JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Article

pubs.acs.org/JAFC

Laboratory Degradation Rates of 11 Pyrethroids under Aerobic and Anaerobic Conditions

Brian N. Meyer, Chung Lam, Sean Moore,[†] and Russell L. Jones*

Bayer CropScience, 2 T.W. Alexander Drive, Research Triangle Park, North Carolina 27709, United States

Supporting Information

ABSTRACT: Degradation of 11 pyrethroids was measured over approximately 100 days in three sediment/water systems under aerobic and anaerobic conditions at 25 °C in the dark. The three California sediments represented a range of textures and organic matter. Test compounds were bifenthrin, cypermethrin, ζ-cypermethrin, cyfluthrin, β-cyfluthrin, deltamethrin, esfenvalerate, fenpropathrin, γ-cyhalothrin, λ-cyhalothrin, and permethrin. A non-standard design was employed to keep conditions essentially the same for all compounds. The test compounds were applied as two test mixtures (six active ingredients per mixture, with bifenthrin common to both) at approximately 50 μg of test compound/kg of sediment (dry weight). Extracts of sediment/water were cleaned up by solid-phase extraction, concentrated, and analyzed by gas chromatography/mass spectrometry (except deltamethrin) against matrix-matched standards, with cyfluthrin-d_6 as an internal standard. Deltamethrin was analyzed by liquid chromatography/tandem mass spectrometry using deltamethrin-phenoxy-$^{13}C_6$ as an internal standard. Similar degradation rates of bifenthrin and for related isomeric compounds (e.g., cyfluthrin and β-cyfluthrin) were generally measured in both mixtures for each sediment. First-order half-lives under aerobic conditions ranged from 2.9 to greater than 200 days, with a median value of 18 days. Under anaerobic conditions, the range was from 20 to greater than 200 days, with a median value of 70 days.

KEYWORDS: *Pyrethroids, aquatic degradation*

INTRODUCTION

Pyrethroids are a class of insecticides, strongly bound to soils and sediments and degraded at varying rates, used to control a wide range of pests with both agricultural and urban uses. After urban uses of organophosphate compounds were discontinued, the amount of pyrethroids applied in urban settings greatly increased. Researchers have found pyrethroids in surface water sediments especially in California, where pyrethroids are used for ant control.[1−3] During the past decade, considerable research has been performed on the environmental fate of pyrethroids in both agricultural and non-agricultural settings (for example, see refs 4−7).

As part of its evaluation of pyrethroids, the California Department of Pesticide Registration (CDPR) requested additional information on the degradation of pyrethroids under aerobic and anaerobic conditions. While considerable information on the degradation rate of individual pyrethroids in aquatic systems is available from registration studies as well as a number of other studies (most of this information is summarized in a review paper by Laskowski[8]), there was no comprehensive study of multiple pyrethroids under similar conditions. Therefore, the study reported in this paper was performed to measure the degradation of 11 pyrethroids in three California sediments under aerobic and anaerobic conditions. The choice by CDPR of the 11 pyrethroids to be included in the study was based on their importance for outdoor applications.

Because the objective was to provide meaningful comparisons of degradation rates between compounds, the general study design deviated significantly from some of the requirements outlined in OPPTS 835.4300 and 835.4400.[9] The study was focused on the degradation of the parent compounds and did not measure metabolites. In addition, the degradation rates were for the overall system, and no attempt was made to distinguish between material in the solution or sediment phases. The high sorption coefficients of pyrethroids[8] would suggest that essentially all of the pyrethroid residues were present in the sediment phase. To permit multiple compounds to be present in the incubated systems, radiolabeled parent compounds were not used. All flasks were incubated at 25 °C. The target nominal concentration for each pyrethroid in the test systems was 50 μg/kg of sediment dry weight and was chosen to provide adequate analytical sensitivity. This starting concentration is a factor of 10 above the limit of quantitation (LOQ) of the analytical method of 5 ppb. The study was conducted according to the Good Laboratory Practice Standards, as noted in 40 CFR Part 160.[10]

MATERIALS AND METHODS

Test materials were grouped into two treatment mixtures, with isomeric analytes (e.g., cyfluthrin and β-cyfluthrin) being placed in different test mixtures. Bifenthrin was selected to be common to both mixtures. Chemical names and characteristics of the different test substances are provided in Table 1.

The test matrices used in this study were sediments collected from three sites in California. These sediments were chosen in consultation with CDPR to represent a range of textures and organic matter content. The geographic location and the physical−chemical properties of each sediment are shown in Table 2. Because water was not present in some of the sediments surveyed for consideration for

Received: January 30, 2013
Revised: May 1, 2013
Accepted: May 3, 2013
Published: May 3, 2013

Table 1. Description of the Test Substances

compound	test mixture	chemical name	CAS registry number	molecular weight	purity (%)
bifenthrin	1 and 2	(2-methyl[1,1′-biphenyl]-3-yl)methyl 3-(2-chloro-3,3,3-trifluoro-1-propenyl)-2,2-dimethylcyclopropanecarboxylate	82657-04-3	422.87	98.8
β-cyfluthrin	1	cyano(4-fluoro-3-phenoxyphenyl)methyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate	68359-37-5	434.29	96.8
		isomers I/II/III/IV = 0.53/31.4/1.78/63.1	68359-37-5	434.29	50.2[a]
cyfluthrin	2	cyano(4-fluoro-3-phenoxyphenyl)methyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate			
		isomers not specified			
γ-cyhalothrin	1	cyclopropanecarboxylic acid, 3-(2-chloro-3,3,3-trifluoro-1-propenyl)-2,2-dimethyl-,cyano(3-phenoxyphenyl)methyl ester, [1*R*-[1*α*(*S**),3*α*(*Z*)]]	76703-62-3	449.85	99.5
λ-cyhalothrin	2	[1*α*(*S**),3*α*(*Z*)]-(±)-cyano(3-phenoxyphenyl)methyl 3-(2-chloro-3,3,3-trifluoro-1-propenyl]-2,2-dimethylcyclopropanecarboxylate	91465-08-6	449.85	98.7
ζ-cypermethrin	1	cyclopropanecarboxylic acid, *cis*-(+)-3-(2,2-dichloroethenyl)-2,2-dimethyl-, (*S*)-cyano(3-phenoxyphenyl)methyl ester and cyclopropanecarboxylic acid, *trans*-(+)-3-(2,2-dichloroethenyl)-2,2-dimethyl-, (*S*)-cyano(3-phenoxyphenyl)methyl ester	67375-30-8	416.30	36.5[b]
cypermethrin	2	(±)-*α*-cyano(3-phenoxyphenyl)methyl (±)*cis*,*trans*-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate	52315-07-8	416.30	93.0
		cis/*trans* =40.6/59.4			
deltamethrin	1	(*S*)-cyano(3-phenoxyphenyl)methyl (1*R*,3*R*)-3-(2,2-dibromoethenyl)-2,2-dimethylcyclopropanecarboxylate	52918-63-5	505.20	99.4
esfenvalerate	1	((*S*)-cyano(3-phenoxyphenyl)methyl (*S*)-4-chloro-*α*-(1-methylethyl)benzeneacetate)	66230-04-5	419.90	98.7
fenpropathrin	2	*α*-cyano-3-phenoxybenzyl-2,2,3,3-tetramethylcyclopropanecarboxylate	39515-41-8	349.42	99.7
permethrin	2	(3-phenoxyphenyl)methyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate	52645-53-1	391.29	96.2
		cis/*trans* = 43.0/57.0			

[a]Solution in cyclohexanone. [b]Dissolved in a solvent not specified by the supplier.

Table 2. Description of the Three California Sediments

parameter	sediment 1	sediment 2	sediment 3
location			
description	sandy creek, east of San Diego	white slough (King Island)	Franks Tract State Recreation Area
county	San Diego	Contra Costa	Contra Costa
latitude	33° 0′ 54.22 N	38° 04.991′ N	38° 02.885′ N
longitude	116° 37′ 49.51 W	121° 26.250′ W	121° 36.850′ W
texture[a]			
class	sand	clay	sandy clay loam
sand (%)	90.3	20.4	49.5
silt (%)	1.8	30.1	25.9
clay (%)	7.9	49.5	24.6
pH[a]			
1:1 soil/water	6.8	6.0	6.9
saturated paste	7.0	6.0	6.8
0.01 M $CaCl_2$	6.4	5.8	6.6
organic matter[a] (%)	1.0	13.7	4.7
organic carbon[a] (%)	0.6	7.4	2.7
cation-exchange capacity[a] (meq/100 g)	6.0	19.0	14.8
moisture capacity[a]			
at 0.33 bar (%)	8.4	80.4	37.2
at 15 bar (%)	3.6	53.7	19.0
bulk density[a] (g/cm^3)	1.19	0.60	0.79

[a]Determined by Agvise Laboratories, Northwood, ND.

inclusion in this study, water was not collected with the sediment. Instead, conditioned water typically used for aquatic studies in the Ecotoxicology Department at the Bayer Facilities in Stilwell, KS, was used. All sediments were sieved (2 mm) and thoroughly mixed. The moisture content of each sediment was determined by heating three aliquots (approximately 10 g each) of sediment repeatedly until the sequential weights were constant. The time between sediment collection and dosing ranged between 2 and 8 weeks.

The aerobic test system consisted of a silanized 500 mL cylindrical flask with an air inlet. Humidified air was supplied continuously to each flask below the liquid level, at a rate that did not disturb the sediment. Aerobic test systems were covered with foil to exclude light and were maintained in the dark at 25 ± 1 °C.

The anaerobic test system consisted of a silanized 250 mL side arm Erlenmeyer flask with a mineral oil bubbler top to exclude air while permitting outgassing. The flasks were purged with nitrogen and were maintained in a temperature-controlled incubator in the dark at 25 ± 1 °C. Untreated test systems were prepared in screw-cap glass jars and incubated under the same conditions. When inconsistent analytical performance developed with sediment 1, various aspects of the method were re-investigated, and this work linked the problems to the jars for incubation of untreated controls, possibly because of not being

silanized. The anaerobic study with this sediment was therefore restarted using identical flasks for all treated and untreated test systems, and no further problems occurred. No problems were encountered with the other sediments, possibly because of their higher organic matter content. Silanization is performed to neutralize active sites on the glass, which may otherwise adsorb analyte molecules and shield them from analysis. This same effect might be accomplished by organic matter in the sediment, If so, then sediments with low organic matter would be more susceptible to active site binding of the analytes.

The quantities of sediment (as dry weight) and water in each test system are shown in Table 3. These quantities varied because of the density and volume of the wet sediment. For example, the dry weight of sediment 2 was reduced to 25 g in the anaerobic test because the volume of sediment that accounted for 50 g exceeded the volume of the incubation flask. In aerobic tests, the volume of water was adjusted to ensure that the air inlet was below the surface of the water but without disturbing the sediment layer.

Table 3. Amounts of Water and Sediment Used in the Degradation Studies[a]

	sediment 1	sediment 2	sediment 3
	Aerobic Study		
sediment (g)	50	50	50
water (mL)	200	270	260
	Anaerobic Study		
sediment (g)	50	25	50
water (mL)	150	150	150
water (mL)	150	150	150

[a]Sediment weights shown represent dry matter. Water quantities include sediment moisture.

For each sediment and test condition (aerobic or anaerobic), 86 test systems were prepared containing sediment and water. In each case, 20 test systems were designated for treatment with test mixture 1 and 20 test systems for treatment with test mixture 2. Six test systems were designated for bioactivity analysis: three untreated and three treated with acetonitrile as a spiking solvent control. The remaining 40 test systems were designated for use as concurrent recovery laboratory spikes and processing into matrix-matched standards and were therefore untreated.

Prior to treatment of the test systems, a pre-incubation period (ranging from 12 to 32 days) was used to acclimate and establish the appropriate conditions (aerobic or anaerobic) as judged by dissolved oxygen (DO) and redox. Also during this period, the analytical method was validated for the specific batch of sediment.

An approximately 100 ppm solution of each test substance was prepared by dissolving 0.01 g of standard in 100 mL of acetonitrile (the exact concentration was adjusted on the basis of standard purity). Application solutions for test mixtures 1 and 2 were prepared by diluting aliquots of the appropriate stock solutions with acetonitrile to a final concentration of 10 ppm per compound. All solutions were refrigerated and stored in the dark when not in use.

The application solution was applied uniformly to the surface of the water using an Eppendorf Repeater Xstream electronic pipet. The applied aliquot was 125 μL for sediment 2 anaerobic test systems, which contained 25 g (dry weight) of sediment. All other test systems contained 50 g (dry weight) of sediment, and 250 μL were applied.

Day 0 systems were analyzed immediately following application. Aerobic test systems were returned to the environmental chamber and attached to the aeration system. Anaerobic test systems were purged with nitrogen before being sealed and transferred to a nitrogen-filled incubator.

Test systems were sampled in duplicate at seven intervals (approximately 0, 3, 7, 14, 28, 60, and 100 days post-treatment). DO and pH were measured in the water layer, and redox potential was measured in both the water and sediment of each sample. On day 0, DO concentrations, pH, and redox were measured in representative flasks prior to treatment. Bioactivity was determined at Agvise Laboratories, Northwood, ND, by aerobic or anaerobic plate counts in representative untreated flasks at day 0 and approximately day 100.

At each sampling interval, two untreated test systems (one for each test mixture) were processed to prepare matrix-matched standards. Also, two previously untreated test systems (one for each test mixture) were spiked with the respective 10 ppm test mixture to generate lab spikes for concurrent recovery determination.

For analysis, acetonitrile (250 mL) was added to the test system and the contents were transferred to a 1 L plastic bottle, which was shaken on a mechanical shaker for 30 min. The contents were vacuum-filtered on Whatman GF/C filters, and the filter cake was rinsed with acetonitrile/water (4:1). The filtrate volume was then adjusted to 700 mL using water.

For analysis of deltamethrin, a 10 mL aliquot of the filtrate was applied to a conditioned 1 g ENVI-Carb cartridge (Sigma-Aldrich, St. Louis, MO), rinsed with acetonitrile/water (3:2) and methanol, and eluted with dichloromethane (DCM). The internal standard (deltamethrin-phenoxy-$^{13}C_6$) was added to the eluate, which was concentrated to dryness and redissolved in methanol/water (9:1). Deltamethrin was analyzed by liquid chromatography/tandem mass spectrometry (LC/MS/MS), using a TSQ Ultra (Thermo Scientific, Waltham, MA) interfaced to a CTC PAL HTC autosampler (Leap Technologies, Carrboro, NC), Surveyor pump (Thermo Scientific), and Gemini, 50 × 2.0 mm, 5 μm, high-performance liquid chromatography (HPLC) column (Phenomenex, Torrance, CA).

For all other analytes, a 70 mL aliquot of the filtrate was applied to a conditioned 1 g ENVI-Carb cartridge, rinsed with acetonitrile/water (3:2) and methanol, and eluted with DCM. The eluate was concentrated to dryness and redissolved in DCM/cyclohexane (2:3). This solution was applied to a conditioned 1 g NH_2 cartridge (Agilent Technologies, Santa Clara, CA) and rinsed with DCM/cyclohexane (2:3). The internal standard (cyfluthrin-d_6) was added to the collected rinse, which was concentrated to dryness and redissolved in cyclohexane for analysis by gas chromatography/mass spectrometry (GC/MS). Analysis used a Trace GC Ultra (Thermo Scientific) and Rtx-5MS, 30 m × 0.25 mm × 0.25 μm, capillary column (Restek Corporation, Bellefonte, PA).

The analytical method was validated with each specific batch of sediment prior to the application of the test substances by analyzing five replicate test systems freshly spiked with each test mixture at 5 ppb (10% of application rate) and 50 ppb of each analyte. Treated flasks were swirled to suspend the sediment immediately after spiking. Additionally, an untreated test system was analyzed to check for background residue.

Kinetic evaluations were performed using KinGUI 1.1, a program developed for kinetic evaluation of degradation studies with crop protection products using criteria specified by FOCUS.[11] The program uses a nonlinear regression method to determine the most appropriate values for the parameters of the specified kinetic model and then provides statistical information describing the comparison of the observed values and the values from the kinetic model using the derived parameters, along with plots of the fit and the residuals.

Kinetic evaluations were performed for the 72 data series (six compounds applied in test mixture 1 and six compounds in test mixture 2, all applied to three sediments under both aerobic and anaerobic conditions) with single first-order (SFO) kinetics and double first-order in parallel (DFOP) kinetics. For selected bifenthrin data series (where concentrations near the start of the experiment were lower than the amount applied, but the degradation curve from later time points extrapolated back to near the amount applied), an additional kinetic evaluation was performed with the starting amount of parent in the kinetic model fixed to 100% of the applied material (concentrations were expressed as the percentage of the applied material). In each data series, there were 14 data points (duplicate samples at 7 time intervals), except for six compounds having 13 data points (in the anaerobic study with sediment 1, one replicate failed at one time interval).

The information presented in this paper was directly obtained from the reports generated by KinGUI. KinGUI provides the 95%

confidence interval in terms of the first-order degradation rate, k. These values of k were transformed to the corresponding half-life $t_{1/2}$ using the following equation:

$$t_{1/2} = \ln(2)/k$$

RESULTS AND DISCUSSION

Redox, pH, and DO measurements are shown in Table 4 for aerobic studies and Table 5 for anaerobic studies. In aerobic flasks, redox (E_h) was generally greater than 200 mV in water and greater than 58 mV in sediment, while DO was greater than 5 mg/L. In anaerobic flasks, redox (E_h) was generally less than 110 mV, with the exception of the first four intervals for sediment 1, and DO was 0.3 mg/L or less. These DO and redox (E_h) values in the aerobic and anaerobic flasks are typical of measurements obtained in such studies.[12] The results of the bioactivity determination by aerobic and anaerobic plate counts showed the systems to be microbially active at the end of the study, with counts remaining the same or increasing or decreasing from the starting levels depending upon the sediment, organism type, and whether the incubation conditions were aerobic or anaerobic.

The method was validated by analyzing five replicate test systems freshly spiked with each test mixture at 5 and 50 ppb. The average recoveries of test mixture 1 spikes were between 74 and 106% [with a relative standard deviation (RSD) of 1−6% for the 5 ppb limit of quantitation (LOQ) spikes and 1−8% for the 50 ppb spikes] for the six analytes (ζ-cypermethrin, β-cyfluthrin, esfenvalerate, bifenthrin, γ-cyhalothrin, and deltamethrin). The average recoveries of test mixture 2 spikes were between 72 and 107% (with a RSD of 1−9% for the 5 ppb LOQ spikes and 1−13% for the 50 ppb spikes) for the six analytes (λ-cyhalothrin, fenpropathrin, cyfluthrin, bifenthrin, permethrin, and cypermethrin). The method LOQ was 5.0 ppb for all analytes in all sediment/water mixtures. The method limit of detection (LOD) ranged from 0.2 to 1.4 ppb, depending upon the analyte and test system.

The detector response was linear over the range from 0.0005 to 0.02 μg/mL (from 2.5 to 100 ppb sample equivalent) for deltamethrin and from 0.02 to 0.5 μg/mL (from 4 to 100 ppb sample equivalent) for the remaining analytes. Untreated sediments were analyzed for background residues or interference. Potential background residues were far below the lowest calibrated standard concentration (4 ppb sample equivalents) and, therefore, negligible for the purposes of this study.

In 504 analyses, concurrent recoveries ranged from 71 to 114%, except for one instance of 65% (bifenthrin, aerobic sediment 2, day 0) and one instance of 122% (fenpropathrin, aerobic sediment 2, day 0). Usual acceptance criteria are between 70 and 120%. The overall mean of concurrent recoveries was 95.8% (standard deviation of 6.2%); therefore, residue values were not corrected for the concurrent recovery results.

In anaerobic sediment 1, day 7 results gave poor concurrent recoveries and poor agreement between replicates; therefore,

Table 4. DO, pH, and Redox (E_h) Measurements of the Test Systems Throughout the Aerobic Study Periods

measurement interval (days)	DO (mg/L)	pH	redox (E_h)[a] in water (mV)	redox (E_h)[a] in sediment (mV)
Sediment 1				
0[b]	5.5	8.1	367	421
3	5.8	8.2	295	277
7	5.4	8.3	284	97
14	5.3	8.2	246	103
28	5.9	6.7	385	372
59	6.2	5.9	480	488
100	6.4	5.9	492	506
Sediment 2				
0[b]	5.5	7.8	243	73
3	4.6	7.2	208	79
7	4.5	8.2	200	87
14	5.8	8.4	213	68
28	4.8	6.8	327	65
60	6	5.6	457	101
103	5.9	7.7	284	150
Sediment 3				
0[b]	5.4	8.1	270	106
3	5.9	8	241	93
7	5	8.1	244	79
14	4.9	8.5	240	59
28	5.3	6.9	378	100
58	6	5.7	462	165
100	6	7	391	193

[a] $E_h = E_{obs} + E_{ref}$, where E_h is the redox potential referred to the hydrogen scale, E_{obs} is the observed redox potential of the electrode, and E_{ref} is the redox potential of the electrode as related to the hydrogen electrode (Ag/AgCl = +197 mV). [b] For day 0, representative test systems were measured prior to treatment.

Table 5. DO, pH, and Redox (E_h) Measurements of the Test Systems Throughout the Anaerobic Study Periods

measurement interval (days)	DO (mg/L)	pH	redox (E_h)[a] in water (mV)	redox (E_h)[a] in sediment (mV)
Sediment 1				
0[b]	0.1	7	178	170
3	0.1	7.1	138	126
7	0.1	7	141	132
11	0.2	6.9	131	126
19	0.1	7.1	114	108
28	0.1	7	88.5	81.4
60	0	7	88.1	73.3
101	0.1	6.9	10.3	0
108	0.4	7	1.6	9.6
Sediment 2				
0[b]	0.2	6.6	104	101
3	0.1	6.7	95	107
7	0.1	6.3	110	113
14	0.1	6.3	105	102
28	0.2	6.7	103	103
61	0.1	6.6	108	105
104	0.1	6.7	101	98.6
Sediment 3				
0[b]	0.1	6.7	59.5	56.9
3	0.1	6.8	54.6	44.3
7	0.3	6.7	59.9	55.7
14	0.1	6.8	53.9	49.8
28	0.3	6.8	49.0	52.6
59	0.1	6.8	58.3	55
100	0.1	6.9	48.6	50.2

[a] $E_h = E_{obs} + E_{ref}$, where E_h is the redox potential referred to the hydrogen scale, E_{obs} is the observed redox potential of the electrode, and E_{ref} is the redox potential of the electrode as related to the hydrogen electrode (Ag/AgCl = +197 mV). [b] For day 0, representative test systems were measured prior to treatment.

dx.doi.org/10.1021/jf400382u | J. Agric. Food Chem. 2013, 61, 4702−4708

Table 6. Characterization of the Degradation Curves in the Aerobic and Anaerobic Studies

	sediment 1			sediment 2			sediment 3		
compound	DT50[a] (days)	DT90[a] (days)	end amount[b] (% of applied)	DT50[a] (days)	DT90[a] (days)	end amount[b] (% of applied)	DT50[a] (days)	DT90[a] (days)	end amount[b] (% of applied)
				Aerobic					
bifenthrin[c]	94	*d*	41, 44	*d*	*d*	70, 68	*d*	*d*	16, 65
bifenthrin[e]	99	*d*	36, 55	*d*	*d*	74, 69	88	*d*	45, 27
β-cyfluthrin	3.1	39	5,[f] 4[f]	7.7	92.4	9,[f] 9[f]	2.6	38	3,[f] 7[f]
cyfluthrin	4.3	49	5,[f] 8[f]	10	*d*	12, 11	3	29	4,[f] 1[f]
γ-cyhalothrin	11	*d*	12, 9[f]	53	*d*	27, 28	17	86	2,[f] 16
λ-cyhalothrin	14	*d*	14, 24	55	*d*	32, 24	13	73	5,[f] 2[f]
ζ-cypermethrin	4.3	57	7,[f] 5[f]	13	*d*	13, 14	4	51	2,[f] 6[f]
cypermethrin	3.6	23	4,[f] 6[f]	8.6	100	9,[f] 9[f]	2.7	23	3,[f] 1[f]
deltamethrin	9.8	88	8,[f] 4[f]	36	*d*	27, 26	12	64	8,[f] 14
esfenvalerate	12	*d*	16, 11	40	*d*	28, 30	22	97	3,[f] 20
fenpropathrin	7.1	*g*	8,[f] 12	63	*d*	26, 25	6.6	57	2,[f] 1[f]
permethrin	2.6	20	5,[f] 6[f]	42	*d*	24, 25	2.4	29	2,[f] 2[f]
				Anaerobic					
bifenthrin[c]	*d*	*d*	96, 80	*d*	*d*	60, 55	*d*	*d*	58, 64
bifenthrin[e]	*d*	*d*	80, 92	*d*	*d*	51, 55	*d*	*d*	60, 63
β-cyfluthrin	14	*d*	21, 15	22	*d*	11, 10[f]	17	89	8,[f] 8[f]
cyfluthrin	15	*d*	18, 24	21	*d*	15, 15	18	*g*	7,[f] 10[f]
γ-cyhalothrin	98	*d*	58, 43	101	*d*	50, 44	73	*d*	31, 35
λ-cyhalothrin	84	*d*	40, 54	93	*d*	43, 46	62	*d*	24, 33
ζ-cypermethrin	33	*d*	30, 23	26	*d*	21, 19	33	*d*	14, 16
cypermethrin	13	*d*	17, 23	20	*d*	13, 12	17	90	7,[f] 9[f]
deltamethrin	106	*d*	53, 46	54	*d*	46, 43	60	*d*	28, 31
esfenvalerate	*d*	*d*	55, 47	73	*d*	42, 39	67	*d*	33, 34
fenpropathrin	89	*d*	48, 53	*d*	*d*	41, 47	95	*d*	30, 45
permethrin	97	*d*	33, 55	52	*d*	37, 38	66	*d*	26, 40

[a]The time to 50 and 90% degradation of the starting material was determined by the best fitting kinetic model if these points were reached during the study period. [b]The duplicate values from the last time interval are reported. The last time interval was 100 days for the aerobic studies with sediments 1 and 3 and the anaerobic study with sediment 3, 103 days for the aerobic study with sediment 2, 101 days for the anaerobic study with sediment 1 (except for deltamethrin, which was 108 days), and 104 days for the anaerobic study with sediment 2. [c]Test mixture 1. [d]Not reached during the study period. [e]Test mixture 2. [f]The concentration in the sample was below the LOQ. [g]The amount remaining in the samples at the end of the study at 100 days corresponded to 90% or greater degraded. The model prediction was slightly longer than the study length.

Table 7. Summary of the Degradation Rates (Expressed as Half-Lives) Obtained with Nonlinear Regression Using Single First-Order Kinetics

		first-order half-life (days)[a]					
		sediment 1		sediment 2		sediment 3	
test mixture	compound	aerobic	anaerobic	aerobic	anaerobic	aerobic	anaerobic
1	bifenthrin	104 (75–173)	>200[b]	>200[b]	121 (65–301)[c]	114 (71–289)	111 (70–267)[c]
2	bifenthrin	99.0 (72–158)	>200[b]	180 (117–365)[c]	111 (72–248)[c]	87.6 (64–139)	104 (69–210)[c]
1	*β*-cyfluthrin	3.8 (3–5)	29.7 (20–58)	12.1 (9–19)	22.0 (18–29)	3.7 (3–5)	21.1 (17–27)
2	cyfluthrin	5.0 (4–7)	24.7 (18–39)	18.3 (14–28)	26.1 (21–35)	4.0 (3–5)	20.7 (18–25)
1	*γ*-cyhalothrin	15.8 (11–28)	97.9 (80–126)	55.6 (48–65)	101 (67–204)	22.1 (16–35)	72.9 (63–87)
2	*λ*-cyhalothrin	25.9 (18–49)	84.4 (69–110)	60.0 (48–80)	92.7 (72–131)	17.2 (14–23)	61.5 (51–78)
1	*ζ*-cypermethrin	5.0 (4–7)	46.3 (34–72)	21.6 16–32)	32.0 (24–45)	5.8 (4–9)	35.0 (32–39)
2	cypermethrin	3.0 (2–4)	23.7 (17–40)	14.1 (11–22)	24.5 (19–34)	3.3 (3–4)	20.1 (18–24)
1	deltamethrin	11.7 (6–18)	100 (81–131)	44.6 (37–56)	68.4 (51–103)	14.4 (11–22)	59.9 (55–66)
1	esfenvalerate	18.6 (13–32)	94.4 (76–124)	50.2 (41–66)	73.0 (56–103)	26.0 (21–35)	66.6 (59–75)
2	fenpropathrin	9.3 (7–14)	85.2 (66–120)	63.1 (50–87)	114 (88–165)	8.8 (7–13)	95.4 (71–131)
2	permethrin	3.0 (2–4)	101 (64–231)	52.9 (41–76)	64.4 (50–91)	2.9 (3–4)	66.3 (58–77)

[a]The number in parentheses is the 95% confidence interval. [b]The exact value cannot be determined given the length of the experiment. [c]Obtained by setting the starting amount to 100% of applied.

data from day 7 were discarded, a sampling interval was added at day 11, and the interval planned for day 14 interval was moved to day 19, to provide good temporal coverage between 3 and 28 days. In addition to this problem with the concurrent recoveries at day 7, two additional problems occurred with analyses of the actual study samples in the anaerobic sediment 1

dx.doi.org/10.1021/jf400382u | J. Agric. Food Chem. 2013, 61, 4702–4708

study. On day 19, the results for three analytes in test mixture 1, replicate 1 (ζ-cypermethrin, deltamethrin, and esfenvalerate) and three analytes in test mixture 2, replicate 1 (cypermethrin, fenpropathrin, and permethrin) were discarded as outliers because of extreme variance from the degradation curve. On day 101, the result for one replicate of deltamethrin was an outlier. Therefore, results for deltamethrin from this sampling interval were replaced with duplicate samples analyzed on day 108.

A listing of residue values has not been included because of the number of analyses. The data showed a decline in residues in all of the total water/sediment systems, and the rate of decline varied among the three sediments. In general, the agreement of results for the duplicate samples was good. Degradation rates appear to follow first-order kinetics until about 50−75% of the compound has degraded, and then degradation rates slow. To provide an indication of the degradation curve, Table 6 provides the times required for 50 and 90% of the material to degrade (in cases where this occurs within the study period) and the amount remaining at the end of the study period. Single first-order degradation rates are provided in Table 7, along with confidence intervals for each of the 72 data series. Figure 1 provides a graphical comparison of

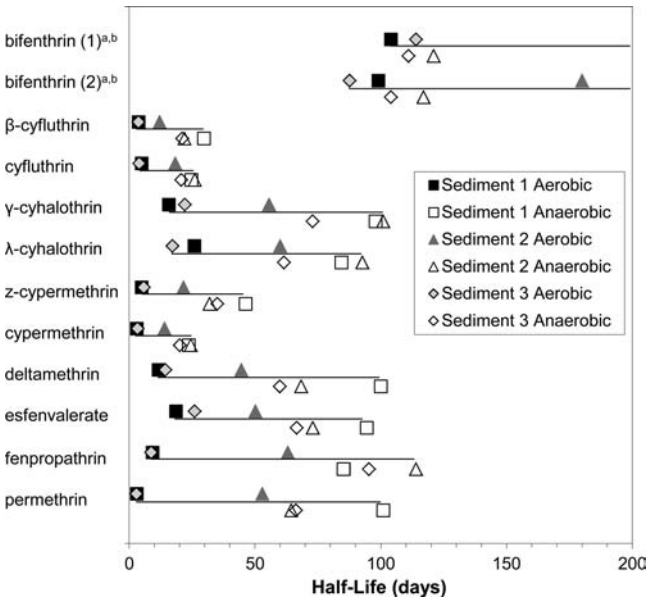

Figure 1. Summary of single first-order half-lives. Note that the lines represent the range of the six study results for each compound. (a) Test mixture numbers are shown in parentheses. (b) Values obtained for bifenthrin in sediment 2, test mixture 1, aerobic and in sediment 1, test mixtures 1 and 2, anaerobic are not included because of the uncertainty associated with half-life values greater than 200 days.

the results. The relatively good agreement of results between the two different bifenthrin series (for half-lives less than 200 days) and between similar compounds (β-cyfluthrin and cyfluthrin, λ- and γ-cyhalothrin, and ζ-cypermethrin and cypermethrin) is an indication of the robustness of the experimental data generated in this study. The degradation rates obtained in this study are in the same range as observed in previous studies[8] with single compounds, indicating that the presence of multiple compounds in incubated samples did not affect the observed degradation rates.

In general, degradation was faster under aerobic conditions than anaerobic conditions. The aerobic degradation rate was generally slower for sediment 2, which had the highest organic matter of the sediments, while the differences in the anaerobic degradation rates among the three sediments were less pronounced. First-order half-lives under aerobic conditions ranged from 2.9 to greater than 200 days, with a median value of 18 days. Under anaerobic conditions, the range was from 20 to greater than 200 days, with a median value of 70 days.

■ ASSOCIATED CONTENT

Supporting Information

Residues (test mixtures 1 and 2) in aerobic and anaerobic test systems (Tables 1−4), microbial plate counts of sediment (Table 5), conditioning of water added to the sediment, GC/MS instrument conditions, and HPLC−MS/MS instrument conditions. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Telephone: 919-549-3912. E-mail: russell.jones@bayer.com.

Present Address

[†]Sean Moore: SynTech Research, 17745 South Metcalf Avenue, Stilwell, Kansas 66085, United States.

Notes

The authors declare the following competing financial interest(s): The study was funded by the Pyrethroid Working Group, a task force of pyrethroid registrants. The authors were employed by Bayer CropScience, which is a member of the Pyrethroid Working Group and a registrant of two of the pyrethroids included in this study.

■ REFERENCES

(1) Weston, D. P.; Lydy, M. J. Urban and agricultural sources of pyrethroid insecticides to the Sacramento−San Joaquin Delta of California. *Environ. Sci. Technol.* **2010**, *44*, 1833−1840.

(2) Weston, D. P.; Holmes, R. W.; Lydy, M. J. Residential runoff as a source of pyrethroid pesticides to urban creeks. *Environ. Pollut.* **2008**, *157*, 287−294.

(3) Ding, Y.; Harwood, A. D.; Foslund, H. M; Lydy, M. J. Distribution and toxicity of sediment-associated pesticides in urban and agricultural waterways from Illinois, USA. *Environ. Toxicol. Chem.* **2009**, *29*, 149−157.

(4) Greenberg, L.; Rust, M. K.; Klotz, J. H.; Haver, D.; Kabashima, J. N.; Bondarenko, S.; Gan, J. Impact of ant control technologies on insect runoff and efficacy. *Pest Manage. Sci.* **2010**, *66*, 980−987.

(5) Jorgenson, B. C.; Young, T. M. Formulation effects and the off-target transport of pyrethroid insecticides from urban hard surfaces. *Environ. Sci. Technol.* **2010**, *44*, 4951−4957.

(6) Jiang, W.; Lin, K.; Haver, D.; Qin, S.; Ayre, G.; Spurlock, F.; Gan, J. Wash-off potential of urban use insecticides on concrete surfaces. *Environ. Toxicol. Chem.* **2010**, *29*, 1203−1208.

(7) Jones, R. L.; Markle, J. C. Management practices for reducing discharge of pyrethroids and sediment in irrigation drainage water from row crops. In *Pesticide Mitigation Strategies for Surface Water Quality*; Goh, K. S., Bret, B. L., Potter, T. L., Gan, J., Eds.; American Chemical Society (ACS): Washington, D.C., 2011; ACS Symposium Series, Vol. *1075*, Chapter 5, pp 65−76.

(8) Laskowski, D. A. Physical and chemical properties of pyrethroids. *Rev. Environ. Contam. Toxicol.* **2002**, *174*, 49−170.

(9) United States Environmental Protection Agency (U.S. EPA). *Fate, Transport and Transformation Test Guidelines, OPPTS 835.4300/4400*; U.S. EPA: Washington, D.C., 2008; U.S. EPA Document 712-C-08-018/019.

(10) United States Environmental Protection Agency (U.S. EPA). *Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA): Good Laboratory Practice Standards; Final Rule*; U.S. EPA: Washington, D.C., 1989; Federal Register 40 CFR Part 160.

(11) Forum for the Co-ordination of Pesticide Fate Models and Their Use (FOCUS). Guidance document on estimating persistence and degradation kinetics from environmental fate studies on pesticides in EU registration. *Report of the FOCUS Work Group on Degradation Kinetics*; European Commission (EC): Brussels, Belgium, 2006; EC Document Reference Sanco/10058/2005 version 2.0, p 434.

(12) Erhardt-Zabik, S.; Wolt, J. D. Design and interpretation of herbicide anaerobic aquatic metabolism studies. *Weed Technol.* **1996**, *10*, 191−201.