

DESORPTION OF PYRETHROIDS FROM SUSPENDED SOLIDS

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Abstract—Pyrethroid insecticides have been widely detected in sediments at concentrations that can cause toxicity to aquatic organisms. Desorption rates play an important role in determining the bioavailability of hydrophobic organic compounds, such as pyrethroids, because these compounds are more likely to be sorbed to solids in the environment, and times to reach sorptive equilibrium can be long. In the present study, sequential Tenax desorption experiments were performed with three sorbents, three aging times, and four pyrethroids. A biphasic rate model was fit to the desorption data with $r^2 > 0.99$, and the rapid and slow compartment desorption rate constants and compartment fractions are reported. Suspended solids from irrigation runoff water collected from a field that had been sprayed with permethrin 1 d before were used in the experiments to compare desorption rates for field-applied pyrethroids with those for laboratory-spiked materials. Suspended solids were used in desorption experiments because suspended solids can be a key source of hydrophobic compounds in surface waters. The rapid desorption rate parameters of field-applied permethrin were not statistically different from those of laboratory spiked permethrin, indicating that desorption of the spiked pyrethroids is comparable to desorption of the pyrethroids added and aged in the field. Sorbent characteristics had the greatest effect on desorption rate parameters; as organic carbon content of the solids increased, the rapid desorption fractions and rapid desorption rate constants both decreased. The desorption rate constant of the slow compartment for sediment containing permethrin aged for 28 d was significantly different compared to aging for 1 d and 7 d, whereas desorption in the rapid and slow compartments did not differ between these treatments. Environ. Toxicol. Chem. 2011;30:1760–1766. © 2011 SETAC

Keywords—Pyrethroids Desorption rate Organic carbon Aging time Suspended solids

INTRODUCTION

Pyrethroid insecticides are used for a wide variety of pest control applications in both urban and agricultural contexts, and their ubiquitous use is a current cause of concern for aquatic ecosystems. Pyrethroid insecticides have been widely detected in sediments at levels that can cause toxicity to aquatic invertebrates [1–4].

Pyrethroids are not registered for direct application to waterways, but they make their way into surface waters via runoff from rainfall or irrigation events because they are bound to suspended solids carried by runoff waters [2]. The low aqueous solubilities ($< 10 \mu\text{g/L}$) and high octanol–water partition coefficients ($\log K_{\text{OW}} > 5$) of pyrethroids result in generally low concentrations in the water column. The largest fraction of pyrethroids released to the environment is therefore found sorbed to sediments, and this fraction can be highly toxic to benthic invertebrates and fish [5].

Toxicity of sediment exposures does not always correlate well with whole-sediment concentrations, but the lower than expected toxicity of pyrethroids has been explained in part by very slow desorption rates [6]. Desorption rates play an important role in determining the bioavailability, and therefore the toxicity, of hydrophobic organic compounds (HOCs) in the environment, because these compounds are more likely to be resistant to desorption than more soluble chemicals [7–10]. Desorption resistance and reduced toxicity have been observed with several types of HOCs following aging on natural sorbents [11,12] and have been related to specific sorbent characteristics such as organic carbon content, quality of organic matter, black

carbon content, and particle size distribution [13–17]. Aging time is the amount of time for which a chemical is in contact with a sorbent before desorption commences, and long aging times have been shown to decrease toxicity of pyrethroids [18]. In California, USA, pyrethroids are often applied to agricultural fields, commercial nurseries, or residential structures or lawns and irrigated within 1 to 7 d; suspended sediments in rainfall and irrigation runoff are a transport route for pyrethroids into surface waters [2]. Thus, aging times of 24 h, 7 d, and 28 d were used in the present study because irrigation or storm events typically occur at frequent intervals when pyrethroids are directly applied.

Sorption of HOCs in soil and sediment is typically dominated by sorption to organic carbon (OC), and it is therefore not surprising that OC can limit desorption [7]. Cooke et al. [19] found that sorption of *cis*-permethrin to five soils showed a trend of increasing sorption with increasing soil OC, and, for two of these soils, less than 2% of the sorbed pyrethroids was released during desorption experiments. Desorption from sorbents with varied OC contents has been examined with other HOCs, and decreased desorption rates have been observed with increasing soil OC content [16,20].

To measure precisely the release rates of low-solubility, highly sorbing chemicals, it is useful to employ a third phase to promote desorption and act as an infinite sink for the solute, producing a boundary condition of approximately zero concentration. In the experiments described here, Tenax was used as the infinite sink to estimate the maximum desorption rate of pyrethroids from the soils and sediments [11,21–23]. The mechanism of desorption is the same as would occur in a natural environment, so this method can provide a quick way to estimate potential bioavailability of pyrethroids. Several researchers have proposed use of a single Tenax extraction at a given time point (6 h) to estimate the quantity of readily desorbed chemicals and the bioavailable fraction [6,11,18,21].

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The objectives of the present study were to measure maximum desorption rates of field-applied and laboratory-spiked permethrin and determine whether spiked permethrin demonstrates a desorption profile that approximates that of field-applied permethrin; to examine the effects of sorbent OC content on permethrin desorption rates; to examine the effects of aging times of 1 d, 7 d, and 28 d on permethrin desorption rates; and to examine the differences in desorption rates of four pyrethroids. Permethrin was selected as the focus of the first three objectives because in California it is the pyrethroid used in the greatest abundance (342,525 lbs [155,367 kg] in 2008), as reported by the California Department of Pesticide Regulation [24], and permethrin-contaminated field samples of suspended solids were available. Bifenthrin, cyfluthrin, and λ -cyhalothrin were chosen to compare with permethrin because their use is moderate or high in California [24], and they have varied aqueous solubilities (0.014, 2.3, and 5.0 $\mu\text{g/L}$, respectively) and log-normalized octanol–water partition coefficients (6.40, 5.97, 7.00, respectively) [25]. Several other studies have examined pyrethroid desorption [18,19,26–29], but no other studies have examined desorption from suspended solids, which has been shown to be a transport route of pyrethroids into surface waters in California [2]. Results for suspended solids might differ from those for bulk soils and sediment because of the preferential removal of particular mineral and/or organic matter fractions during erosion or resuspension events that transport the pyrethroid-containing material into the water column.

MATERIALS AND METHODS

Chemicals

Bifenthrin, λ -cyhalothrin, and cyfluthrin standards in methanol (100 $\mu\text{g/ml}$) were purchased from AccuStandard. Spiking solutions were prepared by adding the appropriate amount of pyrethroid standard to make 5 $\mu\text{g/ml}$ in methanol, and calibration standards were prepared in hexane (5–1,000 $\mu\text{g/L}$) from the pyrethroid standards. The $^{13}\text{C}_6$ *cis*-permethrin standard, purchased from Cambridge Isotope Laboratories, came as 50 $\mu\text{g/ml}$ in 1.2 ml nonane. The nonane was evaporated to dryness under N_2 , and then the $^{13}\text{C}_6$ *cis*-permethrin was resuspended in 1.2 ml methanol, and 5 $\mu\text{g/ml}$ spiking solution was made in methanol. Tenax[®] TA (60/80 mesh; Supelco/Fisher Scientific), a porous polymer adsorbent based on 2,6-diphenylene oxide, was used to capture desorbed pyrethroids from the soils. The Tenax was prepared by sequential washing with methanol, acetone, and hexane. No pyrethroids were found in the blank Tenax extracts. A 5 mM potassium phosphate (KH_2PO_4 , ACS grade; Fisher Scientific) buffer was prepared, and the pH was adjusted to 7 with 1 M NaOH solution (ACS grade). The buffer was used to limit variations in pH, because at pH 7 these four pyrethroids are reported to be stable to hydrolysis or have a very long half-life (183 d for cyfluthrin), whereas hydrolysis half-lives at pH 9 are short for cyfluthrin and λ -cyhalothrin (<10 d) [25]. Sodium azide (98% purity; EM Science) was added to the phosphate buffer at 200 mg/L to suppress biotic degradation during the desorption experiments. Deionized water (Milli-Q; Millipore) was used for all aqueous solutions. All solvents were either Optima or GC Resolv grade (Fisher Scientific).

Instrumentation

Analysis of the four pyrethroids was performed on an Agilent 6890 series gas chromatograph with an electron capture detector (GC-ECD), except in the cases when $^{13}\text{C}_6$ *cis*-permethrin was spiked into Salinas suspended solids, when an Agilent

6890 series gas chromatograph–mass spectrometer (GC/MS; Agilent Technologies) was employed. The GC-ECD was equipped with an Agilent J&W Duraguard DB-5HS column (30 m \times 0.250 mm, 0.25 μm film thickness). The GC/MS was equipped with an Agilent J&W Duraguard DB-5MS column (30 m \times 0.250 mm, 0.25 μm film thickness). The same oven program was used for the GC-ECD and the GC/MS; 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 at 280°C for 10 min. The GC/MS was run in SIM mode, and the quantification and confirmation ions, respectively, were m/z 181 and 165 for bifenthrin, m/z 183 and 184 for unlabeled permethrin, and m/z 189 and 190 for $^{13}\text{C}_6$ *cis*-permethrin. The inlet temperature was 300°C, and pulsed splitless injection was used with a pressure of 40 psi until 1 min. Calibration was based on area using six external standards of 5 to 500 $\mu\text{g/L}$ pyrethroid in hexane. The calibration curves were linear in this concentration range ($r^2 > 0.99$).

Soils

Salinas suspended solids were acquired from Don Weston (Richmond Research Station, University of California—Berkeley). A research lettuce field in Salinas, California, USA, was sprayed with Pounce[™] (active ingredient permethrin) on November 9, 2006, applied at 0.2 pounds active ingredient/acre (0.224 kg a.i./ha), in 60 gallons water/acre (561 L/ha). The field was irrigated on November 10, 2006, and four 5-gallon (18.9-L) stainless-steel kegs of irrigation runoff water were collected. This same field had also been sprayed for the three preceding weeks, with irrigation the following day and cultivation before the subsequent application of Pounce. The collected runoff water samples were at ambient temperature for approximately 24 h during transportation and holding before pick-up of the samples and were then stored at 4°C for 4 d. Suspended solids were separated from the water using a flow-through centrifuge (Aqua-Aerobic). The separated solids were stored wet at 4°C until use in the experiments, up to 20 months. The average moisture content of the Salinas sediment was determined to be 33% by oven drying three subsamples at 105°C for 24 h, each subsample weighing approximately 2 g before drying. The moisture content was used to calculate the dry weight of the suspended solids used in the experiments. The solids were Soxhlet extracted to determine the initial concentration of permethrin from the field application of Pounce. Triplicates of approximately 3 g wet solids were mixed with anhydrous Na_2SO_4 to dry, and then the mixture was Soxhlet extracted with hexane for 24 h. The field-applied permethrin concentration in the suspended solids was determined to be 6.64 ± 0.44 $\mu\text{g/g}$. This concentration was assumed to be a good approximation of an environmentally relevant concentration, and a convenient nominal value of 7.5 $\mu\text{g/g}$ was chosen as the soil spike concentration for the experiments.

Soil was collected from 0 to 20 cm after removing large debris from the surface for both Forbes and Yolo soils. Yolo soil was collected from an organic farm on the UC—Davis campus, and Forbes soil was collected from the Tahoe National Forest in Placer County, California, USA, in 2003. The soils were air-dried and sieved to <425 μm . To prepare the soils for use in the desorption experiments, 5-g subsamples of each were rewetted with Milli-Q water to two-thirds of their percentage moisture content at one-third bar, which was 14% moisture for Yolo soil and 27% moisture for Forbes soil. The soil subsamples were stirred, capped, and allowed to equilibrate with the water for 48 h before use in desorption experiments. The soils were rewetted and allowed to equilibrate before spiking, because

drying has been shown to affect sorption rates significantly, and rewetting restored the rates to their original values [30]. Separate soil aliquots were Soxhlet extracted, as described above, and analyzed for six pyrethroids; none was detected.

The percentage total carbon and nitrogen of all three soils (Table 1) was measured by the Agriculture and Natural Resources Analytical Laboratory at UC—Davis by high-temperature combustion. The soils were pretreated with hydrochloric acid to remove inorganic carbon prior to analysis.

Desorption experiments

All glassware was washed and rinsed with Milli-Q water and baked in a 450°C muffle furnace before use. Glass 50-ml centrifuge tubes and silver foil-lined caps were used in the desorption experiments to minimize sorptive losses [31]. Wet soil (approximately 0.1 g dry) was weighed in triplicate centrifuge tubes; triplicate control tubes containing no soil were also prepared. Both soil and control tubes were spiked with 0.15 ml of the appropriate spiking solution. This volume of spiking solution covered the soil completely, and then the tubes were agitated for about 2 min to distribute the solution throughout the soil. The tubes were stored in the dark, with the caps left off for approximately 8 h to allow the methanol to evaporate. The caps were then replaced and the tubes were stored for 24 h, 7 d, or 28 d since the initial spike was added, depending on the experiment. The short aging times (24 h, 7 d) were chosen to represent California dry season conditions, during which fields are typically irrigated within 1 to 7 d of application of pyrethroids, and 28 d was chosen as the longest aging time because irrigation or storm events would rarely occur at longer intervals where pyrethroids are directly applied and susceptible to runoff. After the appropriate aging period, phosphate buffer was added to almost fill the tubes and then 0.1 g Tenax TA was added to each tube. The tubes were completely covered in foil to prevent photodegradation and agitated on a rotary mixer at 30 rpm. The tubes were removed from the mixer and centrifuged at 3,000 rpm for 15 min so that the soil sank to the bottom and the Tenax floated on the top. The Tenax was removed from the tube with a clean, metal, solvent-rinsed spatula, and clean Tenax (0.1 g) was added to the tube, which was then recapped and returned to the rotary mixer. The 10 time points at which Tenax was removed were 30 min, 1 h, 2 h, 4 h, 8 h, 24 h, 2 d, 3 d, 5 d, and 7 d.

There were 10 different experimental treatments, with various chemical spikes, aging times, and sorbents. The first treatment was prepared to examine the desorption of the preexisting, field-applied permethrin from Salinas suspended solids with no additional chemical spike added (FA Per-1d-Salinas w/o spike). The Salinas fields were irrigated 1 d after application of permethrin, which equates to a 1-d aging time of the permethrin on the soil prior to irrigation. In the next experimental treatment, $^{13}\text{C}_6$ *cis*-permethrin was added to Salinas suspended solids, and the desorption profiles of field-applied and labeled permethrin were distinguished using the GC/MS; the treatment IDs for the field-applied permethrin and

the labeled *cis*-permethrin are FA Per-1d-Salinas w/ spike and $^{13}\text{C}_6$ Per-1d-Salinas w/ spike, respectively. The treatments with and without spikes were designed to determine whether there were competition effects when additional chemical was added to the Salinas suspended solids, which contained field-applied permethrin. The third and fourth treatments had $^{13}\text{C}_6$ *cis*-permethrin as the sorbate and either Yolo soil or Forbes soil as the sorbents, with 1-d aging periods ($^{13}\text{C}_6$ Per-1d-Yolo and $^{13}\text{C}_6$ Per-1d-Forbes). Treatments 5 to 7 used various sorbates (bifenthrin, cyfluthrin, or λ -cyhalothrin) with Salinas suspended solids and 1-d aging periods (Bif-1d-Salinas, Cyf-1d-Salinas, and LCy-1d-Salinas). Treatments 8 and 9 used $^{13}\text{C}_6$ *cis*-permethrin as the sorbate with Salinas suspended solids as the sorbent but used aging periods of 7 d or 28 d ($^{13}\text{C}_6$ Per-7d-Salinas and $^{13}\text{C}_6$ Per-28d-Salinas). Finally, a control treatment was prepared with no soil and pyrethroids were spiked directly onto the glass centrifuge tubes.

The Tenax was extracted with 10 ml acetone, followed by 2×10 ml acetone:hexane (1/1, v/v), with a 5-min ultrasonic bath treatment between each extraction; the solvent was decanted for each step and combined, then dried with anhydrous sodium sulfate, evaporated to 1 ml with a rotary evaporator, transferred to a GC vial, evaporated to near dryness, and resuspended in 0.5 ml hexane for analysis by GC. At the end of the experiment, the supernatant was removed with a pipet, being careful not to remove any of the solid material at the bottom of the tube. The supernatant pH was checked at the end of several experiments, and the pH range was 6.8 to 7.2, so losses from hydrolysis were not expected.

In several experiments, the supernatant was liquid-liquid extracted with 3×40 ml ethyl acetate to ensure that the aqueous concentrations were close to zero in the experiments. All buffer extracts that were from tubes containing soil had nondetectable pyrethroids (<10 ng/L), whereas buffer extracts from control tubes contained detectable, but low, concentrations (<1 $\mu\text{g/L}$), approximately 5% of the total mass spiked. After the supernatant had been removed, the solid material of every tube was mixed with anhydrous sodium sulfate to dry and then Soxhlet extracted with acetone:hexane (1:3, v/v) for 24 h. Glassware was rinsed with solvent and added to Soxhlet extraction solvents to account for adsorption to glassware.

Quality assurance/quality control

A surrogate (150 μl of 500 $\mu\text{g/L}$ pyrethroid in hexane) was added to the Tenax after removal to check the recovery of the extraction and sample preparation steps. Bifenthrin was used as a surrogate for all of the experiments, except for the bifenthrin sorbate experiment, in which λ -cyhalothrin was used. The average surrogate recovery was $102 \pm 14\%$, indicating that losses did not occur in the Tenax extractions and sample preparation steps. The average percentage pyrethroid mass recovered from the Tenax extracts and the cumulative percentage mass recovered from both the Tenax extracts and the Soxhlet extracts are given in Table 2. The total pyrethroid recoveries were 70 to 88%, except for three of the treatments that had recoveries of 54 to 56%. The experiments with recoveries below 70% were the treatments with Forbes soil and 7 d aging and 28 d aging. These poor recoveries could be due to incomplete Soxhlet extractions or degradation. In a preliminary study in which sediments were spiked and Soxhlet extracted on the following day, recovery of four pyrethroids was $90 \pm 15\%$. We suspect that these matrices were more difficult to extract because of the higher organic carbon content of Forbes and the longer contact times in the aging experiments. Reduced

Table 1. Sorbent characteristics^a

	OC (%)	Total N (%)
Yolo	1.08	0.14
Salinas	3.18	0.29
Forbes	3.56	0.17

^a OC = organic carbon; N = nitrogen.

Table 2. Desorption rate constants (k) and desorbed fractions (F) in the rapid and slow compartments for pyrethroids with varying sorbents and contact times^a

	$F_{\text{rapid}} \pm \text{SD}$	$k_{\text{rapid}} (\text{h}^{-1}) \pm \text{SD}$	$F_{\text{slow}} \pm \text{SD}$	$k_{\text{slow}} (\text{h}^{-1}) \pm \text{SD}$	Recovery (%) of Tenax; total
FA Per-1d-Salinas w/o spike	0.306 ± 0.006	0.160 ± 0.037	0.694 ± 0.006	9.95E-04 ± 9.67E-05	41; 68
FA Per-1d-Salinas w/ spike	0.296 ± 0.051	0.198 ± 0.015	0.704 ± 0.051	2.00E-03 ± 5.82E-04	49; 77
¹³ C ₆ Per-1d-Salinas (spike)	0.320 ± 0.040	0.250 ± 0.055	0.680 ± 0.040	1.77E-03 ± 5.24E-04	48; 75
¹³ C ₆ Per-1d-Yolo	0.445 ± 0.018	0.332 ± 0.021	0.555 ± 0.018	2.51E-03 ± 6.92E-05	62; 74
¹³ C ₆ Per-1d-Forbes	0.110 ± 0.015	0.162 ± 0.023	0.890 ± 0.015	8.16E-04 ± 1.71E-04	22; 56
Bif-1d-Salinas	0.430 ± 0.009	0.206 ± 0.074	0.570 ± 0.009	2.13E-03 ± 4.63E-05	64; 85
Cyf-1d-Salinas	0.493 ± 0.011	0.171 ± 0.007	0.507 ± 0.011	1.84E-03 ± 1.75E-04	62; 71
Lcy-1d-Salinas	0.527 ± 0.008	0.162 ± 0.019	0.473 ± 0.008	2.10E-03 ± 2.11E-04	66; 88
¹³ C ₆ Per-7d-Salinas	0.279 ± 0.016	0.243 ± 0.023	0.721 ± 0.016	2.29E-03 ± 2.54E-04	50; 55
¹³ C ₆ Per-28d-Salinas	0.360 ± 0.010	0.195 ± 0.020	0.640 ± 0.010	1.16E-03 ± 9.31E-05	45; 54

^a FA = field-applied; Per = permethrin; Bif = bifenthrin; Cyf = cyfluthrin; Lcy = λ-cyhalothrin; 1d = spike was aged with sorbent 1 d before desorption experiment initiation; 7d = aged 7 d before experiment initiation; 28 d = aged 28 d before experiment initiation. The percentage recovery of pyrethroid from the Tenax desorption steps is listed, followed by the total pyrethroid recovered from both Tenax and the final Soxhlet extraction.

bioavailability and greater than expected adsorption has been observed previously for Forbes soil with other HOCs [32]. Control tubes that contained no sorbent had an average total recovery of $85 \pm 4.5\%$, which indicates that losses did occur during the experiments, although individual steps all show good recovery.

Desorption model

All desorption data were modeled using a dual exponential rate model assuming no significant readsorption [7,11,16]:

$$S_t/S_0 = F_{\text{rapid}}(e^{-k_{\text{rapid}}t}) + F_{\text{slow}}(e^{-k_{\text{slow}}t}) \quad (1)$$

where S_t is the sediment-sorbed mass at time t (ng), S_0 is the sediment-sorbed amount at t_0 (ng), F_{rapid} and F_{slow} are the pyrethroid fractions in rapidly or slowly desorbing compartments, k_{rapid} and k_{slow} are the desorption rate constants for the compartments (h^{-1}), and t is time (h). The pyrethroid mass at t_0 was assumed to be the nominal spike mass for any spiked experiments. For experiments with field-applied permethrin, subsamples of the solid material were extracted shortly before each experiment, and those values were used as S_0 . The assumptions of this model are that the concentration of pyrethroids in the aqueous phase is negligible compared with that in the soil, that the sum of F_{rapid} and F_{slow} is unity, and that the desorption from one compartment is independent of the other compartment [11]. The model outputs were obtained using a nonlinear regression routine within Grapher 4.0 (Golden Software).

RESULTS AND DISCUSSION

The Tenax extract data were examined with a two-compartment empirical model (Eqn. 1), and the parameters are given in Table 2. The mean triplicate data points are plotted with the model results for each experiment in Figures 1, 2, 3, and 4. The two-compartment model fit the data well, with a coefficient of determination (r^2) > 0.99 and a residual sum of squares < 0.005 for all data.

Desorption of spiked and field-applied permethrin

Field-applied permethrin (FA-permethrin) was present in the Salinas suspended solids, and desorptions of the field-applied and spiked permethrin are compared in Figure 1. The desorptions of the field-applied permethrin in the treatments with and without the labeled permethrin spike were compared, and sorption competition was not detected because the desorption

profiles did not differ between the two treatments. All plots in Figure 1 show desorption of permethrin from Salinas suspended solids aged for 1 d at room temperature. FA-permethrin desorption experiments were performed with and without a ¹³C₆ *cis*-permethrin spike, and the rapidly desorbed fraction (F_{rapid}) and rate constant of the rapid fraction (k_{rapid}) were not statistically different for these two experiments. The desorption rate constant of the slow fraction (k_{slow}) was lower for FA-permethrin without the spike than with the spike, but the values are within a factor of two. These results could have been caused by the spiking solution (MeOH) aiding desorption of the slow compartment. Another possibility is that the addition of the ¹³C₆ *cis*-permethrin caused displacement of the FA-permethrin but only in the slow compartment, in which a greater fraction of mass is desorbed, but over a longer period. These findings are consistent with previous work that has shown that competition between field-aged and freshly applied HOCs occurs in the slow compartment [33].

The desorption parameters of the ¹³C₆ *cis*-permethrin spike are very similar to those of the field-applied permethrin. The fraction desorbed and the slow compartment rate constant of the spike are not statistically different from the corresponding parameters for field-applied permethrin. The rapid compartment rate constant of the spike is larger than that for the FA-permethrin, but by less than a factor of two.

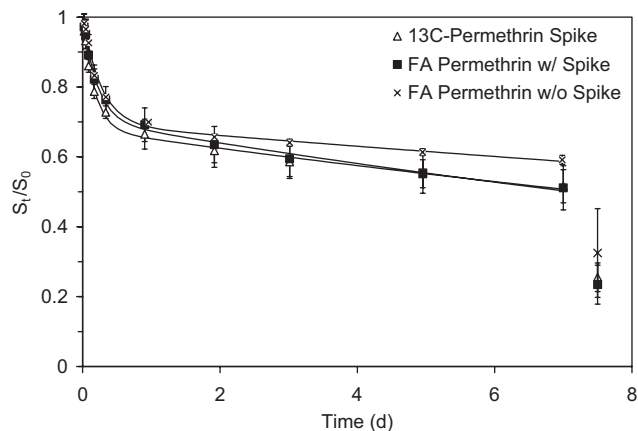


Fig. 1. Desorption of field-applied permethrin and spiked ¹³C₆ *cis*-permethrin from Salinas suspended solids. The spikes had a 1-d aging time. The sorbents were Soxhlet extracted following the Tenax desorption steps, and the cumulative masses of permethrin recovered from the solids are displayed as separate symbols at time 7.5 d.

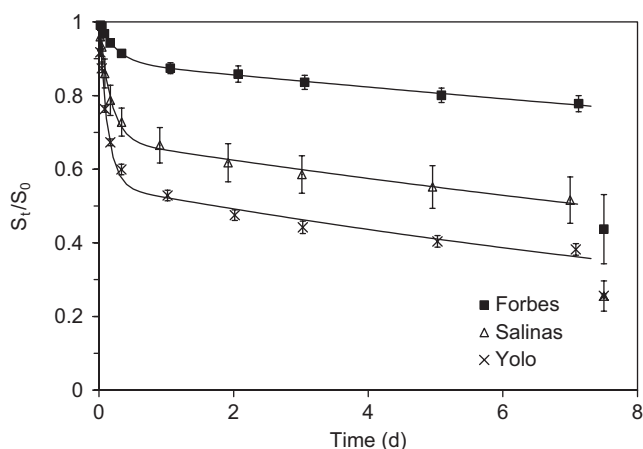


Fig. 2. Desorption of $^{13}\text{C}_6$ cis-permethrin from three sorbents with 1-d aging time. The sorbents were Soxhlet extracted following the Tenax desorption steps, and the cumulative masses of permethrin recovered are displayed as separate symbols at time 7.5 d.

From this comparison, we can conclude that the desorption rates of spiked pyrethroids are a reasonable approximation of rates expected for field applied pyrethroids. Desorption of spiked permethrin from a control tube containing no sorbent exhibited a much larger F_{rapid} (0.729 ± 0.048) and k_{rapid} ($1.422 \pm 0.492 \text{ h}^{-1}$) than desorption from soil organic matter, indicating much less resistance to desorption from glass compared with soil organic matter.

Desorption of permethrin from three sorbents

Spiked permethrin desorptions from Forbes soil, Yolo soil, and Salinas suspended solids after a 1-d aging time are compared in Figure 2. The extent and rates of permethrin desorption are significantly different for the three sorbents, and the results are correlated to the organic carbon content of the sorbent (Table 1). All of the desorption parameters (Table 2) for permethrin desorption from Forbes, Yolo, and Salinas solid matters show significant statistical difference between materials. The rate constants and F_{rapid} decrease with increasing soil OC content and the total mass desorbed during the experiment also decreased with increasing soil OC content. All of these

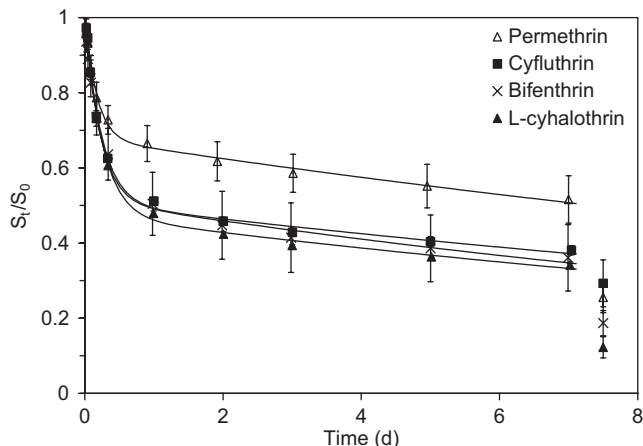


Fig. 3. Desorption of four pyrethroids from Salinas suspended solids with a 1-d aging time. The sorbents were Soxhlet extracted following the Tenax desorption steps, and the cumulative masses of pyrethroid recovered are displayed as separate symbols at time 7.5 d.

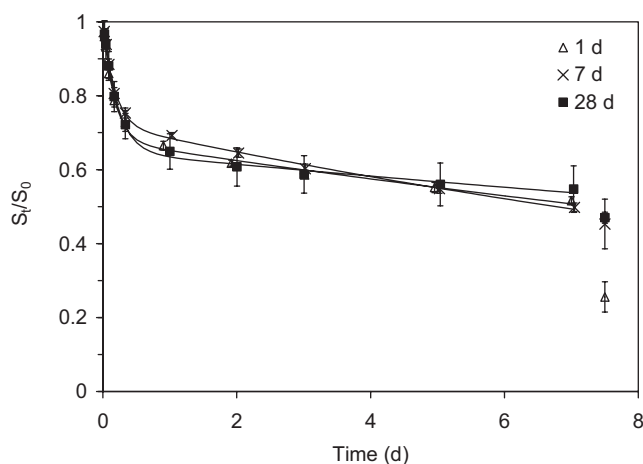


Fig. 4. Desorption of $^{13}\text{C}_6$ cis-permethrin from Salinas suspended solids with three different aging times. The sorbents were Soxhlet extracted following the Tenax desorption steps, and the cumulative masses of permethrin recovered are displayed as separate symbols at time 7.5 d.

trends indicate that OC content is an important factor determining desorption resistance for these sorbents, although other sorbent properties were not examined. Xu et al. (2008) performed similar desorption experiments with bifenthrin, cyfluthrin, fenpropathrin, and λ -cyhalothrin using the Tenax method and found that F_{rapid} generally decreased as soil organic carbon content increased for aging times of 7, 40, and 100 d, in comparing two soils with organic carbon contents of 1.44 and 5.03% [18].

Desorption of four pyrethroids from suspended solids

The rate constants and desorbed fractions for cyfluthrin, bifenthrin, and λ -cyhalothrin are very similar, whereas the values for permethrin are generally lower, demonstrating more resistance to desorption than the other pyrethroids, as displayed in Figure 3. The differences are not large between the compounds and might result simply from experimental variability. No conclusion can be reached about which structural pyrethroid factors determine differences in desorption rates from these data, and a clear trend was not observed, because all desorption parameters were different by less than a factor of two. We expect, based on these four pyrethroids, that other pyrethroids with similar properties likely would have similar desorption rates from a given sorbent and aging time.

Desorption of permethrin at three aging times

The rapid compartment desorption rate constants do not appear to be dependent on aging times for permethrin (Fig. 4). The k_{slow} values for 1 d and 7 d are not statistically different; the 28 d k_{slow} value is lower than these values, but by less than a factor of two. Xu et al. have performed similar experiments with longer aging times (up to 200 d), and an increase in desorption resistance of pyrethroids and degradation of the compounds was seen with longer times and aging in the field [18]. Shorter aging times (1–28 d) were used in the present study because they are relevant to California environmental conditions for agriculture or lawn care, in which irrigation or storm events occur at regular intervals.

Fate of pyrethroids

To predict the fate of pyrethroids in the environment and their bioavailability, sorption and desorption processes must be well understood. The goal of the present study was to

understand better the effect of aging time and sorbent characteristics on desorption rates of pyrethroids and to compare the desorption rates of several widely used pyrethroids. The results showed that the sorbent OC content significantly affected desorption rate constants, with k_{rapid} decreasing as OC content increases. The aging time of permethrin with soil before the introduction of water did not have a significant effect on the rapid rate constant for aging times of 1 to 28 d, although k_{slow} did decrease for the 28-d contact time. In general, k_{slow} was approximately two orders of magnitude smaller than k_{rapid} ; the range of k_{rapid} was 0.160 to 0.332 h^{-1} , whereas the range of k_{slow} was 8.16×10^{-4} to $2.51 \times 10^{-3} \text{ h}^{-1}$ for desorption from soil organic matter. Recent research has shown that rapid desorption rate constants correlate well with ecotoxicity [6,9,34].

Phenanthrene desorption rates for two of the same soils, Forbes and Yolo, were performed by Watanabe et al. [35] with five aging times ranging from 1 h to 18 months. The rapid and slow rate constants for phenanthrene desorption with 1-d aging (1.1 and $6.1 \times 10^{-3} \text{ h}^{-1}$, respectively) are both about an order of magnitude larger than those of permethrin (0.162 and $8.34 \times 10^{-4} \text{ h}^{-1}$, respectively). Phenanthrene is less hydrophobic than permethrin ($\log K_{\text{OW}}$ of 4.57 and 6.1 , respectively), so larger rate constants for the same soils are expected. Permethrin desorption rate constants for two sediments (1.31 and 7.85% OC) were reported by You et al. [34], with k_{rapid} ranging from 0.2287 to 0.5016 h^{-1} , k_{slow} ranging from 0.266 to 0.579 h^{-1} , and initial concentrations ranging from 226 to $1,600 \text{ ng/g}$. The rapid rate constants are similar to those for permethrin desorption from Salinas sediment, but the slow rate constants are an order of magnitude larger.

The pyrethroids tested displayed desorption resistance in all of the experiments: no more than 53% of the nominal spike addition was desorbed in the rapid compartment for any of the experiments, and no more than 65% of the nominal spike addition was desorbed onto the Tenax. These percentages may be overestimates of desorption resistance, because the mass balances were incomplete for most experiments. Additional pyrethroids were recovered from Soxhlet extractions of the sediment for all experiments, so there is clear evidence for desorption resistance, but none of the mass balances was complete following the Soxhlet extractions, so more pyrethroids may remain in the sorbents. These results imply that after 7 d of continuous mixing with an aqueous concentration near zero, pyrethroids may still be associated with the sediment, and some amount may be transported downstream on these particles.

Comparing estimates of rapidly desorbing fraction

A single Tenax extraction at a time point of 6 h has been proposed as a quick and simple method to measure bioavailable pyrethroids, because this time point has been shown to correlate well with the rapidly desorbing fraction and toxicity to *Hyalella azteca* [6]. A single Tenax extraction has also been used to estimate bioavailability of other sorbed HOCs [11,20]. It has been presumed in previous work that the amount of HOC desorbed after 6 h and the fitted value of F_{rapid} can be used interchangeably as predictors of the readily bioavailable fraction. To examine this assumption, we calculated the fraction of the pyrethroid desorbed after 6 h in our experiments, and in all cases the calculated values were within 30% of the F_{rapid} values in Table 2. The time it took for the desorbed mass fraction to reach F_{rapid} was also calculated using the parameters in Table 2, and this ranged from 2.44 to 13.65 h, indicating that the 6-h time point could potentially over- or underestimate the rapidly

desorbed pyrethroid concentration. The geometric mean of the time for the rapid fraction of desorption was 5.13 h, indicating that a 6-h Tenax extraction will give a good estimate of F_{rapid} for desorption of pyrethroids under the given experimental conditions. The time required for the rapid fraction of permethrin to desorb from Yolo soil was the shortest at 2.44 h, whereas that for Forbes soil was the longest at 13.65 h.

This type of rate data provides a crucial input to fate models that predict downstream transport and potential ecotoxicity of pyrethroids. This is especially relevant in areas where irrigation or precipitation events occur within one month of pyrethroid application, because we have observed that aging for less than one month does not significantly decrease the rapidly desorbing fraction of pyrethroids.

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