previously described for the liquid samples. Permethrin, bifenthrin and cypermethrin results were all below the limit of detection at the lowest pyrethroid additions. Lambda-cyhalothrin showed 4% glassware loss at the lowest standard concentration. Spike recoveries were between 75%–99%.

K_{id} calculation

The Freundlich isotherm equation, shown in Equation 1, is an empirical model used to describe the equilibrium distribution between the solid and solution phases.

$$C_{is}=K_{if}\,C_{iw}^{n_i} \quad (1)$$

C_{is} is the equilibrium concentration of the chemical, i, in the solid phase, K_{iF} is the capacity factor, and C_{iw} is the equilibrium concentration in the aqueous phase. The Freundlich exponent, n_i, indicates the linearity of an isotherm. A n_i=1 represents a linear isotherm, where K_{id} does not change with changing sorbate concentrations. With those assumptions, Equation 1 is reduced to Equation 2.

$$K_{id}=\frac{C_{i,solid}}{C_{i,dissolved}} \quad (2)$$

The K_{id} can then be calculated using a mass balance on the pyrethroid-particle system (Eqn. 3)

$$K_{id}=\left(\frac{M_{i,total}}{M_{i,dissolved}}-1\right)\times\left(\frac{V_w}{M_{solid}}\right) \quad (3)$$

where $M_{i,total}$ is the total pyrethroid in the system, which is the sum of any native pyrethroid and the pyrethroid added. $M_{i,dissolved}$ is the mass measured by the SPME extraction, V_w is the sample volume. M_{solid} is the mass of sorbent in the system as measured by the TSS. K_{id}

was not corrected for glassware loss. K_{id} replicates for each event were averaged. Because sorption of hydrophobic chemicals is expected to occur mainly in the organic fraction of soils or sediments, K_{id} is often normalized by the fraction of organic carbon, f_{oc} in the particulate matter.

$$K_{ioc}=\frac{K_{id}}{f_{oc}} \quad (4)$$

24-h composite DFE samples collected during the same time period as our grab samples were analyzed for TSS and particulate organic carbon (POC) by the University of Maryland's Horn Point Laboratory as part of a companion study (Supplemental Data, Table S3). Under the assumption that our centrifugation and reconstitution of the SP did not significantly alter its properties, we used POC/TSS as an estimate of particulate f_{oc} in normalizing our K_{id} to a K_{ioc}.

The particle surface area available in each sample tube was estimated from the PSD measurement. Particles were assumed to be spheres with a diameter equal to the midpoint of the selected particle size bin. Surface area was calculated for the midpoint particle and multiplied by the particle count in the bin. Results were summed and used as an estimate of available surface area.

K_{idoc} measurement and calculation

The FTC supernatant contained the DOC from the DFE. The presence of DOC can alter the solid-liquid distribution of pyrethroids. To estimate pyrethroid sorption or complexation to DOC, a K_{idoc} was calculated using a modified version of the isotherm technique described above. The FTC supernatant was filtered through a 0.45 μm filter (Durapore Membrane, Millipore). A portion was sent to the UC Davis Analytical Lab for analysis of DOC by high temperature oxidation to CO_2. The filtrate was aliquoted into 40 mL amber glass vials and spiked with a mixture of bifenthrin, λ-cyhalothrin, and cypermethrin at the following masses: 5 ng, 10 ng, 20 ng, and 40 ng. Permethrin was added separately in 10 ng, 20 ng, 40 ng and 80 ng amounts. Samples were tumbled at 20 rpm overnight (~16 h). Sample extraction, glassware extraction, and analysis were the same as previously described. Glassware losses were more significant for this experiment, with bifenthrin, λ-cyhalothrin, and cypermethrin losses of 0.8 ng at the lowest addition. Permethrin loss was below the LOD which equates to a maximum of 4 ng of the total mass added. The calculated K_{idoc} values were corrected for the mass associated with the glassware if detectable, which for the permethrin was not until the 40 ng addition.

RESULTS AND DISCUSSION

Overview of pyrethroid distributions

Figure 1 shows the estimated pyrethroid distribution in the DFE based on a mass balance calculation using our experimental K_{id} and K_{idoc} values. Each fraction in the figure is discussed in more detail below. The particle size distributions of the DFE and the reconstituted particle solution were compared and showed good agreement suggesting that the reconstituted solutions provide a reasonable representation of the particulate matter in the DFE (Supplemental Data, Figure S4). The particle associated pyrethroid mass was sub-divided into a less than and greater than 0.8 μm fraction, based on the results of particle fractionation by laboratory centrifugation. The particulate fraction larger than 2.6 μm was ignored and not included in Figure 1 as it did not contain significant quantities of pyrethroid in any case. Complete particle fractionation results for bifenthrin, cypermethrin and permethrin are included in Supplemental Data, Figure S5. The two particulate bound

portions contain the largest amount of the pyrethroid concentration for all four of the pyrethroids examined across all six sampling events. Approximately 40% of the total pyrethroid concentration is associated with the > 0.8 um fraction for bifenthrin, cypermethrin and permethrin. λ-Cyhalothrin has a notably smaller fraction associated with particles that could be removed by centrifugation (average 27%), with one event showing no removal by the lab centrifuge. λ-Cyhalothrin had consistently the lowest whole water concentration of the pyrethroids measured.. Its measurements were near the LOD; consequently, a higher amount of error is associated with the reported values. These results suggest that increased settling times at wastewater treatment facilities are unlikely to remove more than an additional 40% of the pyrethroid concentration. For example, at a tertiary plant in Stockton, CA, detectable pyrethroid concentrations were found in the effluent even after 30 days residence time in settling ponds, albeit at greatly reduced concentrations[5]. In the present study, the calculated dissolved fractions for all pyrethroids measured in the DFE were below 6% across all events. Bifenthrin's dissolved percentage was marginally smaller than the other pyrethroids because of its slightly larger K_{id} value.

Particle fractionation

In Figure 1, the top two portions of the pyrethroid concentration illustrate the results of the particle fractionation. Tukey's test was used to determine significant differences in concentrations between the total effluent and the centrifuged fractions. Removing particles larger than 2.6 μm via centrifugation had no significant effect on pyrethroid concentrations and produced minimal surface area and particulate mass reductions (Supplementary Data, Figure S5). In contrast, removing particles larger than ~0.8 μm produced significant reductions in particulate masses and surface areas. For example, in the January event, available surface area was reduced by 83% when particles larger than 0.8 μm were removed (PSD measurements shown in Supplementary Data, Figure S6) from the DFE and particulate mass was reduced by 95%. The January VSS/TSS ratio of the particulate matter was 0.89 signifying a high organic content, which suggests a low particle density.

A ratio of the cypermethrin concentration to particle surface area was calculated for the DFE and <0.8 μm fraction. With the exception of the April event, the concentration to area ratios were higher for the <0.8 μm fraction than for the whole DFE. This increase is consistent with greater pyrethroid adsorption to fine particulate matter. The April event's ratio was similar for the DFE and centrifuged fraction. This event had the lowest TSS of all events (4 mg/L) and the lowest percentage of surface area removed by centrifugation (57%). The low TSS indicates a lower concentration of high-mass particles for removal. It is likely that this event did not follow the observed trend because an insufficient amount of particulate matter was removed by centrifugation. All events are summarized in Table 3.

Isotherms and distribution coefficients

The concentration range over which an adsorption isotherm can be measured is limited on the low end by the method limit of detection and on the high end by pyrethroid aqueous solubility. As previously mentioned, our bifenthrin spikes exceeded one commonly used literature value of bifenthrin's aqueous solubility. The shape of the bifenthrin isotherm shown in Figure 2 provides further evidence that the true solubility was not exceeded. One would expect an upward inflection of the isotherm indicating that the chemical had started to precipitate instead of simply adsorbing when solubility was exceeded. All of the isotherms obtained were linear (p<0.05), supporting the use of linear distribution coefficients to describe the extent of adsorption. Linear isotherms were also observed in a previous study of bifenthrin and λ-cyhalothrin sorption to suspended solids and bed sediments from the Sacramento River, with values of n_i that did not differ significantly from unity except in one

case [27]. The λ-cyhalothrin and cypermethrin isotherms are quite similar, while that for bifenthrin has a steeper slope, as indicated by the K_{id} values.

The K_{id} values in Table 4 are an average of single point calculations. An alternate method would have been to take the slope of the isotherm to determine the K_{id}. The average *R2* for all isotherms across all sampling dates was 0.73. However, the K_{id} determined by the slope method was very susceptible to outliers. Given the limited domain of our experiments, the single point calculation was selected (number of replicates is shown in Supplementary Data, Table S7).

The particle fractionation shows that at least a portion of the whole water pyrethroid concentration is particle-bound. However, it is still unclear if the remaining part is bound to fine particles or complexed with DOC. Our average log K_{ioc} values (Table 4) across sampling events are higher than others reported in the literature. Sediment log K_{ioc} values measured by SPME and corrected for particle attachment to the SPME fiber were in the range of 5.8 to 6.3 [28]. Budd et al. published log K_{ioc} values between 5.2 to 6.1 for suspended solids collected from constructed wetlands [20]. Lee et al. reported deflation of K_{id} by the artificial increase of $C_{i,dissolved}$ because pyrethroid complexed to DOC and small particles were included in the dissolved portion, however the use of SPME avoids this underestimation [29]. By including the DOC in the SP the opposite effect would be expected (i.e., a downward bias in K_{id} would result). Our SPME measurement of the dissolved concentration excludes pyrethroids sorbed to SP and complexed with DOC [29]. Consequently, the DOC contribution is included with the $C_{i,solid}$ portion. To minimize the relative effect of the DOC on measured sorption coefficients, the reconstituted wastewater used in our experiments has an inflated TSS concentration but the same DOC concentration as the original DFE samples. The K_{idoc} was evaluated for the January event and used to correct all K_{id} values by subtracting off the contribution of K_{idoc} multiplied by the DOC concentration. Within the number of significant figures reported for K_{id} no effect was observed from this adjustment.

The SP appears to be primarily organic, with a large surface area to volume ratio. It would be reasonable to assume that a portion of the SP observed in the effluent is poorly flocculated biomass from the activated sludge reactor. This microbially-derived organic carbon may have different sorption properties than the type of OC investigated in previous work. One potential explanation is that pyrethroids could partition into microbial cells during their contact in the reactor. Jabusch and Swackhamer [30] found that polychlorinated biphenyls (PCBs) had a higher partitioning coefficient into phospholipid membranes than into the neutral lipid triolein or octanol. This increased affinity could have particular importance for lower trophic levels such as phytoplankton where membranes are dominated by polar lipids [30]. Pyrethroids, which are nonpolar contaminants like PCBs, could therefore have a higher distribution coefficient on the microbially derived suspended solids.

Our work suggests that the large specific surface area available in the system can increase K_{id}. Causes of the variation in K_{id} values across sampling events were investigated by determining linear correlation coefficients between experimental and sampling event parameters. Some event parameters considered were influent flow, effluent TSS, VSS, DOC, event type and effluent particle surface area. Sample parameters included reconstituted sample TSS, VSS, f_{oc}, DOC, particle counts and surface area. K_{id} was found to be significantly correlated with surface area present in the particle solution normalized by TSS (α=0.05, bifenthrin p =0.013, λ-cyhalothrin p=0.0021, cypermethrin p= 0.0094, and permethrin p = 0.0433). Parameters describing the organic content of the particles, such as f_{oc}, did not display statistically significant (α=0.05) correlation coefficients. It seems that, in our system, available surface area is at least partially driving the sorption.

Partitioning to DOC

Gan et al. estimated pyrethroid K_{doc} values for surface and sediment pore water and reported "mean" values on the order of 10^5 L/kg, and "corrected" values on the order of 10^6 L/kg. The correction was performed to account for a systematic inflation of $C_{i,dissolved}$ in their measurements caused by the thermal desorption of pyrethroids associated with suspended solids that had become attached to the SPME fiber during sampling [28, 31]. We performed a comparison study of the flocculation method [31], centrifugation only, and direct sampling of the particle solution with no pretreatment (Supplementary Data, Figure S8). We observed particle attachment to our SPME fiber, and the pursuant $C_{i,dissolved}$ increase as reported by Gan et al. However, there was no difference between the flocculated and centrifuged samples and those that had only been centrifuged. We decided to remove particles by centrifuging alone to avoid the introduction of additional surface area into our sample reactors from flocculated material. For samples used to measure the K_{idoc} values, the FTC supernatant was pre-filtered, so centrifugation was unnecessary. Without complete flocculation of the OC in our samples, DOC would still be present. Bondarenko and Gan discuss possible matrix effects associated with non-equilibrium SPME measurements of pyrethroids in pore water samples containing dissolved organic matter (DOM). The unstirred water layer adjoining the fiber could become depleted of pyrethroids, overestimating $C_{idissolved}$. They concluded that with vigorous agitation and relatively low DOM concentration (< 50 mg/L) the effect would be minimized [25]. Our samples had DOM concentrations between 18.9 to 22.4 mg/L and were mixed at 1200 rpm. The K_{idoc} estimates presented here (Table 4) agree well with the uncorrected K_{idoc} values obtained by Gan et al. [28]. The four pyrethroids all had K_{idoc} in the same order of magnitude ($\times 10^5$ L/kg).

While our K_{idoc} values appear to be in range those reported in literature, it would not necessarily be expected. For example, another study [2] derived DOM from three different sources (soil, commercial potting mix and compost) and measured K_{idoc} values from 4.8×10^4 to 3.95×10^5 for bifenthrin, permethrin and cyfluthrin. The K_{idoc} values varied by an order of magnitude between sources. DOM properties can influence pyrethroid affinity for complexation and effluent DOM may differ significantly from the natural sources from which organic matters K_{idoc} are typically derived. Gonsior et al. used ultra high resolution mass spectrometry to investigate the difference between Suwannee River DOM and secondary effluent DOM. Results showed effluent derived DOM had a high abundance of unique features associated with surfactants, their degradates and metabolites [32].

Sensitivity analysis

A sensitivity analysis was performed to evaluate the effect of uncertainties in K_{id} and K_{idoc} values on the dissolved concentration. K_{idoc} was increased by an order of magnitude to more closely resemble previous literature values [28]. Although the distribution between the sorbed and DOC complexed fractions changed, the dissolved concentration was only slightly affected, decreasing to 1–2% of the total concentration. Changing the K_{id} values had a more pronounced effect on the dissolved concentration. Reduction of K_{id} to $\times 10^5$ L/kg, which would be consistent with the K_{ioc} values reported in Laskowski [1] taking into consideration the f_{oc} of our system, produced a sizeable increase in the dissolved fraction from ~5% to ~25% of the total concentration. For the TSS, DOC and whole water concentrations examined here, K_{id} appears to be the most sensitive parameter. The sensitivity of the estimated dissolved concentrations to K_{id} suggests that the values presented here should only be applied to other water systems with care. Given the unique SP produced by wastewater treatment, it would most likely be inappropriate to apply them to environmental solids. The described method could be utilized in other wastewater systems if the treatment technology and solids produced are carefully considered.

Correlation with toxicity

Our sampling events were part of a larger study examining the fate of pyrethroids through the wastewater treatment process [9]. Our grab samples were collected during 24-hr periods during which composite samples were obtained for use in toxicity testing with the amphipod *Hyalella azteca*. Significant paralysis or mortality of *H. Azteca* was observed in 5 of the 6 events [9]. Whole water pyrethroid concentrations did not appear to correlate with observed toxicity. We hypothesized that the association between pyrethroid concentrations and observed toxicity would be improved by using the dissolved pyrethroid concentration measurements instead of whole water concentrations in the correlation. Using our estimated K_{id} and K_{idoc} values and the measured composite sample parameters (whole water pyrethroid concentration, TSS, DOC) we calculated the dissolved concentration for each pyrethroid. Dissolved concentrations were converted to toxic units (TUs) using the half maximal effective concentration (EC50) and the median lethal concentration (LC50) (noted in Figure 1) for each chemical. The EC50 and LC50 presented are not truly freely dissolved thresholds as they may contain a small amount of DOC and suspended particles. Truly freely dissolved toxicity values are not available. We have assumed the literature toxicity values would closely align with a freely dissolved concentration because organic matter levels would be quite low in comparison to our samples. The TU model normalizes pyrethroid concentration by the toxicity threshold for that chemical for a particular animal. An additive toxicity model was assumed for the pyrethroids because of their consistent mode of action [33]. A non-parametric correlation test showed no relationship between observed % *H. azteca* paralyzed/dead and total dissolved pyrethroid TUs. Of the six sampling events, the April event had a total of 2.7 TUs but no significant toxicity, and September had no pyrethroids measured but toxicity was observed [9]. Finding any type of correlation is unlikely with such a small data set with a large amount of scatter. It is also possible that no correlation was observed because toxicity was due to other factors.

CONCLUSION

The pyrethroid K_{id} values presented here are approximately an order of magnitude greater than those previously reported in the literature for pyrethroids, likely because of the unique character of the wastewater derived SP. Surface area in the system showed a strong linear correlation with K_{id}, indicating that high specific surface areas of the wastewater SP may play an important role in producing elevated K_{id} values. Their application to other wastewater treatment systems should be done with careful consideration of treatment method and solids produced. The majority of the pyrethroid mass in the effluent was sorbed to SP, but, only 27–40% of it could be removed by increased settling (approximated by lab centrifugation), indicating that increased settling time in the wastewater treatment process is unlikely to completely alleviate pyrethroid discharges. Turner et al. reports that there was an apparent decrease (although not statistically significant) in permethrin concentration upon tertiary treatment with biologically aerated flooded filtration and rapid gravity filtration [10]. The dissolved concentration, which studies [15, 17, 34] have shown is the portion most readily taken up by organisms in the water column, was less than 6% of the whole water concentration. Neither whole water or dissolved concentrations were well correlated with the *H. azteca* toxicity observed in effluent water samples [9], however the data set was relatively small and contained a great deal of scatter. Further research is needed to conclusively link the observed toxicity to pyrethroids and/or correlate the whole water or dissolved pyrethroid concentrations with observed toxicity.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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References

1. Laskowski DA. Physical and Chemical Properties of Pyrethroids. Reviews of Environmental Contamination and Toxicology. 2002; 174:49–170. [PubMed: 12132343]
2. Delgado-Moreno L, Wu L, Gan J. Effect of Dissolved Organic Carbon on Sorption of Pyrethroids to Sediments. Environmental Science & Technology. 2010; 44:8473–8478. [PubMed: 20945891]
3. Gan J, Lee S, Liu W, Haver D, Kabashima J. Distribution and persistence of pyrethroids in runoff sediments. Journal of Environmental Quality. 2005; 34:836–841. [PubMed: 15843646]
4. Hintzen E, Lydy M, Belden J. Occurrence and potential toxicity of pyrethroids and other insecticides in bed sediments of urban streams in central Texas. Environmental Pollution. 2009:110–116. [PubMed: 18799250]
5. Weston DP, Lydy MJ. Urban and Agricultural Sources of Pyrethroid Insecticides to the Sacramento-San Joaquin Delta of California. Environmental Science & Technology. 2010; 44:1833–1840. [PubMed: 20121184]
6. Weston DP, Holmes RW, You J, Lydy MJ. Aquatic toxicity due to residential use of pyrethroid insecticides. Environmental Science & Technology. 2005; 39:9778–9784. [PubMed: 16475366]
7. Weston DP, Holmes RW, Lydy MJ. Residential runoff as a source of pyrethroid pesticides to urban creeks. Environmental Pollution. 2009; 157:287–294. [PubMed: 18676072]
8. Hwang H, Park E, Young T, Hammock B. Occurrence of endocrine-disrupting chemicals in indoor dust. Science of the Total Environment. 2008; 404:26–35. [PubMed: 18632138]
9. Weston DP, Ramil HL, Lydy MJ. Pyrethroid insecticides in municipal wastewater. Environmental Toxicology and Chemistry. 2013 In press.
10. Turner T, Cartmell E, Lester J, Casse F, Comber S, Scrimshaw M. The Pharmaceutical Use of Permethrin: Sources and Behavior During Municipal Sewage Treatment. Archives of Environmental Contamination and Toxicology. 2011; 61:193–201. [PubMed: 21069313]
11. Gomez M, Bueno M, Lacorte S, Fernandez-Alba A, Aguera A. Pilot survey monitoring pharmaceuticals and related compounds in a sewage treatment plant located on the Mediterranean coast. Chemosphere. 2007; 66:993–1002. [PubMed: 16962638]
12. Kupper T, Plagellat C, Braendli R, de Alencastro L, Grandjean D, Tarradellas J. Fate and removal of polycyclic musks, UV filters and biocides during wastewater treatment. Water Research. 2006; 40:2603–2612. [PubMed: 16797670]
13. Plagellat C, Kupper T, de Alencastro L, Grandjean D, Tarradellas J. Biocides in sewage sludge: Quantitative determination in some Swiss wastewater treatment plants. Bulletin of Environmental Contamination and Toxicology. 2004; 73:794–801. [PubMed: 15669721]
14. Fojut T, Palumbo A, Tjeerdema R. Aquatic life water quality criteria derived via the UC Davis Method: II. Pyrethroid Insecticides. Aquatic Life Water Quality Criteria for Selected Pesticides. 2012:216.
15. Yang W, Gan J, Hunter W, Spurlock F. Effect of suspended solids on bioavailability of pyrethroid insecticides. Environmental Toxicology and Chemistry. 2006:1585–1591. [PubMed: 16764477]
16. Yang WCHW, Spurlock F, Gan J. Bioavailability of Permethrin and Cyfluthrin in Surface Waters with Low Levels of Dissolved Organic Matter. Journal of Environmental Quality. 2007:1678–1685. [PubMed: 17940268]
17. Yang W, Spurlock F, Liu W, Gan J. Inhibition of aquatic toxicity of pyrethroid insecticides by suspended sediment. Environmental Toxicology and Chemistry. 2006:1913–1919. [PubMed: 16833154]

18. Song M, Chu S, Letcher R, Seth R. Fate, partitioning, and mass loading of polybrominated diphenyl ethers (PBDEs) during the treatment processing of municipal sewage. Environmental Science & Technology. 2006; 40:6241–6246. [PubMed: 17120548]
19. Barco-Bonilla N, Romero-Gonzalez R, Plaza-Bolanos P, Frenich AG, Vidal JLM. Analysis and study of the distribution of polar and non-polar pesticides in wastewater effluents from modern and conventional treatments. Journal of Chromatography A. 2010:7817–7825. [PubMed: 21035807]
20. Budd R, O'geen A, Goh K, Bondarenko S, Gan J. Removal mechanisms and fate of insecticides in constructed wetlands. Chemosphere. 2011; 83:1581–1587. [PubMed: 21296378]
21. Barret M, Carrere H, Latrille E, Wisniewski C, Patureau D. Micropollutant and Sludge Characterization for Modeling Sorption Equilibria. Environmental Science & Technology. 2010; 44:1100–1106. [PubMed: 20055462]
22. Hladik ML, Orlando JL, Kuivila KM. Collection of Pyrethroids in Water and Sediment Matrices: Development and Validation of a Standard Operating Procedure. US Geological Survey. 2009
23. Wang DL, Weston DP, Lydy MJ. Method development for the analysis of organophosphate and pyrethroid insecticides at low parts per trillion levels in water. Talanta. 2009; 78:1345–1351. [PubMed: 19362199]
24. APHA. Standard Methods for the Examination of Water and Wastewater. 20. American Public Health Association; Washington, DC: 1998.
25. Bondarenko S, Gan J. Simultaneous Measurement of Free and Total Concentrations of Hydrophobic Compounds. Environmental Science & Technology. 2009; 43:3772–3777. [PubMed: 19544886]
26. Bondarenko S, Spurlock F, Gan J. Analysis of pyrethroids in sediment pore water by solid-phase microextraction. Environmental Toxicology and Chemistry. 2007; 26:2587–2593. [PubMed: 18020696]
27. Fojut T, Young T. Pyrethroid sorption to Sacramento River suspended solids and bed sediments. Environmental Toxicology and Chemistry. 2011; 30:787–792. [PubMed: 21191877]
28. Gan, J.; Spurlock, F.; Hendley, P.; Weston, DP., editors. Synthetic Pyrethroids Occurence and Behavior in Aquatic Environments. American Chemical Society; Washington DC: 2008.
29. Lee S, Gan J, Liu WP, Anderson MA. Evaluation of K_d Underestimation Using Solid Phase Microextraction. Environmental Science and Technology. 2003:5597–5602. [PubMed: 14717169]
30. Jabusch T, Swackhamer D. Partitioning of polychlorinated biphenyls in octanol/water, triolein/water, and membrane/water systems. Chemosphere. 2005; 60:1270–1278. [PubMed: 16018898]
31. Hawthorne S, Grabanski C, Miller D, Kreitinger J. Solid-phase microextraction measurement of parent and alkyl polycyclic aromatic hydrocarbons in milliliter sediment pore water samples and determination of K-DOC values. Environmental Science & Technology. 2005; 39:2795–2803. [PubMed: 15884378]
32. Gonsior M, Zwartjes M, Cooper W, Song W, Ishida K, Tseng L, Jeung M, Rosso D, Hertkorn N, Schmitt-Kopplin P. Molecular characterization of effluent organic matter identified by ultrahigh resolution mass spectrometry. Water Research. 2011; 45:2943–2953. [PubMed: 21477837]
33. Trimble A, Weston D, Belden J, Lydy M. Identification and evalulation of pyrethroid insecticide mixtures in urban sediments. Environmental Toxicology and Chemistry. 2009; 28:1687–1695. [PubMed: 19245272]
34. Yang W, Spurlock F, Liu W, Gan J. Effects of dissolved organic matter on permethrin bioavailability to Daphnia species. Journal of Agricultural and Food Chemistry. 2006:3967–3972. [PubMed: 16719522]
35. Weston D, Jackson C. Use of Engineered Enzymes to Identify Organophosphate and Pyrethroid-Related Toxicity in Toxicity Identification Evaluations. Environmental Science & Technology. 2009; 43:5514–5520. [PubMed: 19708390]
36. Maund S, Hamer M, Warinton J, Kedwards T. Aquatic ecotoxicology of the pyrethroid insecticide lambda-cyhalothrin: Considerations for higher-tier aquatic risk assessment. Pesticide Science. 1998; 54:408–417.
37. Weston D, Lydy M. Focused toxicity identification evaluations to rapidly identify the cause of toxicity in environmental samples. Chemosphere. 2010:368–374. [PubMed: 20018342]

38. Anderson B, Phillips B, Hunt J, Connor V, Richard N, Tjeerdema R. Identifying primary stressors impacting macroinvertebrates in the Salinas River (California, USA): Relative effects of pesticides and suspended particles. Environmental Pollution. 2006; 141:402–408. [PubMed: 16225973]

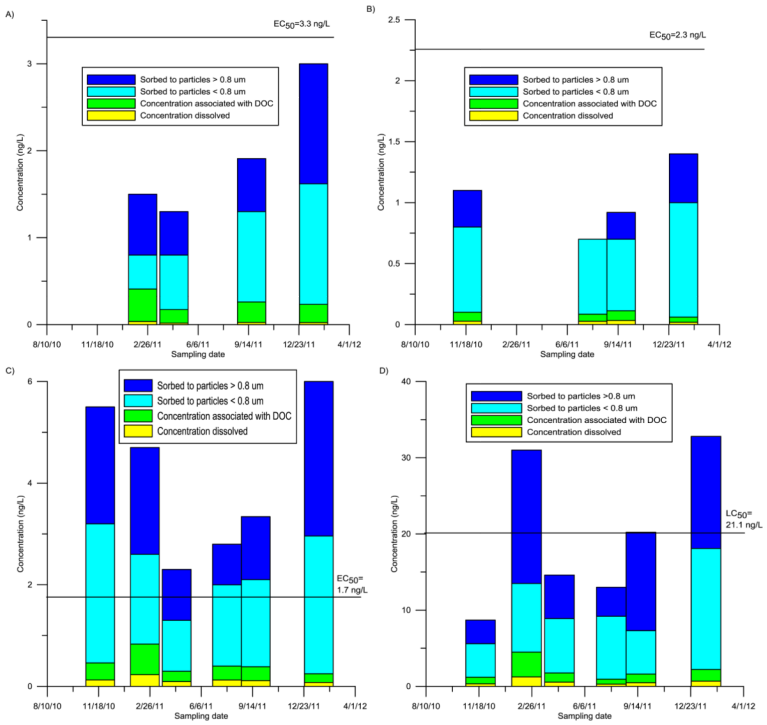

Figure 1.

Distribution of pyrethroid concentration in effluent. a) bifenthrin b) λ-cyhalothrin c) cypermethrin d) permethrin. Lines indicate thresholds for biological effects toward *H. azteca*: Bifenthrin EC50 conc.[35]; λ-Cyhalothrin EC50[36]; Cypermethrin EC50[37]; and Permethrin LC50[38]

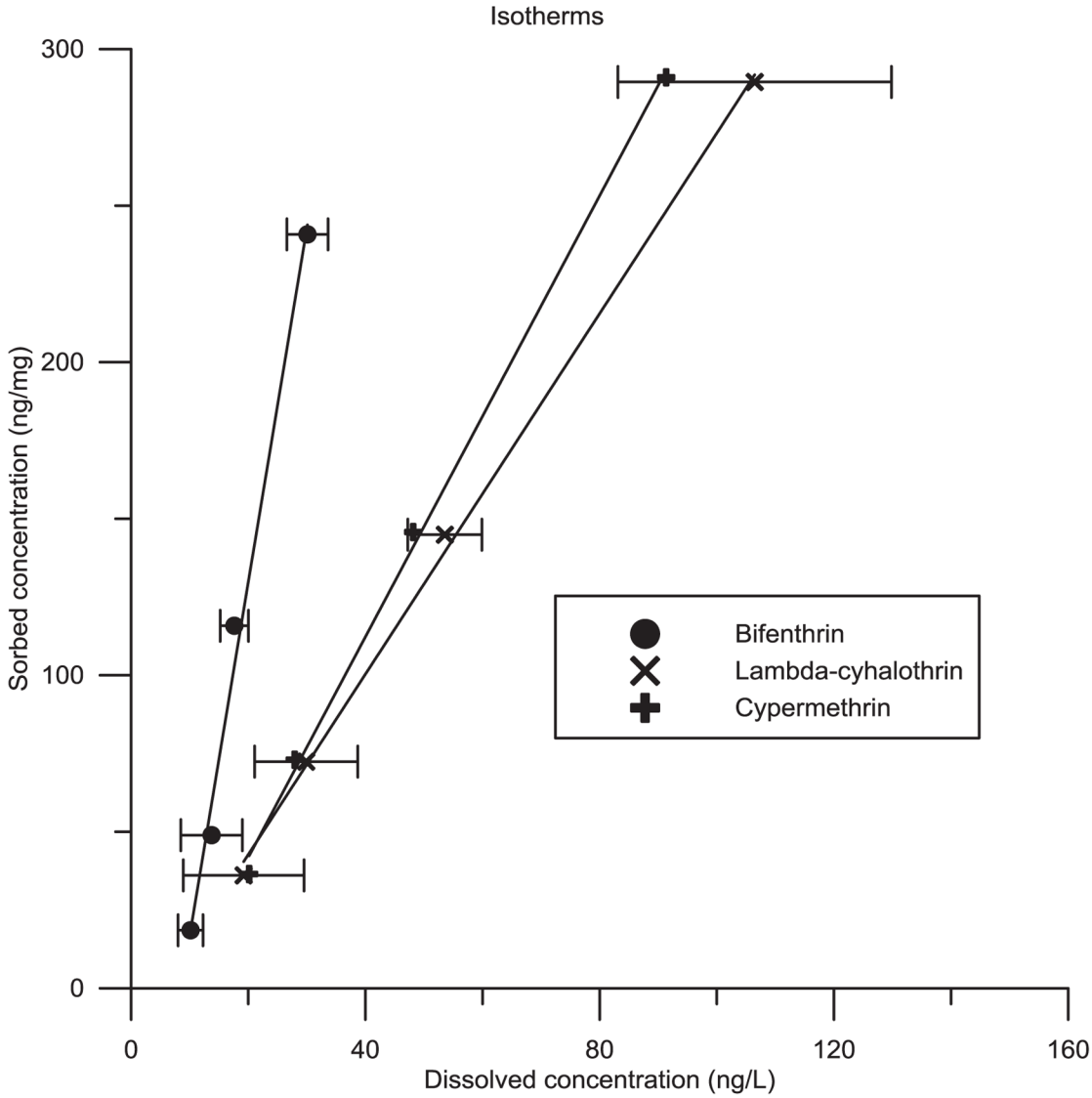

Figure 2.
Adsorption isotherms for the 20 Sep sampling event. Error bars represent the standard deviation between replicates.

Table 1

MS quantification and confirmation ions

Pyrethroid SIM analysis		
Pyrethroid[a]	**Quant. m/z**	**Qualif. m/z**
Bifenthrin	205, 241, 386	205, 241
λ-Cyhalothrin	241	205
Permethrin (NCI)	207	209
Permethrin (EI)	183	
Cis-permethrin (phenoxy-13C6) (EI)	189	
Trans-permethrin (dimethyl D6) (NCI)	213	215
Cyfluthrin	207, 209	209
Cypermethrin	207	209
Esfenvalerate	211	167, 297
Deltamethrin	217	79, 297

[a] NCI - negative chemical ionization and EI-electron impact

Table 2

Limit of Detection (ng/L)

Pyrethroid SPME Analysis		
Pyrethroid	**SPME[a,b]**	**Whole Water[a,c]**
Permethrin	12.2	5.4
Cypermethrin	2.7	0.9
Bifenthrin	4.4	0.4
Lambda-Cyhalothrin	1.3	0.7
Cyfluthrin	NM	0.9
Esfenvalerate	NM	1.0

[a] NM indicates not measured

[b] Method limit of detection

[c] Instrumental limit of dectection

Table 3

Particle Fractionation mass and surface area removal

Sampling Date[a]	% Surface Area Removed	DFE Cypermethrin Concentration Ratio[b,c]	<0.8 um Cypermethrin Concentration Ratio[b,c]
21 Nov (R)	58%	1.08	1.84
16 Feb (R)	67%	1.13	2.27
19 Apr	57%	1.31	1.24
26 Jul	65%	1.26	2.59
20 Sep	71%	1.04	2.24
21 Jan (R)	83%	.623	1.77

[a] R indicates a storm event.

[b] all values are $\times 10^6$.

[c] Calculated by dividing pyrethroid concentration by surface area present in specified fraction; units are ng L^{-1} m^{-2}

Table 4

K_{id} estimates for each event.

Sampling Date[a]	Bifenthrin		Lambda-Cyhalothrin		Cypermethrin		Permethrin	
	K_{id} (L/kg)[b,c]	Log K_{ioc}	K_{id} (L/kg)[b,c]	Log K_{ioc}	K_{id} (L/kg)[b,c]	Log K_{ioc}	K_{id} (L/kg)[b,c]	Log K_{ioc}
21 Nov (R)	9.2 ± 2.2	7.1	3.7 ±0.9	6.7	4.1 ± 1.1	6.8	2.3 ±0.8	6.5
16 Feb (R)	5.6 ± 1.6	7.1	3.0 ± 0.7	6.8	3.1 ± 0.7	6.8	4.0 ± 0.7	6.9
19 Apr	15.7 ± 2.1	7.4	8.4 ± 2.6	7.1	5.3 ±0. 9	6.9	5.8 ± 0.6	7.0
26 Jul	6.0 ± 1.1	7.2	3.2 ± 1.3	6.9	2.6 ±1	6.8	5.5 ± 0.8	7.1
20 Sep	7.2 ± 1.6	7.2	2.6 ±0.4	6.8	2.8 ±0.4	6.8	4.2 ± 0.6	7.0
21 Jan (R)	8.2 ± 2.0	7.4	4.9 ± 0.7	7.2	5.2 ± 0.7	7.2	3.1 ± 0.8	7.0
K_{doc} (L/kg)	0.8 ± 0.1		0.2 ± 0.02		0.2 ± 0.02		0.2 ± 0.1	

[a] R indicates a storm event.

[b] all values are × 10^6.

[c] Error measurements indicate 95% confidence intervals.

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