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Enantioselective Degradation and Chiral Stability of Pyrethroids in Soil and Sediment

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Synthetic pyrethroids contain two or three chiral centers, making them a family of chiral pesticides with a large number of stereoisomers. Recent studies showed significant differences in aquatic toxicity between enantiomers from the same diastereomers of pyrethroids. To better understand the ecotoxicological effect and fate of pyrethroid insecticides, chirality in biodegradation must also be considered. In this study, we examined enantiomer compositions of selected pyrethroids in field sediment samples taken from various locations in southern California. Enantioselective degradation was frequently observed for *cis*-bifenthrin, permethrin, and cyfluthrin under field conditions. We further conducted long incubation experiments under laboratory-controlled conditions using single enantiomers of *cis*-bifenthrin, *cis*-permethrin, and cypermethrin. The half-lives for individual enantiomers were calculated to be 277−770 days for *cis*-bifenthrin enantiomers, 99−141 days for *cis*-permethrin enantiomers, and 52−135 days for cypermethrin enantiomers, respectively. The direction and degree of enantioselectivity in degradation were found to closely depend on the specific compound as well as experimental conditions. Because no significant difference in degradation was observed after samples were sterilized, the observed enantioselectivity may be attributed to preferential biological transformations.

KEYWORDS: Enantioselective; degradation; chiral; enantiomer; pyrethroids

INTRODUCTION

Chiral compounds currently account for about 25% of all pesticides used commercially and for 26% of the total value of the world pesticides market (*1*). Among these compounds, those sold in single isomer form contribute only 6% of the market value (*1*). It is well-known that even though enantiomers from the same compound have identical physical−chemical properties, they may behave enantioselectively in biological processes (*2*, *3*). As compounds with more complex structures are introduced into usage, it may be expected that more chiral compounds will be released into the environment (*4*, *5*). Therefore, there is an increasing interest to evaluate the enantioselective behavior of chiral contaminants in the environment.

Pyrethroids are widely used for controlling insects in crop production and around households. With the restriction of usage of organophosphate insecticides, the use of pyrethroids is expected to further increase. Although pyrethroids are highly hydrophobic and immobile in soil, they may find their way into aquatic systems via runoff or soil erosion (*6*, *7*). This makes them a significant environmental concern because most pyrethroids possess high acute toxicity to fish and aquatic invertebrates, often at concentrations less than 0.5 ppb (*8*−*10*).

All pyrethroids contain two or three chiral centers, making them a family of pesticides with the highest number of enantiomers. The chirality of pyrethroids may arise from the acid moiety, the alcohol moiety, or both (*2*, *3*). In the developmental history of pyrethroids, significant enantioselectivity has been widely observed in insecticidal activity for the enantiomers from the same compound (*2*, *3*, *11*, *12*), and recently, studies show that enantioselectivity also exists in their aquatic toxicity (*4*, *13*). However, in most existing literature, enantioselectivity of pyrethroids has not been adequately considered in their fate and transport processes. Given that most pyrethroids are used in a racemic form, knowledge of the environmental behavior of individual pyrethroid enantiomers will be of great value for improving our understanding of the associated ecotoxicological risks and will be of benefit to the study of other chiral compounds.

Degradation of pyrethroids in soil has been extensively studied. Most studies show that microorganisms play an important role in the degradation of pyrethroid compounds in soils and sediments (*7*, *14*−*18*). Because many studies show that for racemic compounds (e.g., α-HCH, metalaxyl, and metolachlor), certain enantiomers are often preferentially degraded over the others (*19*−*21*); we developed this study to evaluate the occurrence of enantioselective degradation of pyrethroids in soils and sediments under different conditions. In this study, field samples from the southern California region were taken and analyzed to determine if enantioselective degradation occurred for pyrethroids under field conditions. Laboratory incubation experiments under controlled conditions

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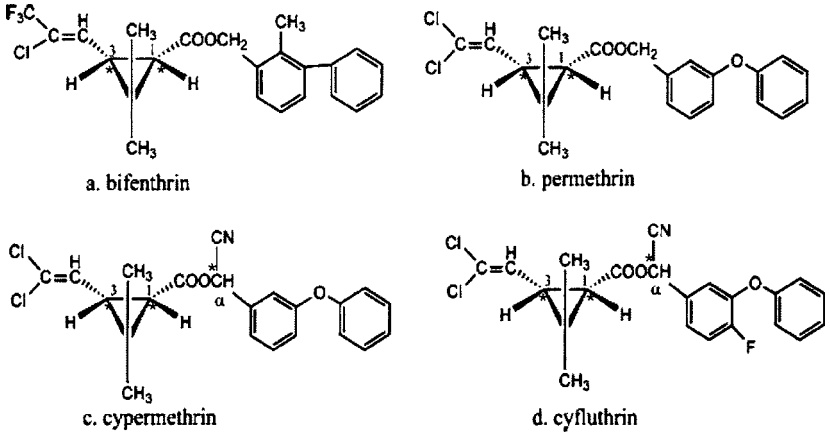

Figure 1. Chemical structures of *cis*-BF, PM, CP, and CF.

Table 1. Textural and Chemical Properties of Soil and Sediment Used in This Study

		%			
	pH	OM	sand	silt	clay
San Diego Creek sediment	7.9	1.09	20	46	34
Arlington soil	6.7	0.82	67	24	9

were further carried out to confirm the occurrence of enantioselective degradation and understand the difference of enantioselective degradation under different conditions.

MATERIALS AND METHODS

Chemicals. Analytical standards of racemic (*Z*)-*cis*-bifenthrin (*cis*-BF, 98%), *cis*-permethrin (*cis*-PM, 99%), cyfluthrin (CF, 98%), and cypermethrin (CP, 98%) were purchased from Chem Service (West Chester, PA). The stereoconfigurations of the selected pyrethroid compounds are shown in **Figure 1**. By using different chiral high-performance liquid chromatography (HPLC) columns, we isolated individual enantiomers of these compounds, which included one pair of enantiomers from *cis*-BF (*R*-*cis*-BF and *S*-*cis*-BF), one pair of enantiomers from *cis*-PM (*R*-*cis*-PM and *S*-*cis*-PM), and one pair of enantiomers from a diastereomer of CP (1*R*-*cis*-α*S*-CP and 1*S*-*cis*-α*R*-CP) by following the methods reported in Liu et al. (*22*). The purity of these enantiomers was determined to be >99% by HPLC and gas chromatography (GC) analysis prior to their use. Other solvents or chemicals used in this study were of analytical or HPLC grade.

Soils. One soil and one sediment were used in the laboratory incubation experiments (**Table 1**). The soil and sediment were collected from the 0−10 cm surface layer from two sites in the southern California region. An Arlington sandy loam was taken from a turfgrass plot at the Agricultural Experiment Station near the University of California, Riverside campus, and the sediment was collected from a location along San Diego Creek in Irvine, CA. The soil and sediment samples were air-dried for 24 h at room temperature, homogenized, and then passed through a 2 mm sieve before use.

Collection of Field Sediment Samples. The Upper Newport Bay is an ecological reserve located within Orange Country, CA. The primary freshwater inlet for the estuary is San Diego Creek. There is evidence for potential toxic effects caused by pyrethroid residues in the Upper Newport Bay (*23*). To determine if given enantiomers are preferentially degraded in the natural environment, samples were taken in the Newport Bay−San Diego Creek watershed based on accessibility and land uses. Information on sampling locations is given in **Figure 2**. For each sampling site, two sets of samples were collected, one in the spring of 2005 after the rainy season and the other in the summer of 2005 during the dry season. For analysis, 100 g of homogenized wet sediment was centrifuged for 25 min at 10000 rpm and the supernatant was decanted. After measurement of sediment water content, 20 g (wet weight) of the sediment was transferred into a 250 mL beaker, mixed with enough anhydrous sodium sulfate (10−30 g) to remove the excess water, and extracted three consecutive times with 50 mL of acetone−methylene chloride (1:1, v/v) by sonication (5 min in 3 s on/1 s off pulse mode). All solvent phases were combined and decanted. The solvent extract was passed though a Whatman no. 41 filter paper (Whatman, Maidstone, United Kingdom) filled with 2 g of anhydrous sodium sulfate. The extract was combined and evaporated to less than 5 mL on a vacuumed rotary evaporator at 40 °C. The residue was transferred into a 5 mL evaporation vial, concentrated to near dryness with a stream of nitrogen gas, and then reconstituted to 1.0 mL with hexane. The sample was further cleaned through a 10 g Florisil column, and pesticides were eluted using 50 mL of ethyl ether−hexane (1:1, v/v). After the sulfur was removed using activated copper (based on EPA method 3660B), the sample was again concentrated to 1.0 mL and an aliquot was analyzed on an achiral GC. For the samples with positive detection of pyrethroids (**Figure 2**), chiral GC analysis was further performed to obtain information on the relative ratio of enantiomers and diastereomers in the field-aged sediment samples.

Laboratory Incubation Experiments. Degradation of pyrethroids was further evaluated through laboratory incubation experiments. Ten grams of soil or sediment (dry weight equivalent) was placed in 150 mL flasks or 20 mL glass vials. For the Arlington soil, the water content was adjusted to about 60% of field holding capacity (w/w) by adding deionized water. For the San Diego Creek sediment, around 6 mL of deionized water was added to each sample to form a 0.5 cm water layer. For *R*-*cis*-BF and *S*-*cis*-BF, two sets of 18 flasks were prepared for each soil or sediment type. One set of samples was exposed to anaerobic conditions by equilibrating the samples in a nitrogen-filled plastic chamber. The other set of samples was used for incubation under aerobic conditions. For PM and CP enantiomers, an additional set of samples was also prepared and subjected to sterilization treatment to determine if enantioselective degradation was a result of microbially mediated transformations. Sterilization was achieved by autoclaving the samples twice at 121 °C for 60 min, with a 24 h interval between the first and the second autoclaving, to remove the microbial activity. Individual enantiomers were spiked into the soil or sediment samples separately, with 10 μg of chemical (in 100 μL of acetone) added into each 10 g soil or sediment using a microsyringe. The initial pesticide concentration was therefore 1.0 μg g^{-1} on an oven-dry weight basis. All spiked samples were incubated at room temperature (20 ± 1 °C). Samples were checked regularly for water content and were also frequently mixed for aeration (for aerobic experiments only).

Three replicate samples were removed from each treatment at different time intervals after pesticide addition and immediately transferred into a freezer (−20 °C) to stop degradation. For extraction, samples were thawed at room temperature and transferred to 250 ml glass centrifuge bottles. The samples were mixed with anhydrous sodium sulfate and shaken with 50 mL of hexane−acetone (1:1, v/v) for 1 h on a mechanical shaker and then centrifuged at 1000 rpm for 20 min. The same extraction step was repeated for a total of three times, and the solvent extracts were filtered through 25 g of anhydrous sodium sulfate for dehydration. The combined extract was evaporated to near

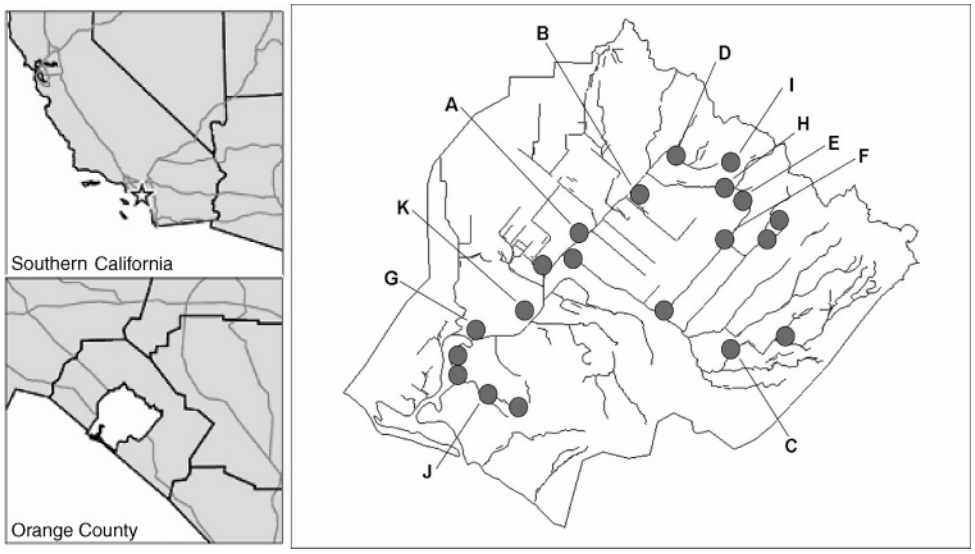

Figure 2. Sampling locations of field sediment samples used in the study (Newport Bay–San Diego Creek watershed in Orange County, California).

dryness on a vacuumed rotary evaporator at 50 °C. The residues were recovered by rinsing the flask with 5.0 mL of hexane−acetone (1:1, v/v), and an aliquot was used for analysis by GC. Preliminary experiments showed that the recovery was >90% for this extraction procedure. The pesticide concentrations measured at the different time points were fitted to a first-order decay model to estimate the first-order rate constant k (days^{-1}) and the half-life $T_{1/2}$ (days).

GC Analysis. Quantification of pyrethroids in soil extracts was carried out on an Agilent 6890N GC system (Palo Alto, CA) with an electron capture detector. The detector temperature was 310 °C, and the makeup gas was nitrogen at 60 mL min^{-1}. The inlet temperature was 260 °C. Achiral analysis was carried out using a nonchiral selective HP-5 column (30 m × 0.25 mm × 0.25 μm, cross-linked 5% diphenyl and 95% dimethyl-polysiloxane, Agilent, Wilmington, DE) with helium as the carrier gas at 1.5 mL min^{-1}. The column temperature was initially held at 210 °C for 1 min and then ramped to 300 °C at 5 °C min^{-1}, followed by holding at 300 °C until complete elution. Preliminary experiments showed that the method detection limits were 0.2−0.5 ppb for these pyrethroids. Chiral analysis was performed on an enantioselective BGB-172 column (30 m × 0.25 mm × 0.25 μm, 20 *tert*-butyldimethylsilyl-β-cyclodextrin dissolved in 15% diphenyl- and 85% dimethyl-polysiloxane, BGB Analytik, Adliwil, Switzerland). The column was initially held at 160 °C for 1 min and then ramped to 230 °C at 1 °C min^{-1}, followed by holding at 230 °C until complete elution of enantiomers. Under the conditions used, all enantiomers from the cis diastereomers were well-separated, while those from the trans diastereomers were not resolved (*4*, *24*), and preliminary experiments showed the method detection limits of the chiral analysis were estimated to be 1−2 ppb for these pyrethroids.

RESULTS AND DISCUSSION

Enantioselective Degradation under Field Conditions. Enantioselective degradation was evaluated for the selected pyrethroids by comparing changes of stereoisomer profiles from the original values. In most field samples with positive detection of *cis*-BF (2−500 ppb), PM (1−10 ppb), or CF (0.5−2.5 ppb, detected only in the spring samples) on achiral GC, reanalysis of samples on chiral GC showed that enantioselectivity in degradation varied among the different compounds, and for the same compound, it varied among different sediment samples. Under the analytical conditions used, the chiral chromatograms contained peaks of separated cis enantiomers but unresolved trans diastereomers due to incomplete chiral separation of the trans enantiomers (**Figure 3**). The peak area of the separated peaks was used to calculate the relative fraction of the resolved stereoisomers by using the same concept as enantiomer fraction

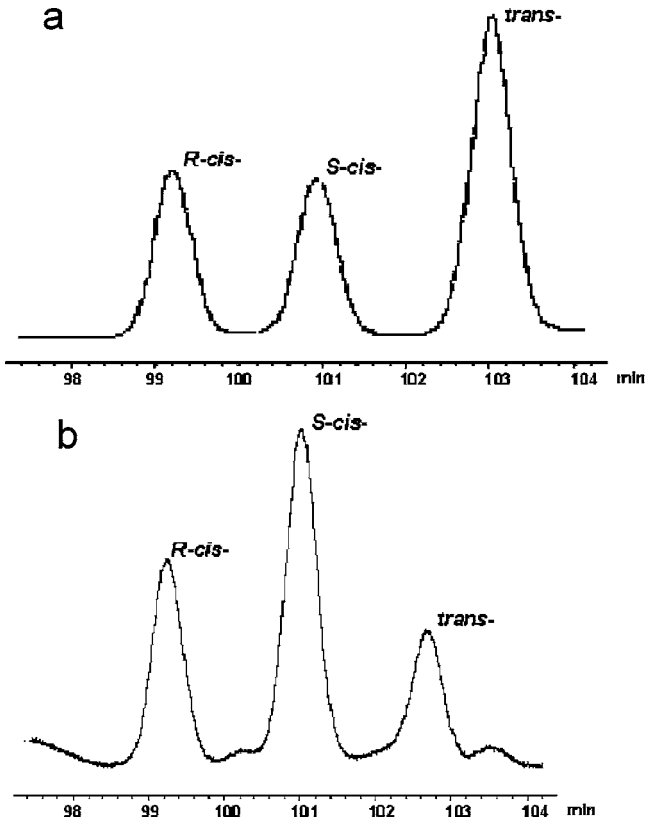

Figure 3. GC chromatograms of PM under enantioselective analytical conditions. (**a**) Standard reference and (**b**) a sediment sample from San Diego Creek in Orange County, California.

(*25*). The stereoisomer fraction (SF) was calculated as the fraction of a given stereoisomer over the total chemical concentration found for the specific compound in a given sample. In racemic formulations, the SF is 0.5 for *R-cis*- and *S-cis*-BF, respectively, in *cis*-BF; 0.25, 0.25, and 0.50 for *R-cis*-, *S-cis*-, and *trans*-PM, respectively, in PM; and 0.125 for each cis enantiomer and 0.25 for each trans diastereomer in CF. The SF values measured for the field sediment samples are summarized in **Tables 2**−**4** for *cis*-BF, PM, and CF, respectively.

The observed SF values remained close to the original value (0.5) for both *R-cis*- and *S-cis*-BF in most samples except for site H in the spring sample set (**Table 2**). A pair *t*-test between

Table 2. SF of *cis*-BF in Stream Sediment Samples

	spring		summer			spring		summer	
site	*R-cis*	*S-cis*	*R-cis*	*S-cis*	site	*R-cis*	*S-cis*	*R-cis*	*S-cis*
A	0.50	0.50	0.45	0.55	G	0.56	0.44	0.52	0.48
B	0.49	0.51	0.49	0.51	H	0.33	0.67		
C	0.51	0.49			I	0.48	0.52		
D	0.47	0.53	0.49	0.51	J	0.44	0.56	0.52	0.48
E	0.45	0.55	0.49	0.51	K	0.53	0.47		
F	0.45	0.55	0.45	0.55	mean	0.47	0.53	0.49	0.51

Table 3. SF of Enantiomers and Diastereomers of PM in Stream Sediment Samples

	spring				summer			
site	*R-cis*	*S-cis*	*cis*	*trans*	*R-cis*	*S-cis*	*cis*	*trans*
A	0.13	0.32	0.45	0.56				
B	0.22	0.35	0.57	0.43	0.57	0.00	0.57	0.43
C	0.34	0.33	0.67	0.33				
E	0.46	0.54	1.00	0.00	0.13	0.72	0.85	0.15
F					0.39	0.33	0.72	0.28
G	0.14	0.71	0.85	0.15	0.25	0.25	0.50	0.50
H	0.17	0.43	0.60	0.40				
J	0.78	0.00	0.78	0.22	0.67	0.14	0.81	0.18
K	0.37	0.38	0.75	0.25				
mean	0.33	0.38	0.71	0.29	0.40	0.29	0.69	0.31

the *R* and *S* enantiomers showed no significant difference in SF. The average SF for *R-cis*-BF was 0.47 for the spring samples and 0.49 for the summer samples, suggesting that there was little preferential degradation of one enantiomer over the other. Analysis of PM in the same sediment samples showed that the trans diastereomer was degraded faster than the cis diastereomer in both spring and summer samples (**Table 3**). One example is shown in **Figure 3**. The averaged SF for the spring samples was 0.71 for *cis*-PM and only 0.29 for *trans*-PM. The corresponding values for the summer samples were 0.69 and 0.31 (**Table 3**). A paired *t*-test showed that in both spring and summer samples, the SF of *trans*-PM was significantly smaller than that of *cis*-PM ($P = 0.007$). The faster degradation of *trans*-PM over *cis*-PM was consistent with previous observations (*1*−*3*, *7*, *15*−*18*). Between the two enantiomers in *cis*-PM, the SF for the individual enantiomers often deviated from the original value of 0.25 for both spring and summer samples (**Table 3**). However, the paired *t*-test did not show a statistically significant trend for the enantioselectivity. It is apparent that in some samples *S-cis*-PM was predominant, while in some other samples the fraction of *R-cis*-PM was greater or similar to that of *S-cis*-PM (**Table 3**). Therefore, the direction and rate of enantioselectivity in the degradation of PM were closely dependent on the sampling location, and a general trend was not identified. Analysis of CF in the sediments showed that while the SF of one trans diastereomer (1*R-trans*-α*R* + 1*S-trans*-α*S*) was consistently smaller than 0.25, the SF of the other trans diastereomer (1*R-trans*-α*S* + 1*S-trans*-α*R*) was consistently greater than 0.25 (**Table 4**). Of the cis enantiomers, the SF remained around 0.125 for some samples but clearly increased or decreased in the other samples (**Table 4**). When enantioselective degradation was observed, the direction of enantioselectivity also appeared to depend on the sampling location and environmental conditions.

The variation in the direction and rate of selectivity for *cis*-PM and *cis*-CF enantiomers was similar to previous observations made for other chiral compounds. For example, metalaxyl was usually found to be environmentally enriched with the *S*-isomer. In one laboratory study, the fungicidally active *R*-enantiomer of metalaxyl degraded more rapidly than the inactive *S*-enantiomer, resulting in residues enriched with *S*-metalaxyl when the racemic compound was incubated. The ratio of *S*-enantiomer over *R*-enantiomer increased from the initial value of 1 to around 11 (*26*). However, a reversed enantioselectivity was observed in anaerobic degradation in sewage sludge, which resulted in residues enriched in *R*-metalaxyl (*27*). In another study, in aerobic soils with pH > 5, the *R*-enantiomer of metalaxyl was degraded faster than the *S*-enantiomer ($k_R > k_S$), resulting in residues with composition [*S*] > [*R*]. However, in aerobic soils with pH 4−5, both enantiomers were degraded at similar rates ($k_R \approx k_S$). In aerobic soils with pH < 4 and in most anaerobic soils, the enantioselectivity was reversed ($k_R < k_S$) (*28*), showing [*R*] > [*S*]. Such discrepancies in degradation rate and ratio between enantiomers from the same compound are possible because there may be variations in the microbial populations at different locations, in different types of soils, and under different environmental conditions.

Laboratory Incubation Experiment. Dissipation of selected enantiomers of *cis*-BF, PM, and CP was measured in a soil and a sediment at ambient temperature under either sterilized, aerobic, or anaerobic conditions. For all treatments, the data fits well to the first-order decay model, with R^2 ranging from 0.87 to 1.00 (**Tables 5**−**7**). All pyrethroid enantiomers exhibited

Table 5. First-Order Rate Constant (k), Half-Life ($T_{1/2}$), and Correlation Coefficient (R^2) for the Degradation of Enantiomers of *cis*-BF in Soil and Sediment

soil	enantiomer	k (days^{-1})	$T_{1/2}$ (days)	R^2
		aerobic		
Arlington soil	*R-cis*	0.0025	277 ± 19	0.98
	S-cis	0.0021	330 ± 28	0.97
San Diego Creek sediment	*R-cis*	0.0012	578 ± 24	0.95
	S-cis	0.0011	630 ± 34	0.98
		anaerobic		
Arlington soil	*R-cis*	0.0009	770 ± 43	0.96[a]
	S-cis	0.0014	495 ± 21	0.96
San Diego Creek sediment	*R-cis*	0.0011	630 ± 46	0.93[a]
	S-cis	0.0017	408 ± 36	0.95

[a] Indicates significant difference between enantiomers at $\alpha = 0.05$.

Table 4. SF of Enantiomers and Diastereomers of CF in Stream Sediment Samples

	spring							
	1*R-cis*-α*R*	1*S-cis*-α*S*	1*R-cis*-α*R* + 1*S-cis*-α*S*	1*R-trans*-α*R* + 1*S-trans*-α*S*	1*R-cis*-α*S*	1*S-cis*-α*R*	1*R-cis*-α*S* + 1*S-cis*-α*R*	1*R-trans*-α*S* + 1*S-trans*-α*R*
B	0.14	0.12	0.26	0.16	0.15	0.08	0.23	0.34
D	0.13	0.12	0.25	0.17	0.08	0.07	0.15	0.43
E	0.20	0.16	0.36	0.14	0.11	0.09	0.20	0.29
J	0.12	0.12	0.24	0.15	0.08	0.07	0.15	0.46
K	0.09	0.19	0.28	0.15	0.09	0.04	0.13	0.43
mean	0.14	0.14	0.28	0.15	0.10	0.07	0.17	0.39

Table 6. First-Order Rate Constant (k), Half-Life ($T_{1/2}$), and Correlation Coefficient (R^2) for the Degradation of Enantiomers of *cis*-PM in Soil and Sediment

soil	enantiomer	k (days^{-1})	$T_{1/2}$ (days)	R^2
		sterilized		
Arlington soil	*R-cis*	0.0049	141 ± 9	0.99
	S-cis	0.0050	139 ± 11	0.98
San Diego Creek sediment	*R-cis*	0.0050	139 ± 10	0.99
	S-cis	0.0050	139 ± 11	0.98
		aerobic		
Arlington soil	*R-cis*	0.0056	124 ± 11	0.91
	S-cis	0.0068	102 ± 12	0.91
San Diego Creek sediment	*R-cis*	0.0056	124 ± 9	0.96
	S-cis	0.0055	126 ± 11	0.98
		anaerobic		
Arlington soil	*R-cis*	0.0061	114 ± 7	0.99
	S-cis	0.0068	102 ± 12	0.96
San Diego Creek sediment	*R-cis*	0.0070	99 ± 7	0.99
	S-cis	0.0057	122 ± 11	0.98

Table 7. First-Order Rate Constant (k), Half-Life ($T_{1/2}$), and Correlation Coefficient (R^2) for the Degradation of Enantiomers of CP in Soil and Sediment

soil	enantiomer	k (days^{-1})	$T_{1/2}$ (days)	R^2
		sterilized		
Arlington soil	1*S-cis*-α*R*	0.0060	116 ± 4	1.00
	1*R-cis*-α*S*	0.0058	120 ± 8	0.99
San Diego Creek sediment	1*S-cis*-α*R*	0.0058	120 ± 2	1.00
	1*R-cis*-α*S*	0.0057	122 ± 11	0.98
		aerobic		
Arlington soil	1*S-cis*-α*R*	0.0097	71 ± 7	0.92[a]
	1*R-cis*-α*S*	0.0110	63 ± 7	0.87
San Diego Creek sediment	1*S-cis*-α*R*	0.0082	85 ± 13	0.95[a]
	1*R-cis*-α*S*	0.0132	53 ± 6	0.98
		anaerobic		
Arlington soil	1*S-cis*-α*R*	0.0058	120 ± 14	0.96[a]
	1*R-cis*-α*S*	0.0097	71 ± 4	0.99
San Diego Creek sediment	1*S-cis*-α*R*	0.0045	154 ± 10	0.94[a]
	1*R-cis*-α*S*	0.0051	136 ± 13	0.95

[a] Indicates significant difference between enantiomers at $\alpha = 0.05$.

relatively long half-lives, with $T_{1/2}$ ranging from 53 to 770 days. The shortest $T_{1/2}$ was found with 1*R-cis*-α*S* CP in the San Diego Creek sediment under aerobic conditions, with a $T_{1/2}$ of 53 days (**Table 7**). In earlier studies on pyrethroid degradation in soil (*15*−*17*), the persistence of pyrethroids was found to be intermediate with $T_{1/2}$ varying from 7 to 112 days. For example, the $T_{1/2}$ of racemic PM was 7−21 days in silt and clay soils and up to 105 days in organic soils. The $T_{1/2}$ of CP racemate was 14−28 days in mineral and organic soils. However, in recent studies on the persistence of pyrethroids in sediments, the $T_{1/2}$ values of racemic PM and *cis*-BF were found to be much longer, and the persistence was consistently prolonged under anaerobic conditions when compared to aerobic conditions (*7*). For instance, the $T_{1/2}$ of *cis*-PM was 98−142 days under aerobic conditions and increased to 209−380 days under anaerobic conditions, respectively. These observations were consistent with the overall long $T_{1/2}$ value found for the selected enantiomers of *cis*-BF, PM, and CP in this study. The increased persistence may be partly attributed to the fact that both the soil and the sediment used in this study contained little organic matter and may be low in microbial activity.

Sterilization treatment in the incubation experiments with enantiomers from PM and CP consistently resulted in a decrease in degradation rate, and the slower degradation was attributable to the removal of microbial activity in the matrix (**Tables 6** and **7**). The degradation rate of both enantiomers was always similar under sterilized conditions, and no significant difference was found between the estimated $T_{1/2}$ values. This suggests that the enantioselective degradation, when observed, was caused by microbial transformations. Incubation conditions such as oxygen status and type of solid matrix may have affected the makeup of microorganisms and hence influenced the rate and direction of the observed enantioselectivity.

The results from laboratory experiments show that enantioselective degradation occurred to some extent for all of these compounds under aerobic or anaerobic conditions. A Wald test was conducted to statistically compare the $T_{1/2}$ of enantiomers from these pyrethroids (*29*). Even though *R-cis*-BF degraded slightly faster in aerobic conditions, no significant difference was detected through the Wald test. Under anaerobic conditions, *S-cis*-BF was degraded faster than *R-S*-BF in both soil and sediment, and the difference was significant at $\alpha = 0.05$. For enantiomers from *cis*-PM, the $T_{1/2}$ values were similar between the enantiomers and no significant difference was found for either aerobic or anaerobic treatments. However, 1*R-cis*-α*S* CP was degraded more rapidly than 1*S-cis*-α*R* in both soil and sediment under either aerobic or anaerobic conditions, and the difference was significant at $\alpha = 0.05$. Sakata et al. (*18*) evaluated degradation of ^{14}C-labeled stereoisomers of selected pyrethroids in soils under aerobic conditions. The selected pyrethroids were generally degraded much faster than those observed in this study. While *R-cis*-PM was degraded faster in a light clay soil, *S-cis*-PM was found to degrade more rapidly in a sandy loam soil (*18*). In the same study, 1*R-cis*-α*S*-CP was found to degrade substantially faster than the 1*S-cis*-α*R* enantiomer and the ratio of $T_{1/2}$ (1*R-cis*-α*S* over 1*S-cis*-α*R*) was estimated to be around 0.45 in both soils (*18*). The preferential degradation of 1*R-cis*-α*S*-CP over 1*S-cis*-α*R*-CP was in agreement with that observed in this study. In this study, CP appeared to degrade at the same or slower rate under anaerobic conditions than under sterilized conditions. The slower degradation under anaerobic conditions may be partly attributable to the fact that photodegradation was completely inhibited under anaerobic conditions, as the samples were kept in the nitrogen-filled chamber. Photodegradation was found to be one of the most important pathways for CP degradation in soil (*30*).

Enantioselective degradation of pyrethroids has been reported in a few previous studies (*4*, *32*−*33*). The *S*-enantiomer of both *cis*-BF and *cis*-PM was found to be preferentially degraded in aged sediment samples at a sediment disposal site, and the deviation in enantiomer ratio from the original value increased with the depth of the sediment samples (*4*). A much larger sampling area was used in the current study, and thus, greater diversity was expected in the sediment properties and environmental conditions. Results from this study show that enantioselective degradation of pyrethroid may not necessarily follow the same direction, and the direction and rate of enantioselectivity appear to closely depend on the sampling location. Enantioselective degradation was also studied for *cis*-BF, PM, and CP using isolated bacterial stains (*32*, *33*). Incubation with pesticide-degrading bacteria showed that the trans diastereomer of PM was selectively degraded over the cis diastereomer, whereas the *S*-cis enantiomer in *cis*-BF or *cis*-PM was preferentially degraded over the corresponding *R*-cis enantiomer (*32*). In the similar study with CP (*33*), it was also found that the isolated bacteria strains preferentially degraded some diastereoisomers or enantiomers over the others. While results from the previous study clearly suggested the dependence of enan-

tioselectivity on microbial makeup, the experiments were carried out only under aerobic conditions and enantioselective degradation was found to follow the same direction. The fact that enantioselectivity may occur in both directions as found in this study suggests that a wider selection of microbial strains should be considered for evaluation of the role of microbial communities in environmental degradation of chiral contaminants.

Heat-induced isomerization has been reported for CP and CF during GC analysis (*31*). The isomerization of CP and CF enantiomers was found to be relatively small in our preliminary experiments (<9%) and was always bidirectional (*31*); the effect of isomerization on enantiomeric compositions of the field samples was not considered in this study. As pure enantiomers were spiked into the sediment or soil samples during the laboratory incubation experiments, isomerization should not affect the transformation kinetics of individual enantiomers. Abiotic isomerization under field conditions or during analysis is an important phenomenon and merits further studies.

In conclusion, this study demonstrated that enantioselective degradation commonly occurred for pyrethroids under both field and laboratory conditions, and the selectivity was attributed to microbial transformations. However, the direction and degree of enantioselectivity were not always predictable. It appears that both stereochemistry of the chiral compound and environmental conditions influenced the direction and rate of enantioselective degradation. As only some stereoisomers of pyrethroids are acutely toxic to aquatic organisms, the selectivity in biodegradation may have ecotoxicological implications. Our study suggests that concentrations of stereoisomers, instead of the total chemical concentration, should be used for better predicting ecotoxicity derived from pyrethroid residues in the environment.

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