

PYRETHROID SORPTION TO SACRAMENTO RIVER SUSPENDED SOLIDS  
AND BED SEDIMENTS

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**Abstract**—Sorption of pyrethroid insecticides to solid materials will typically dominate the fate and transport of these hydrophobic compounds in aquatic environments. Batch reactor isotherm experiments were performed with bifenthrin and  $\lambda$ -cyhalothrin with suspended material and bed sediment collected from the Sacramento River, California, USA. These batch reactor experiments were performed with low spiking concentrations and a long equilibration time (28 d) to be more relevant to environmental conditions. Sorption to suspended material and bed sediment was compared to examine the role of differential sorption between these phases in the environmental transport of pyrethroids. The equilibrium sorption data were fit to the Freundlich isotherm model and fit with  $r^2 > 0.87$  for all experiments. Freundlich exponents ranged from  $0.72 \pm 0.19$  to  $1.07 \pm 0.050$ , indicating sorption nonlinearity for some of the experimental conditions and linearity for others over the concentration range tested. The Freundlich capacity factors were larger for the suspended solids than for the bed sediments, and the suspended material had a higher specific surface area and higher organic carbon content compared to the bed sediment. Calculated organic carbon-normalized distribution coefficients were larger than those previously reported in the literature, by approximately an order of magnitude, and ranged from  $10^{6.16}$  to  $10^{6.68}$  at an equilibrium aqueous concentration of  $0.1 \mu\text{g/L}$ . Higher than expected sorption of pyrethroids to the tested materials may be explained by sorption to black carbon and/or mineral surfaces. Environ. Toxicol. Chem. 2011;30:787–792. © 2011 SETAC

**Keywords**—Pyrethroids Sorption Suspended solids Freundlich isotherms Partition coefficients

## INTRODUCTION

Sorption to particulate matter found in surface water can dominate the fate and transport of hydrophobic organic compounds. In the present study, we compare the sorption of two pyrethroids to suspended solids and a bed sediment at environmentally relevant concentrations employing a long equilibration time and very low sediment to water ratios ( $\sim 1:1,000$ ), conditions more relevant to field conditions than those employed in many previous studies. For example, literature studies of pyrethroid sorption to minerals [1–3] and soils or sediments [4–12] have often employed initial aqueous concentrations well above solubility and short equilibration times ( $\sim 1$  d). Bondarenko et al. [13] examined the distribution coefficient between sediment and water ( $K_d$ ) of pyrethroids at various aging times and concluded that equilibration times should be at least one month for pyrethroids to avoid underestimating the  $K_d$ .

Pyrethroid insecticides have been widely detected in sediments in California, USA in both agricultural and urban areas [14–16]. Bifenthrin and  $\lambda$ -cyhalothrin are two pyrethroid insecticides used in California in agricultural, structural, and residential applications. These compounds have high octanol–water partition coefficients ( $K_{OW} > 10^5$ ) and low aqueous solubilities [17]. Pyrethroids have been shown to be highly toxic to aquatic invertebrates and vertebrates [18–20], but their bioavailability may be decreased by sorption to organic matter (OM) associated with suspended solids present in surface waters or in underlying sediments [21–23].

To examine sorption linearity, empirical data were fit to the Freundlich model, which is widely used for modeling sorption of hydrophobic organic chemicals to OM [24–26],

$$Q_e = K_F C_e^n \quad (1)$$

where  $Q_e$  is the equilibrium concentration in the sorbent ( $\mu\text{g/kg}$ ),  $K_F$  is the Freundlich constant or capacity factor ( $(\mu\text{g/kg})/(\mu\text{g/L})^n$ ),  $C_e$  is the equilibrium concentration in the aqueous phase ( $\mu\text{g/L}$ ), and  $n$  is the Freundlich exponent [27]. The Freundlich exponent,  $n$ , describes the linearity of the sorption process, but the mechanism of sorption cannot be directly inferred from the Freundlich parameters.

Isotherm experiments were performed with bifenthrin and  $\lambda$ -cyhalothrin, pyrethroids frequently detected in environmental monitoring, using bed sediment and suspended solids collected from the Sacramento River, California, USA. Sorption to bed sediment and suspended solids are compared because preferential sorption to suspended solids could facilitate downstream transport of pyrethroids. A rate experiment with each solid material was performed to determine an appropriate contact time to reach apparent equilibrium for the isotherm experiments. Pyrethroid sorption to glassware is widely reported in the literature [1,2,28,29] and is accounted for in the isotherm calculations.

## MATERIALS AND METHODS

## Chemicals

The pyrethroids  $\lambda$ -cyhalothrin and bifenthrin were purchased from AccuStandard as  $100 \mu\text{g/mL}$  in methanol. Other chemicals used in the experiments were sodium sulfate (12–60 mesh, ACS reagent grade, JT Baker), potassium phosphate (ACS grade, 99.7% purity, Fisher Scientific), and sodium azide (98% purity, EM Science). All solvents (dichlorome-

All Supplemental Data may be found in the online version of this article.

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thane, acetone, ethyl acetate, methanol) were purchased from Fisher Scientific and were Optima or GC Resolv grade.

#### Instrumentation

Analyses of bifenthrin and  $\lambda$ -cyhalothrin were performed on an Agilent 6890 series gas chromatograph with an electron capture detector (Agilent Technologies). The oven method was modified from You et al. [30], and the gas chromatograph was equipped with a Zebron ZB-5 column (30 m  $\times$  0.25 mm, 0.25- $\mu$ m film thickness). The oven was set to 100°C, ramped to 270°C at 25°C/min, ramped to 280°C at 2°C/min, and held for 10 min. The inlet temperature was 300°C and pulsed splitless injection was used with a pressure of 40 psi until 1 min. Bifenthrin eluted at 19.9 min and the two  $\lambda$ -cyhalothrin diastereomers eluted at 21.3 and 21.7 min. The method limits of detection for total  $\lambda$ -cyhalothrin and bifenthrin were determined to be 1.5 and 2.6 ng/L, respectively. The method limits of quantification for total  $\lambda$ -cyhalothrin and bifenthrin were determined to be 5.2 and 8.8 ng/L, respectively. Calibration was based on area using five external standards of 1, 10, 50, 100, and 1,000  $\mu$ g/L in ethyl acetate of the appropriate pyrethroid. The calibration curves were linear in this concentration range ( $r^2 > 0.99$ ).

#### Sediment

The water sample collection site was in the Sacramento River (near Rio Vista, CA; U.S. Geological Survey site 711) at GPS coordinates N 38.176, W 121.669, where the river depth was 18 m on June 13, 2006. Surface water was collected at a depth of 1 m below the surface into eight 40-L stainless steel containers. Bed sediment was collected as a grab sample by the UC Davis Aquatic Toxicology Laboratory (Davis, CA, USA) on the same date within 1 h of the surface water collection. The water samples were immediately transported to the lab and stored at 4°C overnight. The next day, the water samples were shaken to resuspend the solid material and were then run through a flow-through centrifuge (Aqua-Aerobic) at an average speed of 10,200 rpm to concentrate the suspended solids. Evolution in the particle size distribution of suspended materials has been reported to occur when sample holding times exceed 6 h [31]; however, replication of particle size distribution was not a focus of the present study and the recovered suspended material is expected to be representative of the original material with respect to composition. Approximately 50 g of wet solids were collected from the centrifuge.

The moisture content of both the suspended solids and bed sediment was measured gravimetrically by drying subsamples in a 105°C oven for 24 h. The suspended solids from the flow-through centrifuge had a moisture content of 73%, and the bed sediment from the grab sample had a moisture content of 25%. The percentage organic carbon (% OC) and total nitrogen were analyzed by the Agricultural and Natural Resources Analytical Laboratory at the University of California, Davis with a high temperature combustion method. Black carbon (soot carbon) was measured in the bed sediment following the procedure of Gustafsson et al. [32]. The black carbon content of the suspended material was not measured due to insufficient sample size. The sample for black carbon analysis was ground and sieved to <425  $\mu$ m, subsamples were baked in a muffle furnace at 375°C for 24 h, followed by sequential acidification with 1 N HCl to remove carbonates. The dried samples were then analyzed for total carbon and nitrogen by the Agricultural and Natural Resources Analytical Laboratory, as described above. Specific surface area ( $S_A$ ) was determined by measuring

a seven-point Brunauer, Emmett, Teller (BET) nitrogen adsorption isotherm (Autosorb I, Quantachrome Instruments). The suspended solids had 1.7% OC, 0.17% total nitrogen, and a surface area of 27.55 m<sup>2</sup>/g. The bed sediment had 0.16% OC, 0.02% black carbon, <0.04% total nitrogen, and a surface area of 5.45 m<sup>2</sup>/g. The suspended solids and bed sediments were extracted sequentially with dichloromethane three times for 10 min in an ultrasonic bath. The extracts were combined and dried with sodium sulfate, evaporated to dryness on a rotary evaporator and resuspended in 1 ml ethyl acetate. Samples were analyzed on the gas chromatograph with electron capture detector; no pyrethroids were detected in either the bed sediment or suspended material at the time of collection.

#### Rate studies

Sorption rate studies were conducted using  $\lambda$ -cyhalothrin as the sorbate, and Rio Vista suspended solids and bed sediment as sorbents. Wet sediment (~50 or 60 mg dry for suspended solids or bed sediment, respectively) was placed in 50-ml glass centrifuge tubes in triplicate. Single control tubes were also prepared without sediment. The exact masses of wet sediment were recorded, and the dry weight was calculated using the moisture content of the sediment. The tubes were covered with foil to inhibit photodegradation, and the Teflon<sup>®</sup> septa of the caps were covered with silver foil to inhibit adsorption to the surface. A 5-mM phosphate buffer was prepared and adjusted to pH 7. The buffer also contained 200 mg/L NaN<sub>3</sub> to inhibit biodegradation. Hydrolysis was not expected to significantly contribute to degradation because both of these compounds are reported to be stable to hydrolysis at pH 7.0 [17]. The initial 0.1  $\mu$ g/L  $\lambda$ -cyhalothrin solution was prepared by adding stock solution of  $\lambda$ -cyhalothrin in methanol to the buffer solution in the appropriate volume. The methanol concentration in the resulting aqueous solutions was <0.5% by volume.

All tubes were filled with approximately 50 ml of the 0.1  $\mu$ g/L  $\lambda$ -cyhalothrin solution and then tumbled end-over-end. At eight times points (0, 12, 24, 72, 168, 336, 504, 672 h) triplicate tubes and one control were removed. The tubes were centrifuged at 2,500 rpm for 15 min, and then the aqueous phase was separated with a pipette and spiked with  $\alpha$ -cypermethrin surrogate solution, which was used to quantify extraction recovery. Surrogate recoveries of individual samples were used to correct the aqueous concentrations for losses due to extraction procedures. The aqueous phase was extracted with 6 ml C<sub>18</sub> solid phase extraction cartridges (Bond-Elut, Varian). The cartridges were conditioned with ethyl acetate, acetone, and water before passing samples through under light vacuum. After the cartridges were dry, they were eluted with 18 ml ethyl acetate by gravity flow. Approximately one of every three sediment samples was spiked with surrogate solution and extracted by sonication, as previously described, to estimate the mass balance of the experiments. All extracts were evaporated to dryness and resuspended in 1 ml of ethyl acetate.

#### Isotherm studies

The isotherm studies followed the same tube preparation procedures as the rate studies, but in addition to the triplicate sediment tubes, duplicate control tubes (containing no sediment) were prepared for each concentration. Four isotherm experiments were performed, bifenthrin and  $\lambda$ -cyhalothrin each with suspended solids and bed sediment. Eight initial pyrethroid concentrations ( $C_0$ ) were prepared: 0.005, 0.01, 0.025, 0.05, 0.1, 0.5, 1, and 10  $\mu$ g/L using the same buffer as described for the rate studies. The solutions were added to the tubes and the tubes

were tumbled end-over-end for 28 d, based on the results of the rate studies. Tubes were removed, centrifuged, and the aqueous phase was separated as described above. The extraction of the aqueous phase and sediment, sample preparation, and gas chromatograph analysis followed the same procedures as the rate studies.

The sorption data was corrected for losses to centrifuge tubes because a substantial amount of sorption to glassware was noted in the control tubes. The procedure for loss correction followed that of Oudou and Hansen [2], in which a sorption isotherm was determined for the centrifuge tube glass using the control data. A distribution constant,  $K_a$ , was calculated as the ratio between the mass of pyrethroid sorbed per glass surface area ( $\text{ng}/\text{cm}^2$ ) and the equilibrium aqueous pyrethroid concentration,  $C_e$  ( $\mu\text{g}/\text{L}$ ), to facilitate comparison with data in the literature.

In the Freundlich equation,  $C_e$  is measured and  $Q_e$  is typically calculated as follows in Equation 2,

$$Q_e = \frac{(C_0 - C_e) \cdot V_w}{M_s} \quad (2)$$

where  $C_0$  is the initial nominal concentration of pyrethroid in the aqueous phase ( $\mu\text{g}/\text{L}$ ),  $V_w$  is the volume of water (L), and  $M_s$  is the mass of dry sediment in a tube (g). To calculate  $Q_e$  incorporating a correction for loss to glassware, Equation 2 is modified as follows:

$$Q_e = \frac{(C_0 - C_e) \cdot V_w - K_a A_{\text{tube}} C_e}{M_s} \quad (3)$$

where  $A_{\text{tube}}$  is the inner surface area of the glass tubes ( $\text{cm}^2$ ), which was assumed to be the same for all tubes. The term  $K_a$  is the slope of the linear regression fit to the data plotted as mass sorbed to the walls per surface area ( $\text{ng}/\text{cm}^2$ ) versus  $C_e$  ( $\mu\text{g}/\text{L}$ ).

## RESULTS AND DISCUSSION

### Rate studies

The rate studies showed that apparent equilibrium for  $\lambda$ -cyhalothrin was reached by 21 d for both sediments, as the average aqueous concentration at 21 d was not statistically different from the values at 14 d and 28 d (within one standard deviation). A contact time of 28 d was chosen for convenience and based on previous results indicating that one month equilibrium times were adequate [13]. Sorption of bifenthrin to these sediments was assumed to follow similar kinetics, and the same contact time was used for the bifenthrin isotherm experiments.

### Isotherm studies

Bifenthrin and  $\lambda$ -cyhalothrin both exhibited sorption to the glassware used in the isotherm experiments of 40 to 60% of the initial mass in the control tubes as calculated using the final measured aqueous concentration in control tubes. These losses are in agreement with several other studies of pyrethroids that report sorption to glassware of 25 to 60% [1,2,4,33]. To correct for these losses, the data for the control tubes, containing no sediment, were plotted and fit with a linear isotherm equation (Fig. 1). The distribution coefficient,  $K_a$ , calculated for  $\lambda$ -cyhalothrin is  $0.81 \text{ cm}^3/\text{g}$ ; this value is almost identical to the  $K_a$  reported by Zhou et al. [33] of  $0.82 \text{ cm}^3/\text{g}$ , and is within a factor of 1.5 of the  $K_a$  reported by Oudou and Hansen [2]. Literature values of  $K_a$  for bifenthrin were not located, but the calculated  $K_a$  of  $0.85$  seems reasonable based on values reported for other pyrethroids.

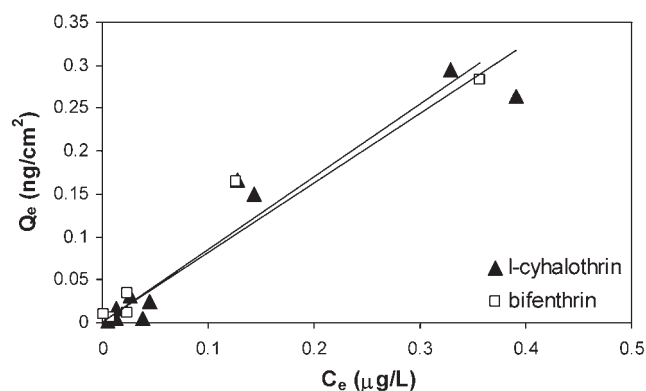


Fig. 1. Isotherm plots for sorption of pyrethroids to glass walls of centrifuge tubes.  $Q_e$  = equilibrium concentration in the sorbent;  $C_e$  = equilibrium concentration in the aqueous phase.

To support subsequent isotherm calculations, the solid phase pyrethroid concentration ( $Q_e$ ) was calculated using Equation 3 (glassware loss correction isotherm) and from the measured solid phase concentrations. The latter calculation is not straightforward, however, because the extracts include both glass tube rinses and the solvent used to sonicate the recovered solids, so the  $Q_e$  calculated from the extraction data include pyrethroids adsorbed to sediment and glassware. Rather than overestimating  $Q_e$ , the extraction-based  $Q_e$ s are systematically lower than those obtained from Equation 3 for  $\lambda$ -cyhalothrin with bed sediment (Fig. 2). In almost every isotherm tube the amount of pyrethroid adsorbed to glassware (based on extraction) is expected to be significantly smaller than the amount on the tube walls (based on Eqn. 3; Fig. 2), suggesting that this approach should still yield reasonable values for  $Q_e$ . This trend was exhibited for both compounds on both types of sediment (data not shown). The lower  $Q_e$ s obtained from extraction are likely due to incomplete sediment extraction, because no reason exists to suppose different reactive loss mechanisms between the control and treatment reactors. We have confidence that our measured  $K_a$  values accurately reflect losses to glassware because they are consistent with available published data.

Data from all four isotherm experiments were log-transformed and fit to the Freundlich model, with measured  $C_e$ s and  $Q_e$ s calculated using Equation 3. For each experiment, mean  $C_e$

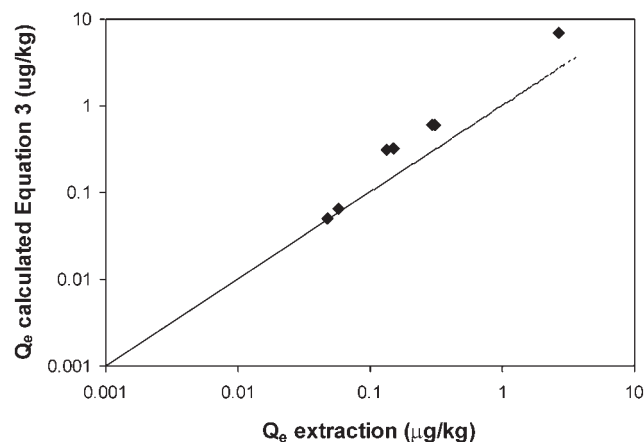


Fig. 2. Comparison of the equilibrium concentrations in the sorbent ( $Q_e$ ) calculated with Equation 3 and those determined from extraction of individual replicate sediments for the case of  $\lambda$ -cyhalothrin with bed sediment. The trendline on the plot is  $y = x$  to compare the values.

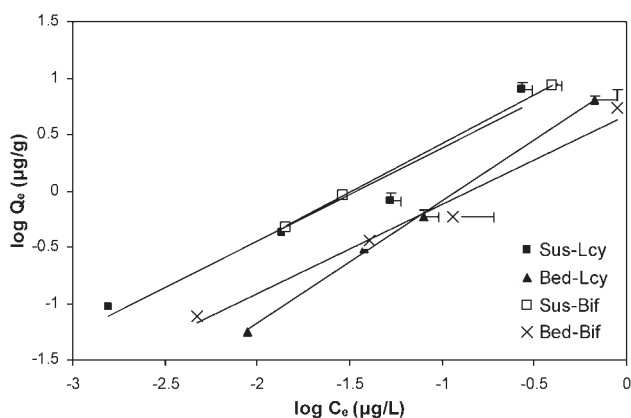


Fig. 3. Sorption isotherms for all four experiments with mean log-normalized aqueous concentration at equilibrium ( $\log C_e$ ) and mean log-normalized equilibrium concentration in the sorbent ( $\log Q_e$ ) for a given nominal concentration. Error bars represent one standard deviation of the mean in both directions.

and  $Q_e$  values were calculated from the triplicates and plotted for a given concentration for clarity of presentation (Fig. 3). The Freundlich isotherm parameters and associated errors for the experiments were calculated using triplicate data, not the mean values (Table 1). Depending on the dataset, isotherm data is generally plotted for the nominal initial concentrations of 0.1, 0.5, 1, and 10  $\mu\text{g/L}$ , and the remaining data were excluded because they were below detection limits in the aqueous phase. The bed sediment exhibits lower sorption capacity than the suspended solids over the entire concentration range studied for both compounds and has a lower Freundlich capacity factor  $K_F$ , indicative of lower sorption at unit concentration (Fig. 3 and Table 1). This is consistent with the lower OC content and lower specific surface area of the bed sediment compared to the suspended solids. Bifenthrin exhibits a greater degree of nonlinearity (lower  $n$ ) than  $\lambda$ -cyhalothrin with both sediments. It should be noted that the 95% confidence intervals for all of the  $n$  values include unity, except Bifenthrin-Bed, indicating that these isotherms are statistically indistinguishable from linear ones at the  $\alpha = 0.05$  level.

For comparison, Freundlich isotherm parameters were also determined using the  $Q_e$ s measured from sediment extractions (Table 1) instead of the  $Q_e$ s calculated from Equation 3. The  $Q_e$ s calculated with Equation 3 are systematically higher than those based on solid-phase extraction data by approximately a factor of 2, and thus the calculated  $Q_e$ s produced higher  $K_F$ s. However, the relative trends and linearity are conserved in both datasets. This comparison was included as an independent check on our isotherm results because of the relatively

large glassware loss corrections required; and because these datasets are rarely compared. Subsequent analyses regarding the isotherms are performed using the calculated glassware loss corrections (Eqn. 3).

Few Freundlich parameters are reported in the literature for these two compounds for comparison, but all Freundlich exponents identified in the literature are listed in Supplemental Data, Table S1. Several of the previously reported sorption isotherms have used initial aqueous pyrethroid concentrations that are well above the accepted aqueous solubilities [4,6,10]. Freundlich exponents that are less than unity indicate that the sorbate is bound with successively less favorable free energies as  $Q_e$  increases. Only one experiment exhibited an exponent slightly greater than unity and the other experiments have confidence intervals that encompass unity, except for the Bifenthrin-Bed experiment. The  $\log K_{OW}$  of  $\lambda$ -cyhalothrin (7.0) is higher than that of bifenthrin (6.4) [17], so it would be expected to have a higher  $K_F$  for a given sediment, which the experimental data follow for both bed sediment and suspended solids.

#### Distribution coefficients

The isotherm results were used to calculate the distribution coefficient,  $K_d$ , and the experimental OC-normalized sorption coefficient,  $\log K_{OC}$ , at a given equilibrium aqueous concentration of 0.1  $\mu\text{g/L}$  (Supplemental Data, Table S1). The  $K_d$  and  $K_{OC}$  were calculated according to the following equations [27]:

$$K_d = \frac{Q_e}{C_e} = K_F C_e^{n-1} \quad (4)$$

$$K_{OC} = \frac{K_d}{f_{OC}} \quad (5)$$

where  $K_F$  is for the loss-corrected  $Q_e$  with units of  $\mu\text{g/kg}$  and  $C_e$  with units of  $\mu\text{g/L}$ ,  $f_{OC}$  is the fraction of OC in the sediment, and  $K_d$  is in units of  $\text{L/kg}$ . The  $K_d$ s calculated for the suspended solids are larger than those calculated for the bed sediments by approximately a factor of 3, and the  $K_d$ s for bifenthrin and  $\lambda$ -cyhalothrin are very similar for a given sediment (Supplemental Data, Table S1). The  $\log K_{OC}$ s were calculated assuming that all of the pyrethroids sorbed to OC. These values are larger than representative average  $\log K_{OC}$ s reported by Laskowski [17] by factors of approximately 1.1–1.2 for  $\lambda$ -cyhalothrin and 1.2 for bifenthrin. The  $K_d$  and  $K_{OC}$  values reported by Laskowski [17] for bifenthrin are likely underestimates of sorption to OM because of a short equilibration time (24 h) and the presence of a cosolvent, acetonitrile, at a concentration of 2% by volume. In addition, large variations in  $K_{OC}$ s for OM with varying physicochemical properties have been reported [34], so the

Table 1. Freundlich isotherm parameters for the four experiments using a sorbent concentration at equilibrium ( $Q_e$ ) calculated from Equation 3 and those measured by sediment extraction; Freundlich capacity factor units are for the aqueous concentration at equilibrium ( $C_e$ ) in  $\mu\text{g/L}$  and  $Q_e$  in  $\mu\text{g/g}^a$

Pyrethroid	Sediment	$Q_e$	$n^b$	$K_F^b$	$R^2$
Bifenthrin	Bed	Eqn. 3	0.74 (0.60–0.89)	4.10 (2.51–6.69)	0.928
		Ext	0.77 (0.60–0.93)	1.84 (1.03–3.26)	0.966
	Suspended	Eqn. 3	0.72 (0.63–1.53)	13.57 (3.23–73.00)	0.875
		Ext	1.21 (0.66–1.75)	19.94 (3.95–100.75)	0.943
$\lambda$ -Cyhalothrin	Bed	Eqn. 3	1.07 (0.96–1.18)	9.60 (6.76–13.62)	0.979
		Ext	0.96 (0.72–1.20)	4.03 (1.78–9.10)	0.954
	Suspended	Eqn. 3	0.84 (0.66–1.01)	16.03 (8.02–32.04)	0.928
		Ext	0.75 (0.21–1.30)	6.04 (0.63–57.69)	0.946

<sup>a</sup> Eqn. 3 = Equation 3; Ext = sediment extraction;  $K_F$  = Freundlich capacity factor.

<sup>b</sup>  $n$  = Freundlich exponent, 95% confidence interval in parentheses.

experimental  $K_{OCs}$  may not be outside of that natural variability. Other researchers have also reported higher  $K_d$  and  $K_{OC}$  values for sediment and suspended materials than the representative values reported by Laskowski [17] (see Supplemental Data, Table S1). Strong evidence exists that measurements of whole water containing fine particles or dissolved organic matter causes an overestimation of freely dissolved aqueous concentrations, and a consequent underestimation of  $K_d$ s for the highly sorptive pyrethroids [13]. Because ratio of solids to solution was very low ( $\sim 1:1,000$ ) in our study, we do not expect significant overestimation of free aqueous concentrations to have affected our results.

Alternatively, larger than expected log  $K_{OCs}$  could be an indication that significant sorption contributions are made by the mineral phases of the sorbents or that the organic carbon in the Sacramento River is highly sorptive, e.g., because it contains black carbon or another highly reactive OC domain. The bed sediment was analyzed and found to contain 0.02% black carbon, which is on the high end of the typical range found in sediments and soils (1–10% of the organic carbon) [35]. In a recent study by Yang et al. [36], pyrethroids were found to sorb strongly to charcoal, but the distribution constants reported for black carbon were not significantly larger than those reported for organic carbon, unlike other compounds that exhibit much higher sorption to black carbon. To estimate the potential sorptive contributions of black carbon in the Sacramento River bed sediment, a black carbon distribution constant ( $K_{bc}$ ) for bifenthrin was used (log  $K_{bc} = 5.32$ ) [36]. The distribution coefficient ( $K_d$ ) of bifenthrin was estimated as the sum of sorption to organic carbon and black carbon ( $K_d = K_{OC}f_{OC} + K_{bc}f_{bc}$ ) using the average literature  $K_{OC}$  of  $10^{5.37}$  [17], the literature  $K_{bc}$  [36], and the measured  $f_{OC}$  and  $f_{bc}$  for bed sediment. This calculation gives a  $K_d$  of 417 L/kg for bifenthrin, compared to the experimental value of 7,460 L/kg. Based on these estimates, sorption to organic carbon and black carbon may not fully account for the experimental distribution constants observed in these experiments.

Because the Sacramento River solids used in this present study had very low levels of organic carbon, it is possible that the mineral phases contributed to the high sorption exhibited. When a sorbent has a very low OC content ( $< 0.1\%$ ), the assumption that OC dominates hydrophobic organic compound sorption may not be valid [27]. It has been demonstrated that when  $f_{OC}$  is below 0.001, mineral surface sorption can be important for nonpolar compounds [37,38]. The  $K_d$ s listed in Supplemental Data, Table S1, for sorption of pyrethroids to several minerals, show that pyrethroids exhibit a moderate affinity for mineral surfaces. To assess whether the measured mineral surface area is able to account for the higher than expected sorption to the tested materials, a mineral sorption term was added to the  $K_d$  estimation, given as Equation 6:

$$K_d = K_{oc}f_{oc} + K_{bc}f_{bc} + K_{min}S_A \cdot 1,000 \frac{g}{kg} \quad (6)$$

where  $K_{min}$  is the mineral surface distribution coefficient ( $L/m^2$ ) and the units of  $S_A$  are  $m^2/g$ , and the mineral term ( $K_{min}S_A$ ) is then multiplied by  $1,000 g/kg$  to correct the units. The calculated  $K_{min}$  for bifenthrin sorption to Rio Vista bed sediment was  $1.3 L/m^2$ . No pure mineral adsorption distribution coefficients are available for bifenthrin in the literature, but the calculated  $K_{min}$  ( $1.3 L/m^2$ ) is greater than those reported for  $\lambda$ -cyhalothrin adsorption to kaolinite and montmorillonite by approximately two orders of magnitude, and lower than the  $K_{min}$ s for  $\lambda$ -

cyhalothrin adsorption to quartz and corundum by a factor of 72 and 39, respectively. Because the mineral content of the Rio Vista bed sediment was not analyzed, the mineral distribution coefficients cannot be directly compared, but the required  $K_{min}$  of  $1.3 L/m^2$  appears to be within the range of reported distribution coefficients for pyrethroids on inorganic surfaces.

It is likely that not all of the mineral surface area and organic carbon are accessible for sorption due to site blocking that occurs when organic matter and minerals form a complex [39]. The surface area measurement by nitrogen sorption is able to measure nanopores that the bulky pyrethroids may not be able to access, so the maximum usable surface area for pyrethroids may be smaller than the total measured surface area. To assess if it is reasonable that sorption to the mineral domain predominates in the sorption of bifenthrin to Rio Vista bed sediment, the specific surface area required for mineral sorption to dominate over sorption to the organic carbon and black carbon domains was calculated with Equation 7:

$$S_A > \frac{K_{oc}f_{oc} + K_{bc}f_{bc}}{1,000 \frac{g}{kg} \cdot K_{min}} \quad (7)$$

where the  $K_{OC}$ ,  $f_{OC}$ ,  $K_{bc}$ , and  $f_{bc}$  are the same values used for previous calculations for bifenthrin sorption to Rio Vista bed sediment, and the  $K_{min}$  ranges from 0.0005 to  $50 L/m^2$ , covering the range of magnitudes reported in Supplemental Data, Table S1. The  $S_A$  required for sorption to the mineral domain to dominate ranges from 0.0083 to  $833 m^2/g$  for the varied conditions; the measured  $S_A$  is in the middle of this range, so a moderate-to-high  $K_{min}$  would be required to account for such a high percentage of mineral sorption.

The fraction of sorption to the mineral and organic matter phases were estimated to assess whether or not the higher than expected sorption could be explained by what is currently known about sorption of pyrethroids to minerals and organic matter, and it appears that significant bifenthrin sorption to mineral surfaces in the Rio Vista bed sediment did occur. The estimates of the contributions to bifenthrin sorption of the organic matter and mineral domains of Rio Vista bed sediment cannot accurately describe the fraction of bifenthrin sorbed to each domain because the distribution coefficients used in the calculations were average values and not specific to the experimental material. Mineral phases and OM do not act independently in bulk suspended solids and bed sediments, thus sorption of a particular chemical may not simply add up to the independent contributions of each domain [40]. Although these calculations were only performed for bifenthrin sorption to Sacramento River bed sediment, similar results would be obtained for  $\lambda$ -cyhalothrin. The Sacramento River suspended material used in the present study also had a low OC content, and yet it showed higher than expected sorption, so the mineral phase likely contributed to sorption for that sorbent as well.

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#### SUPPLEMENTAL DATA

Table S1 Freundlich parameters and distribution coefficients from the present study and the literature, including the range of initial concentrations, solid-water distribution coefficient,

organic carbon-normalized distribution coefficient, and the mineral surface area-normalized distribution coefficient. (72.5 KB DOC)

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