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Aerobic versus Anaerobic Microbial Degradation of Etofenprox in a California Rice Field Soil

Martice E. Vasquez,* Dirk M. Holstege, and Ronald S. Tjeerdema

Department of Environmental Toxicology, College of Agriculture and Environmental Sciences, University of California, One Shields Avenue, Davis, California 95616-8588, United States

Supporting Information

ABSTRACT: The microbial degradation of etofenprox, an ether pyrethroid, was characterized under anaerobic (flooded) and aerobic (nonflooded) California rice field soil conditions by determination of its half-life ($t_{1/2}$) and dissipation rate constant (k) and identification and quantification of degradation products at both 22 and 40 °C using LC-MS/MS. The overall anaerobic $t_{1/2}$ at 22 °C ranged from 49.1 to 100 days (k = −0.0141 to −0.0069 days^{-1}) compared to 27.0 days (k = −0.0257 days^{-1}) at 40 °C, whereas under aerobic conditions the overall $t_{1/2}$ was 27.5 days (k = −0.0252 days^{-1}) at 22 °C compared to 10.1−26.5 days (k = −0.0686 to −0.0262 days^{-1}) at 40 °C. The biphasic dissipation profiles were also fit to a first-order model to determine the $t_{1/2}$ and k for both the fast and slow kinetic regions of the dissipation curves. Hydroxylation at the 4′-position of the phenoxy phenyl ring was the major metabolic process under anaerobic conditions for both 22 °C (maximum % yield of applied etofenprox mass = 1.3 ± 0.7%) and 40 °C (max % yield = 1.2 ± 0.8%). Oxidation of the ether moiety to the ester was the major metabolite under aerobic conditions at 22 °C (max % yield = 0.5 ± 0.1%), but at 40 °C increased amounts of the hydroxylated form were produced (max % yield = 0.7 ± 0.2%, compared to 0.3 ± 0.1% for the ester). The hydrolytic product of the ester, 3-phenoxybenzoic acid (3-PBA), was not detected in any samples. Sterilized control soils showed little etofenprox degradation over the 56-day incubation period. Thus, the microbial population in a flooded soil was able to transform and contribute to the overall dissipation of etofenprox. The simulated summer temperature extreme (40 °C) increased the overall degradation.

KEYWORDS: insecticides, pyrethroids, etofenprox, microbial degradation, anaerobic/aerobic soils

INTRODUCTION

Etofenprox (trade name Trebon or MTI-500) is a synthetic ether pyrethroid insecticide currently undergoing registration for use in California rice fields. Although unregistered for use in rice by the U.S. Environmental Protection Agency (USEPA), in 2007, an emergency use permit was granted in Louisiana for rice water weevil control.[1] However, little information is currently available addressing its dissipation rates and transformation processes once applied to a rice field. For growers to effectively manage crop, soil, and water residues, the environmental fate and transport of etofenprox must be better understood. Pyrethroids in general are highly toxic to aquatic organisms; thus, fate and transport knowledge is necessary to prevent residues (likely in a bound state) from entering the Sacramento River when fields are drained.

The partitioning of etofenprox between air, water, and soil under representative California rice field conditions has been previously reported.[2] Etofenprox volatilization was shown to be an insignificant dissipation pathway from rice field water compared to soil sorption. The extreme insolubility of etofenprox, and pyrethroids in general, drives their high degree of sorption. The movement of etofenprox to soils after aqueous application (EPA application rate = 0.19−0.27 lb/acre)[1] suggests that microbial degradation may play a significant role in field dissipation. In general, soil microbes represent one of the most important vectors for pesticide degradation, and they can greatly reduce persistence in a soil−water matrix such as a rice field.[3] Management practices in rice production create two soil types: anaerobic, when the field is flooded, and aerobic, when it is not. As a result of the presence of both conditions in rice fields (although flooded fields have aerobic microsites), it is important to characterize both etofenprox degradation rates and transformation product formation under aerobic and anaerobic conditions.

Pyrethroid-degrading bacteria have been isolated from aerobic sites and assessed for esterase presence and activity.[4] Although etofenprox is an ether pyrethroid, not an ester, it is hypothesized that the microbial community in California rice fields will be able to efficiently degrade it. Changes in the redox conditions within the rice field system have been shown to change the microbial community structure.[5] It is also hypothesized that degradation rates will be greater under aerobic conditions than anaerobic conditions and that the rates will increase with increased temperature. Therefore, the objectives of this study were to determine the effects of water regimen and summer temperature extremes on the microbial degradation of etofenprox in a representative California rice soil by determination of its dissipation rate constant (k) and the half-life ($t_{1/2}$) and by identification and quantification of degradation products, under both anaerobic and aerobic conditions, at 22 and 40 °C. A comparison of the relative aerobic and anaerobic soil persistence of etofenprox to other currently used pyrethroids will be made.

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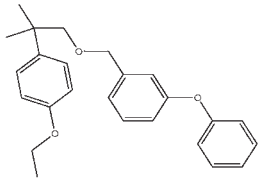
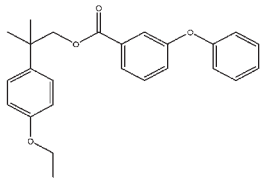
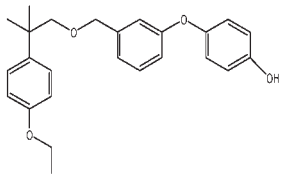
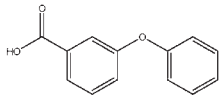
Compound	Name	Structure
1	Etofenprox	
2	α-CO	
3	4′OH	
4	3-PBA	

Figure 1. Chemical structures of etofenprox and targeted metabolites by LC-MS/MS.

MATERIALS AND METHODS

Chemicals. Etofenprox (CAS Registry No. 80844-07-1; 2-(4-ethoxyphenyl)-2-methylpropyl 3-phenoxybenzylether), α-CO (2-(4-ethoxyphenyl)-2-methylpropyl 3-phenoxybenzoate), and 4′OH (2-(4-ethoxyphenyl)-2-methylpropyl 3-hydroxybenzyl ether) were supplied at no charge by Mitsui Co. (Tokyo, Japan). Sodium azide and 3-phenoxybenzoic acid (3-PBA) were purchased from Sigma, whereas $NaSO_4$ (anhydr), Optima hexane, Optima acetone, Optima methanol, and HPLC-grade water and acetonitrile were purchased from Fisher Scientific (Hampton, NH). Stock solutions of etofenprox were prepared in methanol and used to prepare microcosm samples.

Soil and Irrigation Water: Collection and Characterization. Soil (no history of insecticide application) was collected from the Rice Experiment Station (Biggs, CA) in May 2008 and is classified as an Esquon-Neerdobe thermic clay loam.[6] The rice field soil was composed of 21% sand, 32% silt, and 46% clay, with an organic matter content of 0.7%. It is characteristic of the Sacramento Valley rice-growing region, having very low amounts of organic matter and high clay content. It was air-dried, ground to pass through a 2 mm sieve, and then stored at 4 °C until used. Soil particle size was characterized by the University of California at Davis (UCD) Analytical Laboratory, and description of the methods can be found in Sheldrick and Wang[7] or the laboratory Website (http://anlab.ucdavis.edu).[8] Water (pH 7.5) used for flooding the microcosms was collected from an irrigation outfall (Berryessa Irrigation District) located at UCD in July 2008 and stored at 4 °C until used.

Microbial Degradation Experimental Design. Anaerobic microcosms were constructed with a 2.5 cm soil layer (50 g) and flooded to a depth yielding a 1.5 cm water layer (60 mL) in a 300 mL amber screw-cap bottle. Aerobic microcosms were constructed similarly except soils were maintained at approximately 40% moisture-holding capacity and bottle tops (uncapped) were covered with foil. All microcosms were prepared in triplicate for each time point (t = 0, 1, 3, 7, 14, 21, 28, 35, 42, 56, and/or 126 days) and were incubated at either 22 ± 2 or 40 ± 0.1 °C in the dark. Control soils (triplicate) were autoclaved three times before water addition and application of etofenprox, and control sample water contained 200 mg/L sodium azide for microbial inhibition. The redox potential of the flooded soil was monitored to determine when anaerobic conditions were achieved; conditions were considered anaerobic when the soil redox potential reached E_h < 200 RmV (relative millivolts), the average redox potential of a flooded rice field soil.[9] Acetone extraction of the sacrificial microcosms (representing the entire water, soil, and bottle wall residues) at the defined time intervals following etofenprox addition (150 μg in 150 μL of methanol) was used to determine degradation rates and metabolite formation over the course of the experiments.

Extraction and Analysis. Acetone (60 mL) was added to the sacrificial microcosms at the end of each defined time interval and placed on a platform shaker (135 rpm) for 24 h. The soil extract was vacuum filtered, and the filter cake was washed with acetone. For anaerobic samples, the acetone was removed from the acetone−water extract by evaporation under N_2 gas, and the remaining aqueous phase was liquid/liquid extracted using hexane (20 mL) three times. The combined extract was dried with sodium sulfate (anhydr) and evaporated to dryness under N_2 at room temperature. The residue was dissolved in 2 mL of 40:60 acetonitrile (0.1% ammonium acetate)/water (0.1% ammonium acetate), filtered (0.45 μm), and then analyzed by LC-MS/MS. For aerobic samples, water (50 mL of 200 ppm NaN_3) was added to the acetone extract before evaporation under N_2. The remaining aqueous phase was then extracted in the same manner as the anaerobic samples.

The chemical structures of the parent compound and the targeted metabolites are presented in Figure 1. LC-MS/MS analysis was performed using a HP 1100 HPLC (Palo Alto, CA) coupled to an Applied Biosystems Sciex 2000 triple-quadrupole LC-MS/MS (South San Francisco, CA) using electrospray ionization (ESI). The chromatographic column used was a 100 mm × 2.1 mm i.d., 5 μm, Titan C_{18} analytical column (Peeke Scientific, Sunnyvale, CA), with a flow rate of 0.25 mL/min and a 40 μL injection volume. The solvent gradient profile was as follows: 0−4.5 min, 40:60 acetonitrile (0.1% ammonium acetate)/water (0.1% ammonium acetate); 4.5−10 min, 95:5 acetonitrile (0.1% ammonium acetate)/water (0.1% ammonium acetate); 11−20 min, 40:60 acetonitrile (0.1% ammonium acetate)/water (0.1% ammonium acetate). The gradient profile for compound **4** determination was as follows: 0−6 min, 20:80 acetonitrile (0.1% acetic acid)/water (0.1% acetic acid); 6−15 min, 40:60 acetonitrile (0.1% acetic acid)/water (0.1% acetic acid).

Compounds **1**−**4** were quantified in multiple-reaction monitoring mode (MRM) against a second-order calibration curve generated in Analyst software version 1.2.4 using matrix-matched standards. Mass transitions monitored were as follows: m/z 394 → 177, m/z 408 → 177, m/z 410 → 177, and m/z 203 → 93, for compounds **1**−**4**, respectively. Positive ionization mode was used for compounds **1**−**3** and negative mode for compound **4**. Collision energies and declustering potentials were optimized for each compound. Prior to sample injection for compound **1** quantification, extracts were diluted (1/100 or 1/200) with mobile phase to produce an area response within the calibration range. The instrument detection limits were 0.01, 0.05, 0.05, and 0.05 mg/L for compounds **1**−**4**, respectively, as determined by multiplying 3 times the standard deviation of replicate injections of low-level standards. Target analyte soil extraction efficiencies at a 3 mg/kg spike level were 95.6, 92.4, 89.6, and 69.7% for compounds **1**−**4**, respectively. Soil extraction efficiencies at a 0.5 mg/kg spike level were 80.8, 74.0, 73.2, and 51.2% for compounds **1**−**4**, respectively.

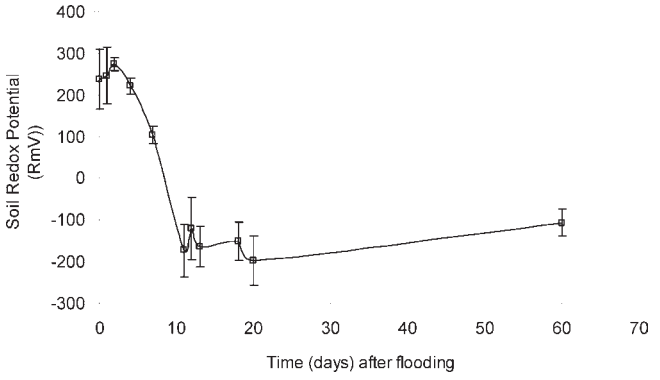


Figure 2. Redox profile of flooded soil at various time intervals. Anaerobic conditions (−100 to −200 RmV) were achieved within 14 days of soil flooding. Points represent the mean ± SD ($n \geq 2$).

Redox Potential. Soil redox potential (E_h) was monitored to ensure anaerobic conditions were achieved before etofenprox was applied and maintained over the course of each experiment. Separate microcosm samples were prepared at least in duplicate using 50 mL wide-mouth tubes with a 2.5 cm soil layer and a 1.5 cm water layer. Measurements were taken using a calibrated redox electrode (Thermo, Waltham, MA) according to the manufacturer's directions. The probe was allowed to stabilize while submerged in the soil layer before the redox value was recorded.

Data Analysis. Aerobic and anaerobic degradation rate constants were calculated on the basis of first-order kinetics where the rate constant (k) is calculated from the equation

$$C_t = C_0\, e^{-kt} \quad (1)$$

and C_0 is the initial concentration (ug/g) of etofenprox, C_t is the concentration (μg/g) at time t (days), and k is the first-order degradation rate constant. The half-life ($t_{1/2}$) is calculated according to the equation

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

One-way ANOVA was used for comparison of degradation rates between control (sterile) and nonsterile (biologically active soils).

RESULTS AND DISCUSSION

Redox Potential of Flooded Soil. Anaerobic soil conditions ($E_h \leftarrow 200$ RmV) were achieved within 10 days of flooding microcosms according to the soil redox potential profile (Figure 2), and thus etofenprox was added on day 14 to the system after the microcosm soil became anaerobic. A rise in redox potential occurred over time, although not to aerobic levels. This phenomenon has been reported by other researchers without explanation.[10−12] The pH of the soil/water solution was 6.9.

Comparison of Anaerobic and Aerobic Degradation Rates and Half-Lives. The overall pseudo-first-order dissipation rate constants of etofenprox are summarized in Table 1. Dissipation occurred at a faster rate under aerobic soil conditions (overall $t_{1/2}$ = 27.5 days, k = −0.0252 day^{-1}) compared to anaerobic conditions (overall $t_{1/2}$ = 100 days, k = −0.0069 day^{-1}) at 22 °C (Figure 3,; Table 1). Decreasing recoveries of etofenprox in anaerobic control samples after 126 days (72.8%) required that overall anaerobic kinetics be modeled over both 56 and 126 days. The overall anaerobic half-life after 56 days of incubation at 22 °C was 49.1 days compared to the overall half-life of 100 days calculated after 126 days of incubation (Table 1). After 56 days of incubation under nonsterile anaerobic conditions, 31.9% of etofenprox remained compared to 20.0% under aerobic conditions at 22 °C. After 126 days, 27.3% remained under anaerobic conditions.

Table 1. Pseudo-First-Order Kinetic Summary of Etofenprox Dissipation in Anaerobic (Flooded) and Aerobic (Nonflooded) Soils at Representative California Temperatures

kinetic parameter	k (days^{-1})	$t_{1/2}$ (days)	r^2
Anaerobic Kinetics at 22 ± 2 °C			
overall kinetics (0−56 days)	−0.0141	49.1	0.6047
overall kinetics (0−126 days)	−0.0069	100	0.5081
fast kinetics (0−3 days)	−0.1967	3.5	0.6873
slow kinetics (7−56 days)	−0.0074	93.6	0.8738
Aerobic Kinetics at 22 ± 2 °C			
overall kinetics (0−56 days)	−0.0252	27.5	0.7978
fast kinetics (0−3 days)	−0.1839	3.8	0.9768
slow kinetics (7−56 days)	−0.0154	45.0	0.8975
Anaerobic Kinetics at 40 ± 0.1 °C			
overall kinetics (0−56 days)	−0.0257	27.0	0.8689
fast kinetics (0−3 days)	−0.0746	9.3	0.8639
slow kinetics (7−56 days)	−0.0218	31.8	0.8492
Aerobic Kinetics at 40 ± 0.1 °C			
overall kinetics (0−21 days)	−0.0686	10.1	0.8750
overall kinetics (0−56 days)	−0.0262	26.5	0.6492
fast kinetics (0−3 days)	−0.1843	3.8	0.9714
slow kinetics (7−56 days)	−0.0117	59.2	0.4382

Etofenprox dissipation occurred at similar overall rates under both soil conditions at 40 °C (anaerobic overall $t_{1/2}$ = 27.0 days, k = −0.0257 day^{-1}; and aerobic overall $t_{1/2}$ = 26.5 days, k = −0.0262 day^{-1}; Figure 4; Table 1). Decreasing recoveries (61.3%) of etofenprox in aerobic control samples after 56 days and steady-state conditions after 21 days resulted in kinetics modeled over both 21 and 56 days. The aerobic $t_{1/2}$ over 21 days of incubation at 40 °C was 10.1 days compared to a 26.5 day overall $t_{1/2}$ calculated after 56 days of incubation (Table 1). After 56 days, 18.1% of etofenprox remained in nonsterile soil under aerobic conditions, compared to 23.9% under anaerobic conditions at 40 °C. After 21 days, 23.1% remained in aerobic soil and 32.6% in anaerobic soil. In this regard, aerobic dissipation occurred at a faster rate ($p < 0.2$) at both 22 and 40 °C compared to anaerobic dissipation.

Etofenprox dissipation under both oxic and temperature conditions showed a fast initial decrease (0−3 days) in the percent-applied mass (Figures 2 and 3), followed by a slower decrease as the time course progressed (7−56 days). As a result, the first-order model does not fit the overall data very well, considering the correlation coefficients of the regression equation (Table 1). To account for the biphasic nature of the kinetic data, the first-order model was applied to the fast initial concentration decrease phase (0−3 days) and then separately to the slower concentration decrease phase (7−56 days). The results of the fast and slow kinetics analyses are presented in Table 1. The first-order model fits the data best when applied to each phase separately, as indicated by the improved correlation coefficients. All soil incubation types showed similar $t_{1/2}$ values (3.5−3.8 days) for the fast kinetics region of the degradation data, except

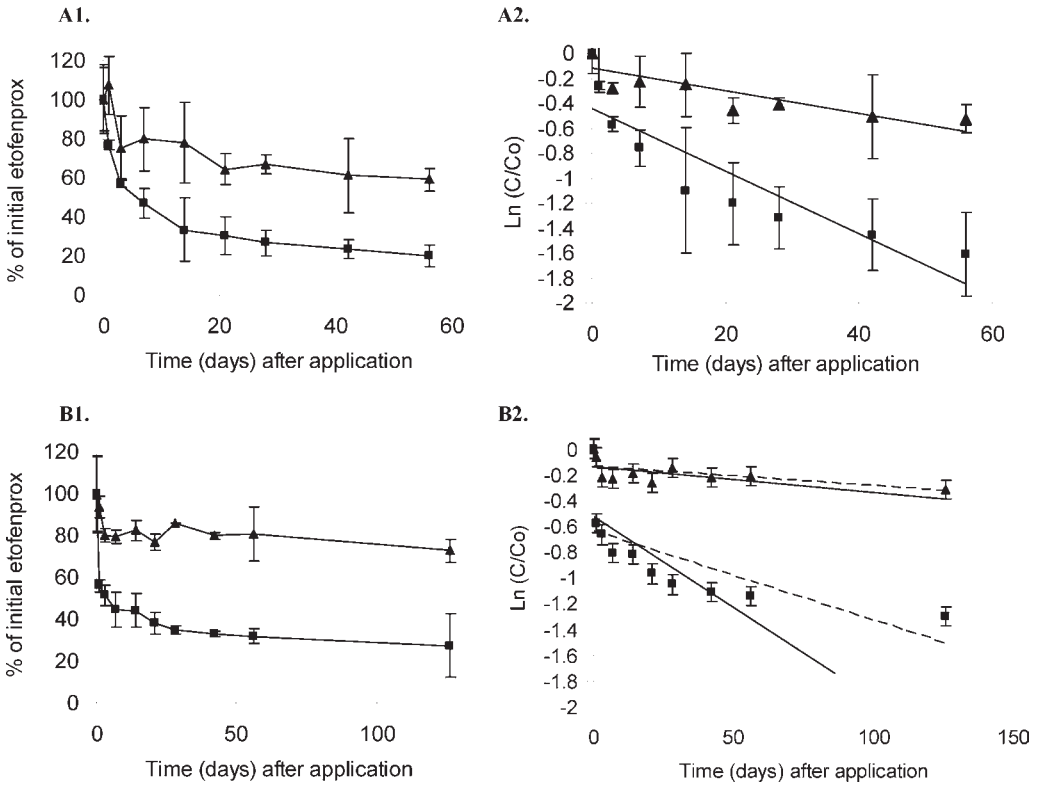


Figure 3. Decrease in the percent applied mass (A1 and B1) of etofenprox and pseudo-first-order degradation kinetics (A2 and B2) of etofenprox under aerobic (A) and anaerobic (B) soil conditions at 22 °C. Points represent the mean ± SD ($n = 3$) for sterile (▲) and nonsterile (■) soils. Regression lines represent 0−126 days (dashed) kinetics and 0−56 days (solid line) kinetics.

the anaerobic soil at 40 °C, with a $t_{1/2}$ value of 9.3 days. The slow kinetics $t_{1/2}$ values for all soil types suggest a possible underestimation on the overall $t_{1/2}$ when using the first-order kinetic model. Biphasic pesticide degradation data results have been reported by Cavoski et al.[14] for rotenone degradation in soils at 40% moisture-holding capacity. Kinetics data were modeled using both the pseudo-first-order model and a first-order multicompartment model for biphasic data to establish $t_{1/2}$ values. The authors attributed the initial fast decrease to equilibrium being established between the soil−water phases and this being the most available time for biodegradation of sorption-prone pesticides.

Dissipation of etofenprox in sterilized controls was significantly different ($p < 0.05$) compared to its degradation in biologically active soils over the course of the experiment, indicating dissipation was mediated by microbes. Controls showed little degradation except for the 126 day anaerobic (22 °C) and 56 day aerobic (40 °C) control samples, and thus the respective $t_{1/2}$ values were calculated with and without these time points. Low control recovery was possible due to residue aging or changes in soil sterility. A previous investigation by Jordan et al.[13] showed nonextractable permethrin residues did not exceed 11.4% in flooded and nonflooded soil (20.8% sand, 54.0% silt, 25.2% clay), and most nonextractable residues were in the fulvic acid fraction of the organic matter (1%).[13]

Different rates of etofenprox dissipation under aerobic and anaerobic conditions are suggested to be attributed to different microbial communities functioning as different terminal electron acceptors are depleted over time.[5,15] As oxygen becomes limited in a flooded soil, capable microbes will switch from aerobic to anaerobic respiration, by which inorganic compounds of decreasing redox potential are used for energy production.[15] Microbial community activity is suggested to rise and fall depending on the availability of both carbon sources and terminal electron acceptors.

Temperature Effect on Degradation Rates. The simulation of hot Sacramento Valley summers (40 °C) decreased the relative persistence of etofenprox under both flooded and nonflooded conditions by increasing the k of etofenprox dissipation (Figures 3 and 4; Table 1). The increase in temperature from 22 to 40 °C decreased the value of $t_{1/2}$ under anaerobic conditions by half, with a similar magnitude being observed for aerobic conditions if the 0−21 day incubation was considered. Although longer anaerobic periods may contribute to greater etofenprox persistence, elevated temperatures during periods of anaerobic field conditions should increase the degradation rate. The authors note that the soil and water temperature in the rice fields will not likely reach 40 °C, but it is seen as an extreme air temperature value encountered in the Sacramento Valley during summer. Elevated temperature has also been reported to increase the degradation rate of cyfluthrin under anaerobic conditions.[16] Increased periods of winter flooding (at low temperatures), as a result of restrictions on postharvest combustion of straw residues because of air-quality concerns, could ultimately increase the persistence of residual etofenprox due to longer anaerobic periods.

Identification and Quantification of Degradation Products. Two main degradation products were identified under both aerobic and anaerobic conditions: (i) compound **2**, the product of ether-to-ester oxidation; and (ii) compound **3**, via hydroxylation at the 4′ carbon of the phenoxy phenyl ring (Figure 5). The maximum yields formed under both oxic and

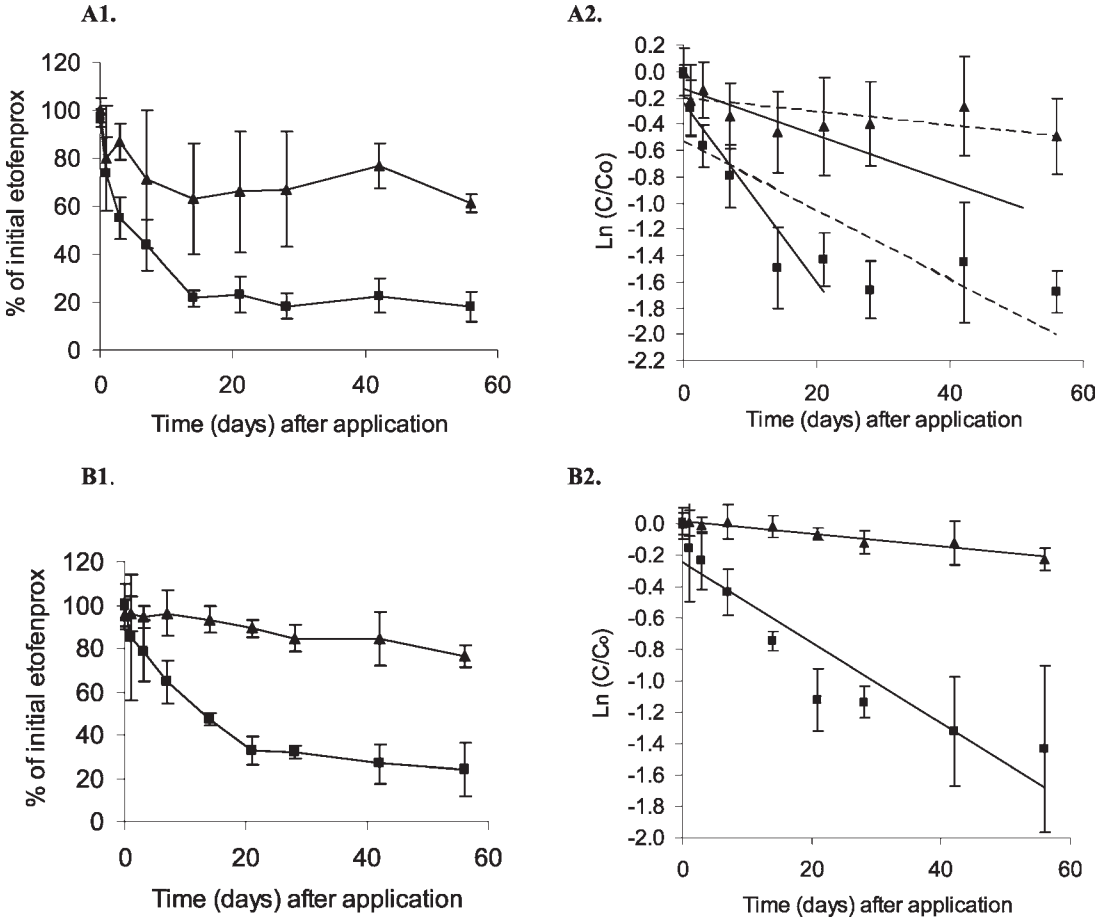


Figure 4. Decrease in the percent applied mass (A1 and B1) of etofenprox and pseudo-first-order degradation kinetics (A2 and B2) of etofenprox under aerobic (A) and anaerobic (B) soil conditions at 40 °C. Points represent the mean ± SD ($n = 3$) for sterile (▲) and nonsterile (■) soils. Regression lines represent 0−56 days (dashed) kinetics and 0−21 days (solid line) kinetics.

temperature conditions are presented in Table 2. The major metabolite under anaerobic conditions at both temperatures was compound **3**, whereas under aerobic conditions compound **2** predominated at 22 °C but not at 40 °C. In a reductive environment, such as a flooded rice field, O_2 is also not available for cytochrome P450-mediated reactions, which may explain the lack of compound **2** under anaerobic conditions.[17] Conversely, hydroxylation under anaerobic conditions may result from water serving as the oxygen donor in an enzyme-catalyzed reaction mediated by microbes.[18] It has also been more recently suggested that hydroxyl radical derived from the microbial cell membrane could serve as the oxygen donor.[19] Increased oxidative activity levels of different microbes may have led to an increase in compound **3** production under aerobic conditions at 40 °C.

Persistence of the identified degradation products should be further investigated as a result of their presence at the end of each incubation period; their potential environmental fate, ecotoxicity, and insecticidal activity also warrant further investigation. The hydrolytic product of compound **2**, compound **4**, was not detected in either anaerobic or aerobic samples. Accumulation of compound **4** after ester hydrolysis of cypermethrin was shown under anaerobic, but not aerobic, soil conditions.[20,21] Low yields of compound **2** under anaerobic conditions leave little potential for quantifiable levels of accumulated compound **4** after hydrolysis. Reduced analytical recovery (51.2% at 0.5 mg/kg spike) of compound **4** is possibly due to lack of acidification before hexane extraction (thus, lack of partitioning into the organic layer), which was avoided so as to not potentially hydrolyze compound **2** already in the sample extract. If compound **4** residues were above instrument detection levels in the water phase, direct injection of the microcosm water could have been an option.

The overall mass balances of recovered etofenprox and its metabolites were 20.8 ± 5.5 and 34.1 ± 4.4% for aerobic and anaerobic degradation at 22 °C, respectively, and 19.0 ± 6.4 and 25.6 ± 13.7% for aerobic and anaerobic degradation at 40 °C, respectively. The possible fate of the unrecovered fraction of etofenprox includes tight soil sorption of both etofenprox and metabolites leading to unextractable residues. Mineralization or incorporation into microbial biomass could also contribute to the low overall mass balance of the applied mass, as these fractions were not monitored. Recoveries of targeted analytes decreased with decreasing concentration, and extraction loss can be at least 30% at the lower limits of analyte detection. The final fate for other pyrethroids is suggested to likely be a combination of mineralization and tight soil sorption.[22] Etofenprox is likely to have a similar fate.

Comparison of Pyrethroid Aerobic and Anaerobic Soil Degradation. Etofenprox is less persistent (10.1−27.5 days, depending on temperature) under aerobic soil conditions compared to λ-cyhalothrin (42.6 days),[22] a pyrethroid currently used in California rice culture;[23] anaerobic degradation data for λ-cyhalothrin are not currently available. Caution must be taken

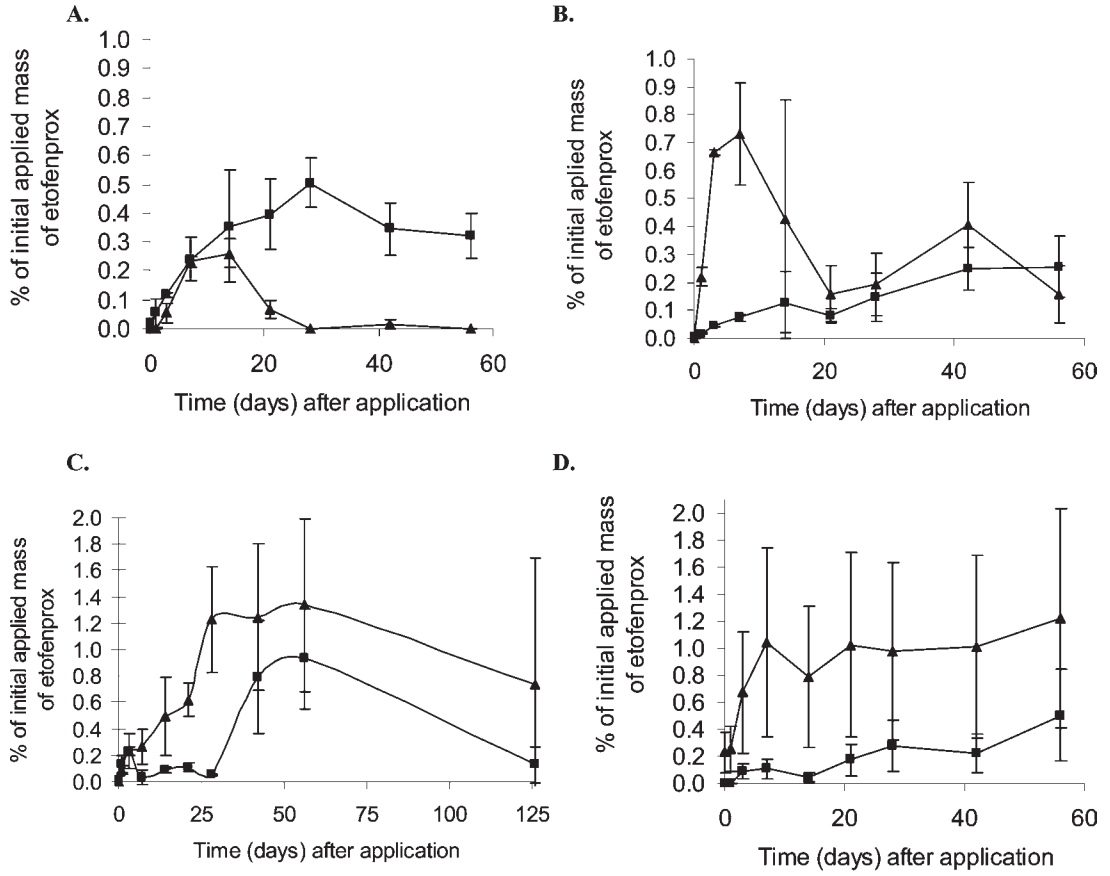


Figure 5. Major etofenprox metabolite formation under anaerobic (flooded) and aerobic (nonflooded) soil conditions at 22 and 40 °C: compound **2** (■) and compound **3** (▲). Points represent the mean ± SD ($n = 3$). Panels A and B represent aerobic degradation products at 22 and 40 °C, respectively. Panels C and D represent anaerobic degradation products at 22 and 40 °C, respectively.

Table 2. Maximum Yield of Detected Metabolites (% ± SD of Initial Applied Mass of Etofenprox, where $n = 3$) under Anaerobic and Aerobic Soil Conditions at 22 and 40 °C

	22 °C		40 °C	
	compd **2**	compd **3**	compd **2**	compd **3**
anaerobic	0.9 ± 0.4	1.3 ± 0.6	0.5 ± 0.3	1.2 ± 0.8
aerobic	0.5 ± 0.1	0.3 ± 0.1	0.2 ± 0.1	0.7 ± 0.2

with this comparison due to the lack of information on comparability of test conditions between this study and those studies used to generate kinetic values for other pyrethroids. Under aerobic conditions bifenthrin is the most persistent ($t_{1/2}$ = 96.3 days; see the Supporting Information and ref 24) when compared to either etofenprox (10.1−27.5 days) or cyfluthrin (11.5 days).[22] The extreme insolubility of bifenthrin compared to the other pyrethroids suggests bioavailability is significantly reduced by sorption.[25,26] Of the pyrethroids reviewed by Laskowski,[22] all except bifenthrin are reported to degrade at a faster rate under aerobic versus anaerobic soil conditions.

Microbial populations in both flooded and nonflooded California rice soils were able to transform etofenprox, thus contributing to its field dissipation. Air temperature extremes (40 °C) characteristic of the Sacramento Valley during the peak of rice production increased the degradation of etofenprox compared to the milder 22 °C, representative of the early growing season. Etofenprox has been shown to have a shorter aerobic soil $t_{1/2}$ compared to λ-cyhalothrin, a pyrethroid currently used in California rice culture for weevil control. Knowledge of dissipation processes and kinetics, and of the influence of environmental factors, is essential to an understanding of how an agrochemical such as etofenprox will behave in California rice fields.

■ ASSOCIATED CONTENT

Supporting Information. Soil degradation half-lives of etofenprox and selected ester pyrethroids. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Phone: (530) 752-2534. Fax: (530) 752-3394. E-mail: mevasquez@ucdavis.edu.

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REFERENCES

(1) U.S. Environmental Protection Agency. Etofenprox; pesticide tolerances for emergency exemptions. *Fed. Regist.* **2006**, *71*, 54922−54928.

(2) Vasquez, M.; Gunasekara, A.; Cahill, T.; Tjeerdema, R. Partitioning of etofenprox under simulated California rice field conditions. *Pest Manage. Sci.* **2010**, *66*, 28–34.

(3) Mabury, S.; Cox, J.; Crosby, D. *Rev. Environ. Contam. Toxicol.* **1996**, *147*, 71–114.

(4) Lee, S.; Gan, J.; Kim, J.; Kabashima, J.; Crowley, D. Microbial transformation of pyrethroid insecticides in aqueous and sediment phases. *Environ. Toxicol. Chem.* **2004**, *23*, 1–6.

(5) Liesack, W.; Schnell, S.; Revsbech, N. Microbiology of flooded rice paddies. *FEMS Microbiol. Rev.* **2000**, *24*, 625–645.

(6) Soil Survey Staff, Natural Resources Conservation Services, USDA. Soil survey of Butte area, California, parts of Butte and Plumas Counties, 2006. http://soildatamart.nrcs.usda.gov/Manuscripts/CA612/0/Butte_CA.pdf (accessed June 22, 2010).

(7) Sheldrick, B. H.; Wang, C. Particle-size distribution. In *Soil Sampling and Methods of Analysis, Canadian Society of Soil Science*; Carter, M. R., ed.; Lewis Publishers: Ann Arbor, MI, 1993; pp 499−511.

(8) UC Davis College of Agricultural and Environmental Sciences Analytical Laboratory, http://anlab.ucdavis.edu/ (accessed Jan 12, 2011).

(9) Tomco, P.; Holstege, D.; Tjeerdema, R. Microbial degradation of clomazome under simulated California rice growing conditions. *J. Agric. Food Chem.* **2010**, *58*, 3674–3680.

(10) Smith, S., Jr.; Willis, G.; Cooper, C. Cyfluthrin persistence in soil as affected by moisture, organic matter and redox potential. *Bull. Environ. Contam. Toxicol.* **1995**, *55*, 142–148.

(11) Parr, J.; Smith, S. Degradation of toxaphene in selected anaerobic soft environments. *Soil Sci.* **1976**, *121*, 52–57.

(12) Oyamada, M.; Kuwatsuka, S. Effects of soil properties and conditions on the degradation of three diphenyl ether herbicides in flooded soils. *J. Pestic. Sci.* **1988**, *13*, 99–105.

(13) Jordan, E.; Kaufman, D. Degradation of *cis*- and *trans*-permethrin in flooded soil. *J. Agric. Food Chem.* **1986**, *34*, 880–884.

(14) Cavoski, I.; Caboni, P.; Sarais, G.; Miano, T. Degradation and persistence of rotenone in soils and influence of temperature variations. *J. Agric. Food Chem.* **2008**, *56*, 8066–8073.

(15) Parr, J.; Smith, S.; Willis, G. Soil anaerobiosis 1. Effect of selected environments and energy sources on respiratory activity of soft microorganisms. *Soil Sci.* **1970**, *110*, 37–43.

(16) Noble, R.; Hamilton, D. Stability of cypermethrin and cyfluthrin on wheat in storage. *J. Pestic. Sci.* **1985**, *16*, 179–185.

(17) Crosby, D. *Environmental Toxicology and Chemistry*; Oxford University Press: New York, 1998.

(18) Vogel, T.; Grbic-Galic, D. Incorporation of oxygen from water into toluene and benzene during anaerobic fermentative transformation. *Appl. Environ. Microbiol.* **1986**, *52*, 200–202.

(19) Chakraborty, R.; Coates, J. Hydroxylation and carboxylation − two crucial steps of anaerobic benzene degradation by *Dechloromonas* Strain RCB. *Appl. Environ. Microbiol.* **2005**, *71*, 5427–5432.

(20) Roberts, T.; Standen, M. Degradation of the pyrethroid cypermethrin NRDC 149 (±)-α-cyano-3-phenoxybenzyl (±)-*cis*,*trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate and the respective *cis*- (NRDC 160) and *trans*- (NRDC 159) isomers in soils. *J. Pestic. Sci.* **1977**, *8*, 305–319.

(21) Roberts, T.; Standen, M. Further studies of the degradation of the pyrethroid insecticide cypermethrin in soils. *J. Pestic. Sci.* **1981**, *12*, 285–296.

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

(23) California Department of Pesticide Regulation. *Summary of Pesticide Use Report Data 2008; Indexed by Chemical*; California Environmental Protection Agency: Sacramento, CA, 2008; p 338 (available online at http://www.cdpr.ca.gov/docs/pur/pur08rep/chmrpt08.pdf, accessed June 22, 2010).

(24) Tomlin, C. D. S., Ed. *The Pesticide Manual*, 15th ed.; British Crop Production Council: Hants, U.K., 2009; p 454.

(25) Weber, J.; Coble, H. Microbial decomposition of diquat adsorbed on montmorillonite and kaolinite clays. *J. Agric. Food Chem.* **1968**, *16*, 475–478.

(26) Subba-Rao, R.; Alexander, M. Effect of sorption on mineralization of low concentrations of aromatic compounds in lake water samples. *Appl. Environ. Microbiol.* **1982**, *44*, 659–668.