JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Article

Cite This: J. Agric. Food Chem. XXXX, XXX, XXX−XXX

pubs.acs.org/JAFC

Influence of Flooding, Salinization, and Soil Properties on Degradation of Chlorantraniliprole in California Rice Field Soils

Zachary C. Redman,*[,†] Sanjai J. Parikh,[‡] Mathew J. Hengel,[†,§] and Ronald S. Tjeerdema[†]

[†]Department of Environmental Toxicology, [‡]Department of Land, Air and Water Resources, and [§]IR-4 Laboratory, College of Agricultural and Environmental Sciences, University of California, One Shields Avenue, Davis, California 95616-8588, United States

Supporting Information

ABSTRACT: Chlorantraniliprole (3-bromo-*N*-[4-chloro-2-methyl-6-(methylcarbamoyl)phenyl]-1-(3-chloro-2-pyridine-2-yl)-1*H*-pyrazole-5-carboxamide; CAP) was granted supplemental registration for use in rice cultivation in California through December, 2018. Previous work investigated the partitioning of CAP in California rice field soils; however, its degradation in soils under conditions relevant to California rice culture has not been investigated. The degradation of CAP in soils from two California rice fields was examined under aerobic and anaerobic conditions with varying salinity via microcosm experiments. Results indicate that soil properties governing bioavailability may have a greater influence on degradation than flooding practices or field salinization over a typical growing season. Differences between native and autoclaved soils ($t_{1/2}$ = 59.0−100.2 and 78.5−171.7 days) suggest that biological processes were primarily responsible for CAP degradation; however, future work should be done to confirm specific biotic processes as well as to elucidate abiotic processes, such as degradation via manganese oxides and formation of nonextractable residues, which may contribute to its dissipation.

KEYWORDS: *chlorantraniliprole, soil dissipation, degradation, microcosm, rice, insecticide*

INTRODUCTION

The Sacramento Valley of California produces more short- and medium-grain rice than any other rice-growing region in the United States and accounts for 95% of California's total rice production.[1] Pyrethroids, such as λ-cyhalothrin (trade name Warrior), are the most frequently applied insecticides in California to mitigate yield losses caused by the rice water weevil (*Lissorhptrus orysophilus*); however, management efficacy has begun to decline in California rice fields.[1] Chlorantraniliprole (CAP, trade name Coragen, Figure 1), an anthranilic diamide insecticide, was granted supplemental labeling in September, 2016, for use through December, 2018, on California rice fields as a preflood treatment for the prevention of yield losses attributable to rice water weevil larvae. While comparatively less toxic than pyrethroids to nontarget species such as crayfish and pollinators, CAP is highly toxic to aquatic invertebrates.[2−5] Furthermore, freshwater planarians and nontarget soil arthropods have shown reduced activity, reproduction, and feeding after short-term exposure to CAP, indicating potential for ecological impacts at sublethal concentrations that could result from spray drift, weir leakage, or release with tailwater.[6,7] Previous investigation of CAP partitioning using simulated California rice field conditions concluded that it is unlikely to volatilize (calculated Henry's Law constant of 1.69×10^{-16} to 2.81×10^{-15} atm·m^3·mol^{-1} from 15−35 °C) and it exhibits moderately weak sorption to soil (log K_{OC} = 2.59−2.96), resulting in an estimated 76.58−87.58% of the applied amount remaining in the soil or pore water of a typical rice field.[8] Therefore, CAP degradation in California rice field soils should be investigated to ensure adequate dissipation prior to the release of tailwater into the Sacramento River system.

Biotic pesticide degradation in soils is carried out by the microbial community present and is influenced by the physical and chemical properties of the local environment. When a rice field is flooded, anaerobic conditions are rapidly established with oxic regions persisting only within a few millimeters of the surface and rhizosphere, causing dramatic changes in the dominant microbial communities.[9−12] As a result, degradation rates under preflood aerobic conditions can differ greatly from those measured under flooded anaerobic conditions.[13−16] Extended flooding periods, combined with elevated temperature and rapid evapotranspiration in California rice fields, exacerbate the evapoconcentration of salts, resulting in measured electrical conductivities exceeding 4.0 dS·m^{-1}.[17,18] Increased salinity has been shown to negatively impact microbial and enzyme activity in soils; however, to our knowledge the impact of soil salinity on pesticide degradation is limited, and its impact on the degradation of CAP in soils has not been previously investigated.[19−22]

The half-life of CAP in three Chinese paddy soils (fraction of organic carbon, f_{oc}, and percent clay between 0.0151−0.0218 and 19.18−34.46%, respectively) under aerobic conditions ranged from 41−53 days, and applications of up to 1 mg·kg^{-1} were not observed to significantly alter the microbial population after the first 14 days of exposure.[23,24] The aerobic soil and anaerobic aquatic degradation half-lives for CAP reported by the registrant were 228.0−924.1 and 208 days, respectively.[2] To our knowledge, no investigation has derived soil-degradation rates for CAP under anaerobic

Received: May 10, 2019
Revised: June 13, 2019
Accepted: July 1, 2019

DOI: 10.1021/acs.jafc.9b02947
J. Agric. Food Chem. XXXX, XXX, XXX−XXX

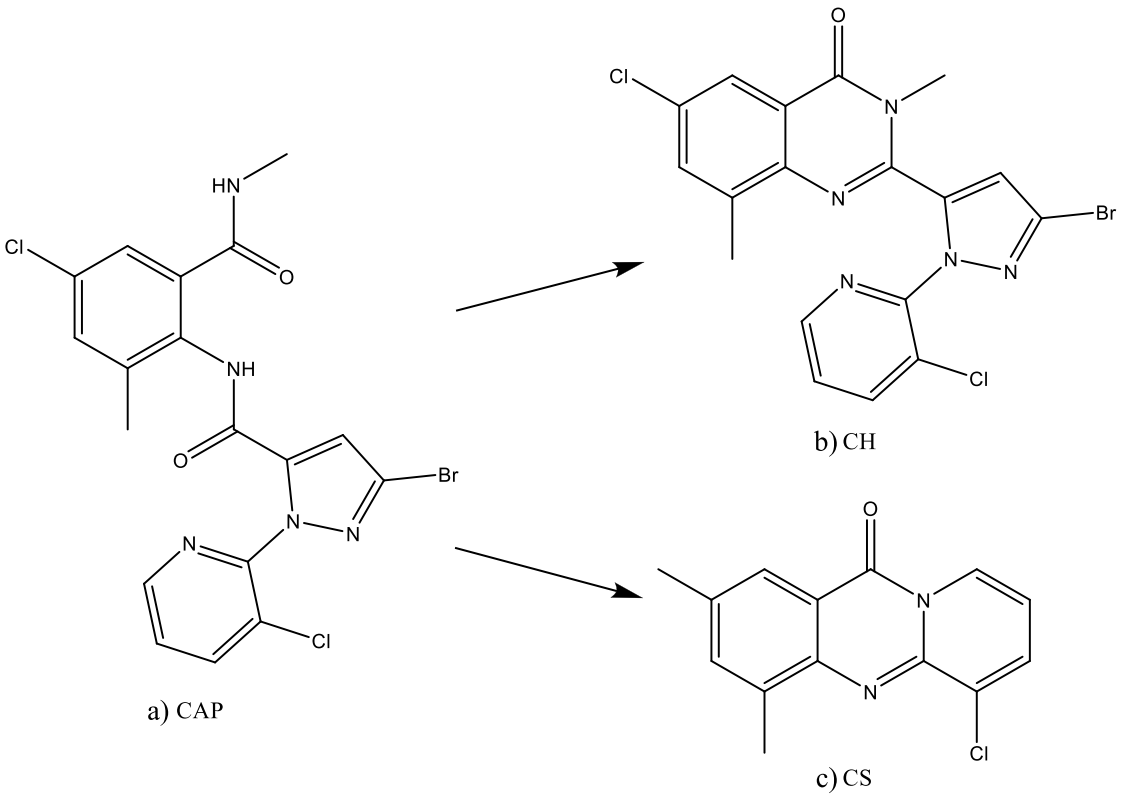

Figure 1. Chemical structures of (a) chlorantraniliprole (CAP) and its (b) hydrolysis (CH) and (c) soil (CS) degradates.

Table 1. Soil Properties Determined by UCD Analytical Laboratory

soil	pH	f_{oc} [a]	f_{om} [a]	EC[a] (dS/m)	CEC[a] (meq/100 g)	texture classification	sand (%)	silt (%)	clay (%)
Princeton (PS)	6.30	0.023	0.046	0.59	26.4	silty clay loam	10	54	36
Biggs (BS)	4.74	0.020	0.039	0.26	12.3	clay loam	33	40	27

[a]Abbreviations used for fraction of organic carbon (f_{oc}), fraction of organic matter (f_{om}), electrical conductivity (EC), and cation-exchange capacity (CEC).

conditions. Thus, this investigation aims to (1) characterize the degradation of CAP in soil under simulated California rice field conditions and (2) determine the influence of (a) soil properties, (b) flooding, and (c) salinity on reaction rates. To achieve this, (1) degradation half-lives were determined via microcosm experiments with (2a) two rice field soils, characterized by different clay and organic matter contents (27−36% and 3.9−4.6%, respectively) from the Sacramento Valley maintained at (2b) 50% water holding capacity (aerobic) or flooded (anaerobic) at (2c) three different salinities.

MATERIALS AND METHODS

Chemicals. 3-Bromo-*N*-[4-chloro-2-methyl-6-(methylcarbamoyl)-phenyl]-1-(3-chloro-2-pyridine-2-yl)-1*H*-pyrazole-5-carboxamide (CAP; analytical grade, 99.7%), 2-[3-bromo-1-(3-chloro-2-pyridinyl)-1*H*-pyrazol-5-yl]-6-chloro-3,8 dimethyl-4(3*H*)-quinazolinone (CH; analytical grade, 99.8%), and 2-[3-bromo-1-(3-chloro-2-pyridinyl)-1*H*-pyrazole-5-yl]-6-chloro-3,8-dimethyl-4(3*H*)-quinazolinone (CS; analytical grade, 98.9%) were donated by DuPont Chemical (Wilmington, DE). Water (Optima grade), methanol (Optima grade), acetone (HPLC grade), calcium chloride (certified ACS grade), and sodium chloride (certified ACS grade) were purchased from Fisher Scientific (Hampton, NH). *N*,*N*′-Bis(5-chloro-2-methoxyphenyl)phthalamide (IS), water (HPLC grade), methanol (HPLC grade), ethyl acetate (HPLC grade), magnesium sulfate (reagent grade, >99.5%), sodium sulfate (ACS reagent grade, 99%), C18 (Discovery), primary secondary amine (PSA), and formic acid (99.8%) were purchased from Sigma-Aldrich (St. Louis, MO).

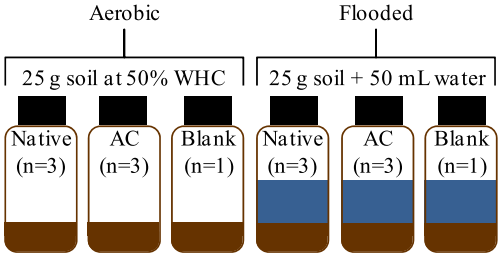

Figure 2. Native (n = 3), AC (autoclaved, n = 3), and blank (n = 1) rice field soil microcosms were prepared for both Biggs and Princeton soils under both aerobic and flooded conditions. Flooded microcosms were prepared separately with 50 mL of water containing 0, 0.01, or 0.05 M NaCl, $CaCl_2$, $MgSO_4$, and Na_2SO_4 (10:1:2:1 mol ratio).

Soil Sample Preparation and Analysis. Soils having no history of CAP application were collected from two Sacramento Valley rice fields near (1) Princeton, CA (PS), Marvin silty clay loam classified as fine, thermic Mollic Haploxeralfs (39° 26′ 11.5′′ N, 122° 2′ 41.7′′ W), and (2) Biggs, CA (BS), Esquon−Neerdobe classified as fine, smectitic, thermic Xeric Epiaquerts (39° 25′ 5.7′′ N, 121° 40′ 34.4′′ W).[25] Each soil was collected according to ISO 18400 sampling guidelines from the top 10 cm of each field, air-dried, sieved (<2 mm) to remove large particles and debris, and then stored at 4 °C in the dark until use.[26]

DOI: 10.1021/acs.jafc.9b02947
J. Agric. Food Chem. XXXX, XXX, XXX−XXX

Soil water-holding capacity was determined according to ASTM D2216-10.[27] Briefly, soils were saturated over a period of 24 h, drained for 24 h, and oven-dried at 110 °C. Water-holding capacity (WHC, in %) was calculated using eq 1,

$$\mathrm{WHC} = \frac{m_{cw} - m_{cd}}{m_{cd} - m_c} \times 100 \quad (1)$$

where m_{cw} is the mass of the container and wet soil (g), m_{cd} is the mass of the container and dry soil (g), and m_c is the mass of the container (g). Water-holding capacities for Princeton and Biggs soils were 28.03 ± 1.86% and 24.51 ± 0.22% (n = 5), respectively.

Clay mineralogy and metal (hydr)oxide content were qualitatively determined via X-ray diffraction (XRD) and attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) as described in the Supporting Information. All other soil physicochemical properties (Table 1) were determined by the University of California, Davis Analytical Laboratory (methods available at anlab.ucdavis.edu).[28]

Microcosm Equilibrium. Microcosms were constructed with 25 g of soil and 50 mL of aqueous phase in tightly capped sterilized 250 mL amber polypropylene bottles (Dynalab Corp, Rochester, NY). They were prepared using either sterilized water or a solution of 0.05 M NaCl, $CaCl_2$, $MgSO_4$, and Na_2SO_4 (10:1:2:1 mol ratio) to simulate the salt composition of California rice field water.[29] Microcosms were incubated at room temperature (21.8 ± 0.5 °C) and sampled in triplicate at 0, 1, 3, 7, 21, and 28 days. Oxidation−reduction potential (ORP) and pH were measured using a HI991002 m (Hanna Instruments, Woonsocket, RI), while electrical conductivity (EC) was measured with an ECTester 11+ meter (Oakton Instruments, Vernon Hills, IL).

CAP Degradation in Soil. The degradation of CAP in each rice field soil was characterized using microcosms of 25 g of soil maintained either at 50% WHC, selected based on Organisation for Economic Co-operation and Development (OECD) recommendations for optimal microbial growth in aerobic soils in loosely capped sterilized 250 mL amber polypropylene bottles (aerobic treatments) or with 50 mL of sterile water in tightly capped sterilized 250 mL amber polypropylene bottles (anaerobic treatments).[30] Additional saline anaerobic treatments were prepared using 50 mL of 0.01 or 0.05 M aqueous solutions of NaCl, $CaCl_2$, $MgSO_4$, and Na_2SO_4 (10:1:2:1 mol ratio) (Figure 2). Microbe activity was inhibited in control microcosms through triplicate autoclaving. Microcosms were incubated at room temperature (21.8 ± 0.5 °C) for 3 weeks before spiking with 50 μL of 250 $\mu g \cdot mL^{-1}$ CAP in methanol; negative checks were prepared identically and spiked with 50 μL of methanol. Hydrolysis controls were prepared by spiking 10 mL of sterilized water in amber borosilicate vials with 40 μL of 250 $\mu g \cdot mL^{-1}$ CAP in methanol. For all treatments, microcosms and sterilized controls were sampled in triplicate along with a negative check and extracted (described below) 0, 3, 7, 14, 21, 28, 63, 91, and 119 days after spiking. Triplicate hydrolysis controls were diluted 1:10 (v/v) with methanol at each time point prior to analysis by liquid chromatography tandem mass spectrometry (LC-MS/MS).

Extraction. A solid−liquid extraction method was developed for the analysis of CAP and its hydrolysis (CH) and soil (CS) degradation products in soil. First, 50 mL of water (HPLC grade; aerobic samples only) and 100 mL of ethyl acetate were added to each sample. Samples were shaken (250 rpm, 1 h) on an Innova 2000 platform shaker (New Brunswick Scientific, Edison, NJ) and centrifuged (4066g, 10 min), and the supernatant was decanted into a separate 250 mL polypropylene bottle (Thermo Fisher Scientific, Waltham, MA). This process was repeated two additional times with 50 mL of acetone. Next, 10 g of NaCl and 20 g of $MgSO_4$ were added to the combined supernatants, which were then shaken (250 rpm, 5 min) and centrifuged (4066g, 10 min). Following centrifugation, 100 mL of the organic layer was transferred into a 500 mL borosilicate cylindrical flask (Labconco, Kansas City, MO) and evaporated to dryness in a RapidVap (40 °C, 20% speed, 169 mbar; Labconco, Kansas City, MO). Samples were reconstituted with 10 mL of methanol (HPLC grade), and 5 mL was transferred to a 15 mL polypropylene centrifuge tube (Corning, Corning, NY) containing 150 mg of C18 and 150 mg of PSA. Samples were shaken by hand for 1 min, centrifuged (1397g, 5 min), filtered through a 13 mm syringe tip filter with a 0.2 μm PTFE membrane (VWR Internationl, Radnor, PA), transferred to an amber LC vial with IS (final concentration 0.08 $\mu g \cdot g^{-1}$), and analyzed by LC-MS/MS. Average spike recoveries for CAP, CH, and CS ranged from 100−129%, 94−122%, and 60−109%, respectively (Table S1). The observed recovery enhancement for CAP and CH from the Princeton soil that was not sufficiently corrected by the internal standard at the 0.01 $\mu g \cdot g^{-1}$ fortification level likely resulted from the multiple solvent extractions necessary to achieve acceptable recovery of CS from the Princeton soil. While use of deuterated or ^{13}C labeled compounds would have corrected for the enhancement, they were not available at the time of the experiment. However, because the concentration of CAP was not observed to be <0.2 $\mu g \cdot g^{-1}$ and all rate constants were calculated based on relative concentrations, the enhanced recovery from the Princeton soil at low concentrations was not anticipated to influence the results of these experiments.

Degradation Kinetics. Degradation rate constants and half-lives were calculated via a first-order kinetics model using eq 2,

$$C_t = C_0\, e^{-k_{deg} t} \quad (2)$$

where C_t is the concentration of CAP ($\mu g \cdot g^{-1}$) at time t (days), C_0 is the initial concentration of CAP ($\mu g \cdot g^{-1}$), and k_{deg} ($days^{-1}$) is the first-order rate constant. Equation 2 can be rearranged to eq 3:

$$\ln\left(\frac{C_t}{C_0}\right) = -k_{deg} t \quad (3)$$

k_{deg} is then the negative slope of the linear regression line obtained by plotting the natural log of the relative concentration of CAP versus time. The half-life ($t_{1/2}$) of CAP can be calculated using eq 4:

$$t_{1/2} = \frac{\ln(2)}{k_{deg}} \quad (4)$$

LC-MS/MS Analysis. Soil extracts were analyzed on a 1260 Infinity Series liquid chromatography system coupled to a 6420 triple quadrupole mass spectrometer controlled by MassHunter version B.06.00 (Agilent, Santa Clara, CA). Injections (5 μL) were made onto a Luna C18(2) column (150 mm × 4.6 mm; 3 μm) with a Security Guard C18 cartridge (4 mm × 3 mm i.d.; Phenomenex, Torrence, CA). A gradient mobile phase of 0.1% formic acid in water (Optima grade) and 0.1% formic acid in methanol (Optima grade) was used; gradient parameters are available in the Supporting Information (Table S2). The retention times for CAP, IS, CH, and CS were 6.04, 9.13, 9.94, and 12.23 min, respectively, and the total run time was 16 min; a representative chromatogram is available in the Supporting Information (Figure S2). Atmospheric pressure chemical ionization in positive ionization mode was used with gas and vaporizer temperatures of 325 and 350 °C, respectively. The nebulizer gas was set to 40 psi, and the drying gas flow was 5 $mL \cdot min^{-1}$. Monitored ion transitions and mass spectrometer acquisition parameters are available in the Supporting Information (Table S3).

Blank extracts (n = 7) spiked to 0.005 $\mu g \cdot mL^{-1}$ were analyzed to determine method limit of detection (MLOD) and method limit of quantification (MLOQ). The standard deviation of spiked blank extract responses was multiplied by 3.1427 (Students t-value for 98% two-tail confidence limits) and 10 for the calculation of MLOD and MLOQ, respectively (Table S4).

Statistics. JMP Pro 13 (SAS Institute, Cary, NC) was used to determine first-order rate constants via linear regression and all following statistical analysis. The impacts of soil, flooding, salinity, and sterilization on degradation as well as the impact of time, soil, and salinity on equilibrium microcosm EC, pH, and ORP were assessed using analysis of variance (ANOVA; significance level $P \leq 0.01$). Model assumptions of normally distributed residuals and equal variance were confirmed via Wilk−Shapiro ($W \geq 0.95$) and Levene (P

DOI: 10.1021/acs.jafc.9b02947
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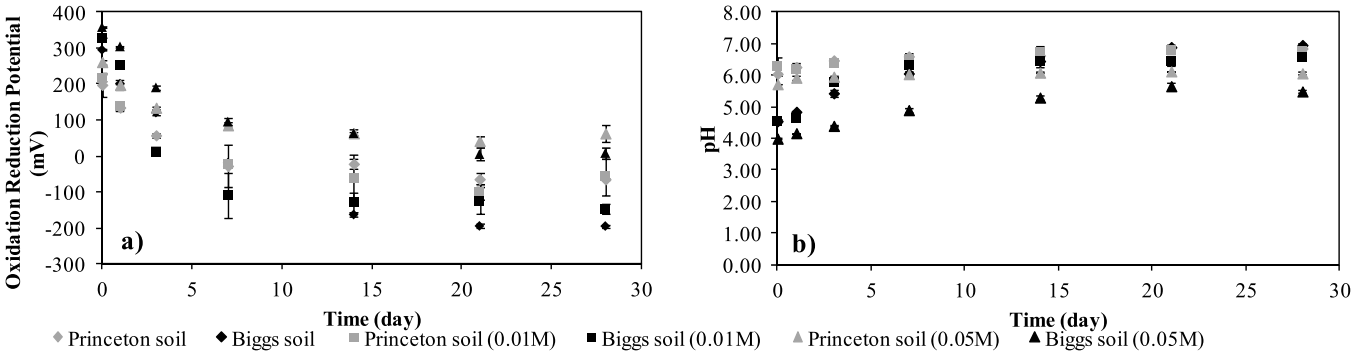

Figure 3. Flooded microcosm equilibrium (a) oxidation reduction potential and (b) pH; error bars represent standard deviation (n = 3). Ionic strength (M) is based on a mixture of NaCl, $CaCl_2$, $MgSO_4$, and Na_2SO_4 (10:1:2:1 mol ratio).

≤ 0.05) tests, respectively. Post hoc analysis was performed using Student's t test and Tukey HSD pairwise comparisons (α = 0.05).

RESULTS AND DISCUSSION

Microcosm Equilibrium. Flooded microcosm ORP and pH reached equilibrium after 21 days (Figure 3); equilibrium pH was significantly impacted by both salinity and soil type (P < 0.0001) with significant differences between all treatments (α = 0.05) except PS, BS, and PS (0.01 M). For both soil types, equilibrium pH values following saline treatment were lower than those measured with nonsaline treatments and are likely attributable to the displacement of protons from clay mineral surfaces via cation exchange at elevated salinity. Both salinity and soil type had a significant effect on equilibrium ORP (P < 0.0001) with the 0.05 M salinity resulting in elevated ORP (α = 0.05). EC was stable for the duration of the incubation period with small, yet statistically significant (P < 0.0001; α = 0.05), differences observed between soils at each level (Table 2) and attributable to differences in clay content and cation-exchange capacity (Table 1).

Table 2. Princeton (PS) and Biggs (BS) Soil Microcosm Electrical Conductivities (Average ± Standard Deviation; n = 21) (dS/m)[a]

salinity	PS	BS
0 M	0.329 ± 0.073	0.139 ± 0.051
0.01 M	1.250 ± 0.102	1.063 ± 0.103
0.05 M	4.27 ± 0.39	4.70 ± 0.25

[a]Ionic strength (M) based on a mixture of NaCl, $CaCl_2$, $MgSO_4$, and Na_2SO_4 (10:1:2:1 mol ratio)

CAP Degradation Kinetics. Degradation in soil followed first-order kinetics (R^2 = 0.50−0.89) for 63 days, after which no further degradation was observed (Figure 4). Degradation

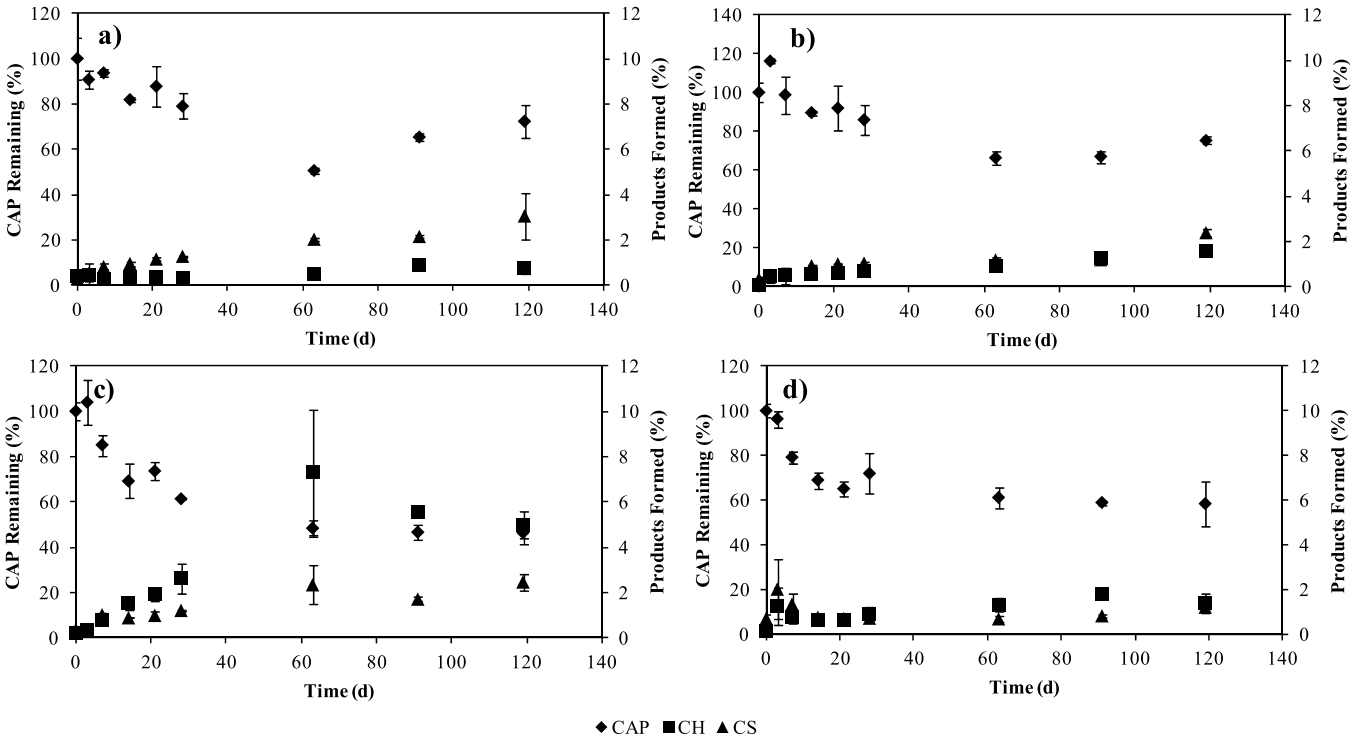

Figure 4. Degradation of CAP and the formation of its hydrolysis (CH) and soil (CS) degradation products as a molar percentage of initially applied CAP in native (a) aerobic Biggs soil, (b) aerobic Princeton soil, (c) anaerobic Biggs soil, and (d) anaerobic Princeton soil microcosms. Points and error bars represent average and standard deviation, respectively (n = 3).

DOI: 10.1021/acs.jafc.9b02947
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Table 3. Degradation Rate Constants (k_{deg}), Half-lives ($t_{1/2}$), and R^2 for the Dissipation of CAP from Princeton (PS) and Biggs (BS) California Rice Field Soils (n = 3)[a]

		aerobic		flooded		flooded (0.01 M salinity)		flooded (0.05 M salinity)	
soil	parameter	native	autoclaved	native	autoclaved	native	autoclaved	native	autoclaved
BS	k_{deg} ($days^{-1}$) (±SE)	1.011×10^{-2} ($\pm 8.30 \times 10^{-4}$)	8.176×10^{-3} ($\pm 9.01 \times 10^{-4}$)	1.174×10^{-2} ($\pm 1.238 \times 10^{-3}$)	8.833×10^{-3} ($\pm 7.81 \times 10^{-4}$)	6.915×10^{-3} ($\pm 9.79 \times 10^{-4}$)	4.037×10^{-3} ($\pm 9.22 \times 10^{-4}$)	9.058×10^{-3} ($\pm 8.64 \times 10^{-4}$)	5.174×10^{-3} ($\pm 8.89 \times 10^{-4}$)
	$t_{1/2}$ (days) (±SE)	68.6 (±5.6)	84.8 (±9.3)	59.0 (±6.2)	78.5 (±6.9)	100.2 (±14.2)	171.7 (±39.2)	76.5 (±7.3)	134 (±23.0)
	R^2	0.89	0.81	0.83	0.87	0.72	0.50	0.85	0.64
PS	k_{deg} ($days^{-1}$) (±SE)	7.495×10^{-3} ($\pm 9.18 \times 10^{-4}$)	7.312×10^{-3} ($\pm 8.70 \times 10^{-4}$)	6.954×10^{-3} ($\pm 1.392 \times 10^{-3}$)	6.471×10^{-3} ($\pm 9.30 \times 10^{-4}$)	7.544×10^{-3} ($\pm 1.462 \times 10^{-3}$)	5.414×10^{-3} ($\pm 6.56 \times 10^{-4}$)	8.503×10^{-3} ($\pm 1.149 \times 10^{-3}$)	6.093×10^{-3} ($\pm 9.11 \times 10^{-4}$)
	$t_{1/2}$ (days) (±SE)	92.5 (±11.3)	94.8 (±11.3)	99.7 (±20.0)	107.1 (±15.4)	91.9 (±17.8)	128.0 (±15.5)	81.5 (±11.0)	113.8 (±17.0)
	R^2	0.78	0.79	0.57	0.73	0.60	0.78	0.74	0.70

[a]Ionic strength (M) based on a mixture of NaCl, $CaCl_2$, $MgSO_4$, and Na_2SO_4 (10:1:2:1 mol ratio).

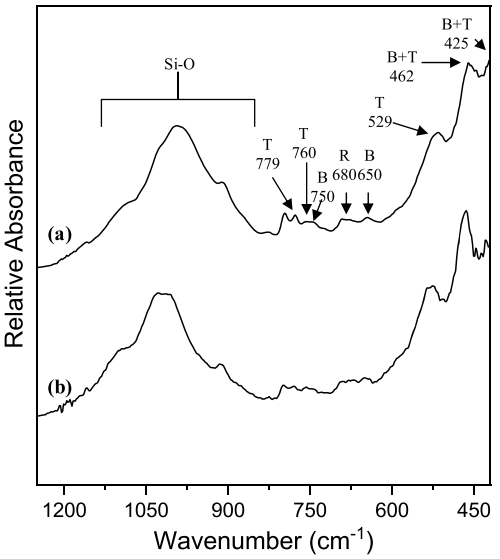

Figure 5. ATR-FTIR spectra for (a) Biggs and (b) Princeton soil clay fractions normalized to relative Si−O absorbance intensity. Annotations denote the silicate vibrational region and the wavenumbers (cm^{-1}) associated with the manganese oxide lattice vibrations for birnessite (B), todorokite (T), and ranicite (R).

rate constants and half-lives for CAP during this period are presented in Table 3. CAP is reportedly stable to hydrolysis under both neutral and acidic conditions; however, a loss of ~32% of CAP was observed in the hydrolysis controls after 119 days ($t_{1/2}$ = 204.6 ± 28.9 days; R^2 = 0.69).[2,31] While hydrolysis controls were autoclaved to inhibit microbial activity, the observed half-life is in close agreement with the anaerobic and aerobic aquatic metabolism half-lives (208 and 231 days, respectively) reported to the USEPA.[2] Autoclaving was generally observed to cause a decrease in the degradation of CAP ($P < 0.0001$); however, the differences were small and only significant (α = 0.05) for BS microcosms at 0.05 M salinity. Half-lives for BS autoclaved and native microcosms at 0.05 M salinity were 76.5 and 134 days, while those for all treatments ranged from 59.0−100.2 and 78.5−171.7 days for autoclaved and native microcosms, respectively (Table 3). Incomplete elimination of degradation via autoclaving may be attributable to the recovery of surviving microbial communities or residual soil enzyme activity after autoclaving.[16,32] However, abiotic degradation of organic compounds in soil by metal (hydr)oxides, in particular manganese oxides, has been previously observed and could account for the degradation of CAP in autoclaved soils.[33] While qualitative XRD analysis indicated that the soils are composed of chlorite, kaolinite, and glauconite and lacked evidence of crystalline metal (hydr)-oxides (Figure S1), subsequent ATR-FTIR analysis revealed the presence of amorphous manganese oxides although no iron or aluminum (hydr)oxides (Figure 5). As annotated in Figure 5, tetravalent manganese oxides were identified by the Mn−O vibrational bands in the 400−800 cm^{-1} region; birnessite was identified based on bands in the regions of 425, 462, 650, and 750 cm^{-1}, while todorokite was identified by bands in the regions of 425, 529, 760, and 779 cm^{-1}.[34] The band near 680 cm^{-1} may indicate the presence of ranicite, which is reportedly only distinguishable from disordered birnessite and todorokite by the presence of the 680 cm^{-1} band and the absence of bands located at 750 and 760 cm^{-1}.[35] Overall, inhibition by autoclaving, faster dissipation in soil microcosms than

DOI: 10.1021/acs.jafc.9b02947
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Table 4. Formation of Hydrolysis (CH) and Soil (CS) Degrades As a Molar Percentage (%) of CAP Degraded (±SD, n = 3) in 63 Days Biggs (BS) and Princeton (PS) Soil Microcosms[a]

	aerobic		flooded		flooded (0.01 M)		flooded (0.05 M)	
	CH (%)	CS (%)	CH (%)	CS (%)	CH (%)	CS (%)	CH (%)	CS (%)
BS	0.98 (±0.14)	4.12 (±0.27)	14.06 (±5.11)	4.47 (±1.36)	15.29 (±2.06)	6.99 (±0.68)	10.50 (±2.48)	3.64 (±0.38)
PS	2.77 (±0.57)	3.52 (±0.29)	3.47 (±1.07)	1.79 (±0.49)	3.81 (±1.97)	2.43 (±1.09)	3.46 (±0.81)	2.50 (±0.43)

[a]Ionic strength (M) based on a mixture of NaCl, $CaCl_2$, $MgSO_4$, and Na_2SO_4 (10:1:2:1 mol ratio).

hydrolysis controls, and the presence of manganese oxides indicate that the degradation of CAP in soils is likely driven by biotic processes and assisted via abiotic degradation on manganese oxides.

An end to the first-order degradation of CAP 63 days after application provides additional evidence to support the conclusion that the degradation of CAP in soil is biologically mediated. Some amide-containing heterocyclic compounds have shown antimicrobial activity; however, CAP was not observed to negatively impact the microbial population in soil microcosms at an application rate double that used in this experiment.[23,24,36] While differences in local community structures and soil properties could theoretically lead to enhanced toxicity of CAP and its degradates to soil microorganisms, cessation of degradation was likely caused by depletion of available micronutrients, such as nitrogen and phosphorus, resulting in the death or dormancy of the microbial population responsible for the degradation of CAP. Nutrient depletion (i.e., ammonium) from unfertilized rice field soil microcosms was observed after 70 days of incubation, consistent with the 84 day (total incubation time) period to potential depletion in our microcosms.[37] Large pulses in microbial activity following the rewetting of soils have been observed previously, and it is plausible for soils that commonly undergo long periods of drought followed by wet periods, such as rice fields, to have microbial communities adapted to wetting cycles, leading to resuscitation, use of available substrate, and dormancy.[38−40] Previous work has shown that the application of fertilizers can have an impact on microbially mediated processes; however, the impact of fertilizer amendment on the degradation of CAP was outside the scope of this investigation's aim to evaluate the impact of California relevant flooding practices and salinization on the degradation of CAP in soil.[37,41−43]

The half-life of CAP in native soils was 59.0−100.2 days (Table 3) and was generally faster in BS treatments, although not significantly impacted by flooding conditions or salinity within a single soil treatment. A significant difference in degradation rate was only observed between BS and PS native flooded treatments (α = 0.05) with half-lives of 59.0 and 99.7 days, respectively. Relative IR absorbance of BS versus PS clay fractions suggests a greater quantity of amorphous manganese oxides in the BS soil, inferred based on the relative intensities of the ATR-FTIR spectra presented in Figure 5, which may explain the dissipation rate increase observed in BS treatments; however, this interpretation necessitates that future work characterize the interaction between CAP and manganese oxides. CAP degradation in all treatments was slower than previously measured aerobic half-lives by Wu et al. (41−53 days) although faster than those reported to USEPA (228.0−924.1 days); these results indicate that, while the dissipation of CAP is not expected to vary greatly in a California rice fields based on flooding practices and salinization, variability between fields as a result of microbial diversity or differences in bioavailability may be significant.[2,24,44,45]

Degradation Products and Nonextractable Residue Formation. The degradation products CH and CS (Figure 1) were observed to increase with time in all treatments as CAP was degraded. Figure 4 provides a plot of CAP, CH, and CS as a molar percentage of the initial amount of CAP applied in native microcosms. The amount of CH and CS formed in each treatment, expressed as a molar percentage of CAP lost, is presented in Table 4. A larger percentage of CAP was converted to CH rather than CS in all anaerobic treatments, consistent with the maximum observed 9.5 and 4.9% conversion of applied CAP to CH and CS, respectively, as reported to USEPA.[2] However, much less CH was formed in aerobic microcosms. It is likely that the difference in water content between aerobic and anaerobic microcosms led to changes in the rate of hydrolysis, which could have occurred via both biotic and abiotic processes.

As seen in Figure 4, it is clear that the formations of CH and CS alone do not account for the loss of CAP in these soils. Mass balance, as a molar percentage of initial CAP, at 63 days ranged from 53 to 76%. Subsequent analysis by Orbitrap mass spectrometry did not result in the identification of any nontarget compounds in 63 days microcosms. Because CAP is nonvolatile, possible explanations for lack of mass balance include mineralization and the formation of bound or biogenic nonextractable residues, although this cannot be stated with certainty without the application of unavailable radiolabels. Nonextractable residue formation can occur through chemical or biological mechanisms and can vary greatly based on chemical properties, soil organic matter content, pH, moisture content, redox state, and microbial activity.[46−48] Furthermore, increased contact time, or aging, of pesticides with soils has been shown to increase sequestration or decrease the extractability of organic compounds from soils.[49−52] Previous observation of an increase in the sorption of CAP to soils after brief aging suggests that the interaction of CAP with soils may be time-dependent.[8] The formation of nonextractable residues may also decrease bioavailability and could explain the cessation of degradation observed after 63 days in these microcosm experiments. The observation that CAP degradation was slower in PS microcosms, characterized by higher soil organic matter and clay content (Table 1), is consistent with the hypothesis that increased sorption or nonextractable residue formation may reduce bioavailability and be responsible for the observed differences between soil treatments.

Overall, the dissipation of CAP from California rice field soils is expected to proceed slowly via biological processes and may be assisted by the formation of nonextractable residues and abiotic degradation by manganese oxides. Future work using radiolabels is necessary to fully characterize the extent and nature of potential nonextractable residue formation, and additional field studies could yield further insight into the overall dissipation of CAP in soils.

DOI: 10.1021/acs.jafc.9b02947
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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jafc.9b02947.

Liquid chromatography mobile phase gradient, mass spectrometer acquisition parameters, average extraction recoveries, method limits of detection, clay separation, X-ray diffractograms, and a representative chromatogram (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*Phone: (530) 752-2534. Email: zcredman@ucdavis.edu.

ORCID

Zachary C. Redman: 0000-0002-4158-524X

Funding

This work was funded by the California Rice Research Board (Award Number RP-5), the William G. and Kathleen Golden International Agricultural Fellowship, the Donald G. Crosby Fellowship in Environmental Chemistry, and the Donald G. Crosby Endowed Chair in Environmental Chemistry.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank K. Tran, J. Khuu, M. Maier, and K. Williams for their assistance and C. Li for XRD operation. We are grateful to R. Stogsdill and R. Hansen for allowing us access to fields for soil collection. We also thank Du Pont Crop Protection for generous donation of chlorantraniliprole and its degradates.

■ ABBREVIATIONS USED

CAP, chlorantraniliprole; USEPA, United States Environmental Protection Agency; K_{oc}, organic carbon normalized partition coefficient; f_{oc}, fraction of organic carbon; WHC, water-holding capacity; CH, 2-[3-bromo-1-(3-chloro-2-pyridinyl)-1*H*-pyrazol-5-yl]-6-chloro-3,8 dimethyl-4(3*H*)-quinazolinone; CS, 2-[3-bromo-1-(3-chloro-2-pyridinyl)-1*H*-pyrazole-5-yl]-6-chloro-3,8-dimethyl-4(3*H*)-quinazolinone; IS, *N*,*N*′-bis(5-chloro-2-methoxyphenyl)phthalamide; BS, Biggs soil; PS, Princeton soil; XRD, X-ray diffraction; ATR-FTIR, attenuated total reflectance Fourier transform infrared spectroscopy; ORP, oxidation reduction potential; EC, electrical conductivity; OECD, Organisation for Economic Co-operation and Development; AC, autoclaved; PTFE, polytetrafluoroethylene; C18, octadecyl ligand; PSA, primary secondary amine; LC-MS/MS, liquid chromatography tandem mass spectrometry; MLOD, method limit of detection; MLOQ, method limit of quantitation; ANOVA, analysis of variance; k_{deg}, first-order degradation rate constant; $t_{1/2}$, half-life

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DOI: 10.1021/acs.jafc.9b02947
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