Degradation of [^{14}C]Carfentrazone-ethyl under Aerobic Aquatic Conditions

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Carfentrazone-ethyl (CF-E) is an aryl triazolinone reduced-risk herbicide for use on corn, wheat, and soybean. As part of the assessment of its metabolic fate, the aerobic aquatic metabolism of [^{14}C]CF-E at a concentration of 0.22 μg/g was investigated. Two separate aquatic sediments (silty clay loam and clay loam soils, flooded with water) were used in the study. At each of eight samplings throughout the 30-day study, the distribution of radioactivity between surface water, sediment, and volatile fractions was assessed. At zero time, the majority of the applied radioactivity was contained in the water layer (83−90%), declining to 70−80% after 30 days. This was coupled with an increase in the percent radioactivity in the soil layer from 4−6% at day 0 to 13−19% after 30 days. Nonextractable soil residues and volatile degradation products were formed in negligible amounts. Analysis of the incubation extracts from either aquatic sediment indicated a rapid conversion (<2 days) of the parent CF-E ester to carfentrazone−chloropropionic acid. Over time, increasing amounts of a cascade of acidic degradation products comprising >90% of the applied radioactivity were formed. Identification of these degradation products was initially achieved through chromatographic comparison with reference synthetic standards and subsequently confirmed using LC-MS analysis. A degradation pathway for CF-E under aerobic aquatic conditions is proposed.

Keywords: *Aerobic; aquatic; metabolism; aryl triazolinone; carfentrazone-ethyl; Aim*

INTRODUCTION

Carfentrazone-ethyl (CF-E, **1)**, ethyl α,2-dichloro-5-[4(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1*H*-1,2,4-triazol-1-yl]-4-fluorobenzenepropanoate, is a low-use-rate aryl triazolinone herbicide registered by FMC Corp. (Aim) for postemergence use on corn, wheat, and soybeans. This rapid-acting herbicide was among the first to receive a fast-track approval under the EPA's reduced-risk guidelines because of its low toxicity (*1*, *2*). CF-E acts by inhibiting protoporphyrinogen oxidase, causing an induction of lipid peroxidation and resulting in a rapid desiccation (cell wall disruption) of susceptible weed species (*3*, *4*). In Europe, the product is especially effective against *Galium*, *Lamium*, and *Veronica* spp. (*2*, *5*, *6*). In the United States, it is effective in the selective control of broad-leaved weeds such as lambsquarter, morning-glory, nightshade, and velvetleaf (*4*). At higher use rates, CF-E provides the burn-down properties characteristic of the aryl triazolinones and can be used, in combination with other herbicides, as a total vegetation control herbicide (*7*). Several studies revealed that CF-E is extensively metabolized in plants (*8*, *9*) and mammals (*7*, *10*). This study was undertaken to determine the degree and pathway of CF-E degradation under aerobic aquatic conditions as part of an overall evaluation of its environmental fate. The study was conducted according to U.S. EPA Pesticide Assessment Guidelines.

MATERIALS AND METHODS

Chemicals. *Radiolabeled Test Substance.* Two types of ^{14}C-labeled parent chemical were used: uniformly phenyl-labeled CF-E ([*phenyl*-^{14}C]CF-E), with a specific activity of 31.0 mCi/mmol and a radiopurity of 98.1%, and triazole-5-labeled CF-E ([*triazole*-^{14}C]CF-E), with a specific activity of 37.6 mCi/mmol and a radiopurity of 98.5%. The position of the label in each of the two isotopes used is shown in Figure 1.

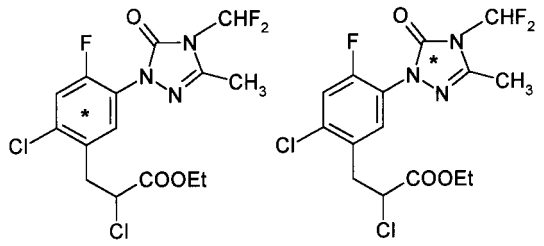

Figure 1. Label positions in [^{14}C]carfentrazone-ethyl (CF-E). Asterisks (∗) denote the position of ^{14}C labels.

Reference Standards. Non-radiolabeled CF-E, ethyl α,2-dichloro-5-[4(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1*H*-1,2,4-triazol-1-yl]-4-fluorobenzenepropanoate (CAS Registry No. 128639-02-1, as provided by the author), and reference standards of the degradation products encountered in the study were synthetically prepared at FMC (unpublished data). A review on the synthesis of the aryl triazolinone class of herbicides has been reported previously (*11*). The synthetic compounds were used as reference standards for high-performance liquid chromatography (HPLC) and thin-layer chromatography (TLC) analysis and included carfentrazone−chloropropionic acid (CF-ClPAc), carfentrazone−cinnamic acid (CF-CAc), carfentrazone−propionic acid (CF-PAc), carfentrazone−benzoic acid (CF-BAc), and 3-(hydroxymethyl)carfentrazone−benzoic acid (3-OH-CF-BAc).

Reagents. Solvents used for extraction and for chromatographic analysis were of HPLC grade or ACS reagent grade (J. T. Baker, Phillipsburg, NJ). Scintillation cocktails used were Hydrocount, Baker Analyzed (J. T. Baker), Hionic Fluor

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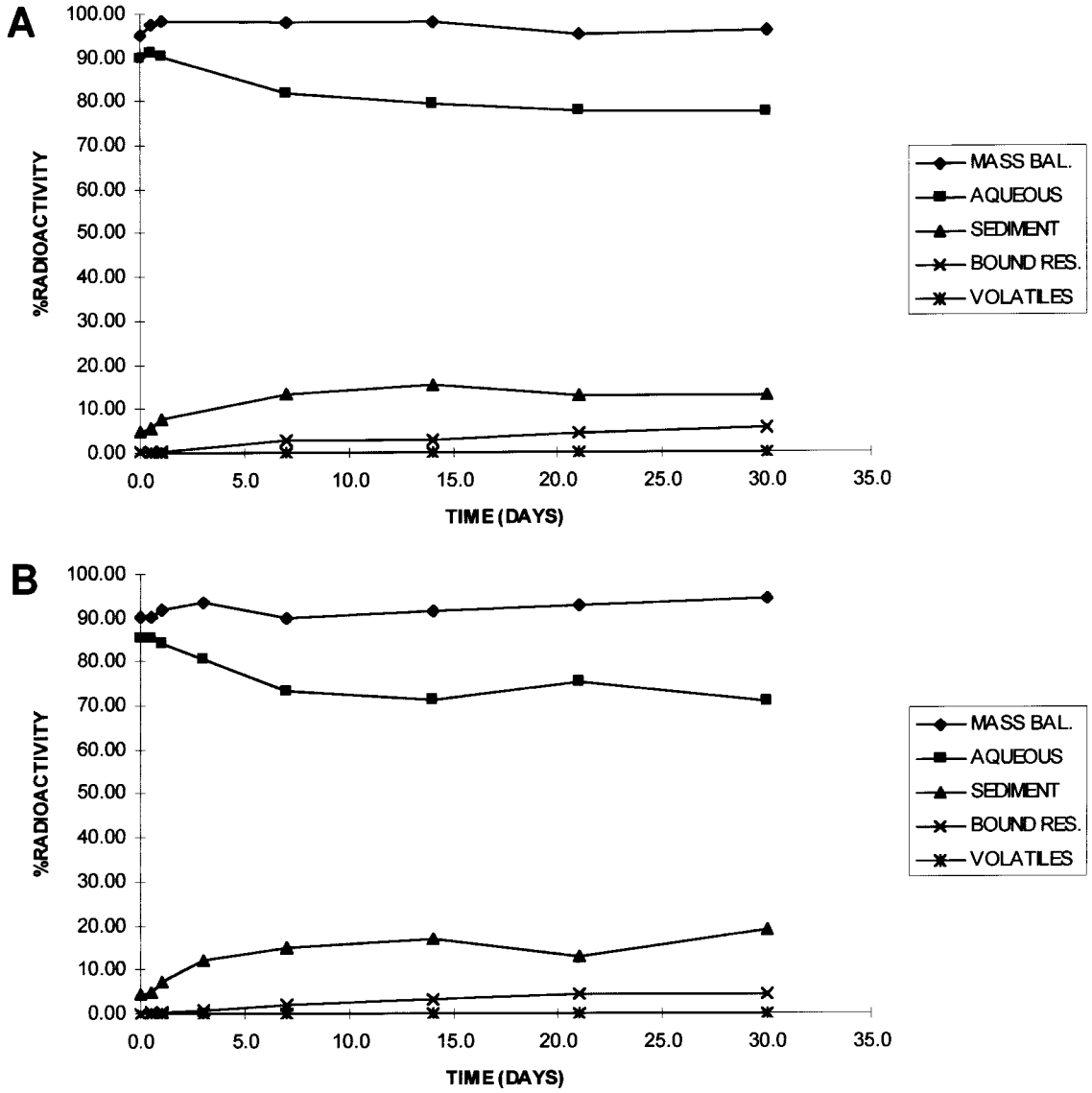

Figure 2. Distribution of radioactivity and mass balance in aquatic clay loam sediment: (A) [*phenyl*-^{14}C]CF-E; (B) [*triazole*-^{14}C]CF-E.

(Packard, Meriden, CT), and Carbon 14 Cocktail for Harvey Biological Oxidizers (R. J. Harvey Instrument Corp., Hillsdale, NJ).

Aquatic Sediments. The test matrices (sediment and water) used in this study were collected from two different rice-growing sites, one located in Live Oak, CA, and the other in Washington, LA. Characterization of the sediment was done at A&L Great Lakes Laboratories, Inc., Fort Wayne, IN, according to USDA guidelines. On the basis of the characterization results, the Louisiana sediment was classified as silty clay loam (11% sand, 54% silt, and 35% clay) and the California sediment as clay loam (37% sand, 28% silt, and 35% clay). Water samples were also analyzed for their physical characteristics including pH, dissolved oxygen, hardness, and conductivity at FMC laboratories except for water hardness determination, which was performed at A&L Great Lakes Laboratories. Collected test samples (water and sediment) were stored at ~4 °C in the dark until used shortly after receipt. An estimate of the microbial population was performed at least twice for each incubation, and the presence of aerobic organisms was clearly demonstrated. A standard quantitative plating method was used for that purpose (*12*). The moisture content for each sediment was determined prior to use. Each test system with a sediment-to-water ratio of 1:4 (w/v) was contained in a vessel (250 mL Nalgene bottle) with 25 g of sediment (dry weight basis) per 100 mL of water so that the sediment was completely covered with water during the study.

Aerobic Incubation. Each sample series was connected to a setup that maintains aerobicity of the water and permits common trapping of evolved volatile organic products and CO_2. The samples were incubated in the dark and generally maintained at a constant temperature of 25 ± 1 °C throughout the study. Each test vessel was wrapped with aluminum foil to prevent exposure to light. Two nine-vessel sets (including a control vessel) were established for each label. A common outlet port for each set was connected to a series of trapping containers. These traps included an ethylene glycol trap to collect evolved volatile organic products followed in series by a potassium hydroxide solution trap to collect $^{14}CO_2$. An indicator (phenolphthalein) was added to the potassium hydroxide trap to allow quick visual monitoring of the solution alkalinity during the study.

Dosing. The purified test substance (radiopurity > 98%), dissolved in acetonitrile (40−60 μL total volume/vessel), was applied to the water layer of the test system following a 2-week preincubation period. The test system was not mixed after dosing. The dosing solution was analyzed by liquid scintillation counting (LSC) to determine the actual amount of radioactivity applied to each test system. Dosing was done at a nominal concentration of 0.220 μg/g (based on the combined weight of water and sediment). This concentration approximated the proposed application rate of 0.30 lb of active ingredient (ai)/acre when applied to a 6-in.-deep body of water.

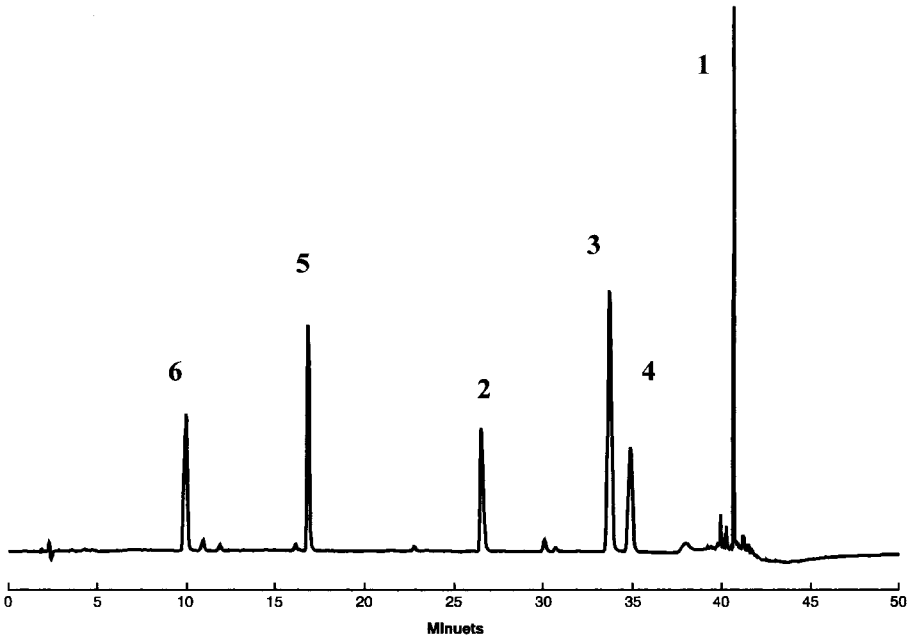

Figure 3. HPLC chromatogram (UV, 246 nm) of reference standards of CF-E and its degradation products. Peaks: 1, CF-E; 2, CF-ClPAc; 3, CF-CAc; 4, CF-PAc; 5, CF-BAc; 6, 3-OH-CF-BAc.

Sampling. Samples were taken at days 0, 0.2, 1, 3, 7, 14, 21, and 30 post-treatment for all incubations except for one (clay loam, phenyl label), for which the 3-day sampling was not done due to limited pure test substance availability at the time of dosing. Duplicate samples were analyzed at each sampling interval. Conductivity, pH, and the oxygen content of the water layer were measured at each sampling interval. At selected intervals (typically, 0, 14, and 30 days), aliquots of the test matrix were plated to check for and estimate the presence of aerobic organisms. The volatile traps were removed and replaced periodically (at each sample collection) to prevent saturation and were subsequently analyzed by LSC.

Extraction, Fractionation, and Workup Methods. *Water Layer.* Prior to separating the water from the sediment, samples of water were removed at selected intervals for microbial plating, as described earlier. Separation of water and sediment was then achieved by centrifugation (Beckman GS-6, 3000 rpm) for 15 min. The amount of radioactivity in the water was determined by LSC. The water layer was then directly analyzed by reversed phase HPLC. In cases when aqueous samples were subjected to TLC analysis, the pH was adjusted to ~2.0 followed by methylene chloride extraction. The organic extracts were then used for TLC analysis.

Sediment. The sediment was extracted (four times) using a solvent mixture composed of acetonitrile/water (70:30, v:v) with sonication for ~15 min. The combined extracts were concentrated and then analyzed directly by HPLC. Subsamples of these sediment extracts were subjected to further methylene chloride extraction (1:1, v/v, two times). The concentrated methylene chloride extracts were subsequently used for TLC confirmatory analysis. The air-dried, homogenized, previously extracted sediment was then combusted (in triplicate) to estimate the amount of unextractable bound residue. The amount of unextracted radioactivity was consistently below ≤6% of the total applied radioactivity, and characterization of this fraction was not attempted.

Radiometric Analysis. *LSC.* Radioactivity in aqueous solutions and sediment fractions was routinely counted in 10 mL of Hydrocount cocktail (J. T. Baker). KOH traps were counted using Hionic Fluor (Packard). All samples were counted for 5 min or until a statistical limit of 2% of 2σ was reached. Background values were generated for each individual cocktail and were automatically subtracted. Evolved $^{14}CO_2$ from samples subjected to combustion analyses was trapped in Carbon-14 Cocktail (Harvey Instruments) as discussed below.

Combustion of Extracted Sediment. Extracted sediment samples were air-dried and ground in an electric mill (Miracle Mill) to a homogeneous state prior to subsampling for combustion. Triplicate aliquots of each sample (~500 mg) were combusted in porcelain boats. Cellulose (~50 mg) was also added to each sample to enhance combustion efficiency. In each case, evolved $^{14}CO_2$ was trapped in ^{14}C cocktail (15 mL, R. J. Harvey Instrument Corp.) and radioassayed by LSC. Oxidizer efficiency was monitored by combustion of a measured quantity of [^{14}C]mannitol before and after each set.

High-Performance Liquid Chromatography (HPLC). Reversed phase HPLC was utilized for purity check of the test substance and as the primary means of quantitative analysis in this study. HPLC analysis of the samples was performed using a Hewlett-Packard 1050 LC system equipped with a diode array and a Ramona (Raytest, Wilmington, DE) radioisotope detector. A Zorbax SB-C8, 3.5 μm (4.6 × 150 mm) column was used. Analysis was done at 246 nm with a typical flow rate of 1.0 mL/min and 40 °C temperature. The mobile phases consisted of 25 mM ammonium acetate, pH 4 (A) and methanol (B). HPLC gradient method A was routinely utilized as follows: 0−3 min (isocratic at 90% A and 10% B); 3−15 min (linear to 65% A and 35% B); 15−20 min (linear to 60% A and 40% B); 20−24 min (linear to 55% A and 45% B); 24−26 min (isocratic at 55% A and 45% B); 26−35 min (linear to 50% A and 50% B); 35−37 (linear to 25% A and 75% B); 37−39 min (linear to 100% B); 39−41 min (isocratic at 100% B); 41−50 min (linear to 90% A and 10% B). Samples were injected using an autoinjector (typical injection volume = 50−100 μL), and 1-min fractions of each analysis were routinely collected and assayed for ^{14}C by LSC. In some cases, 15-s fractions were collected to enhance the resolution of radiocomponents. Initial determination of the degradation product's identity was made by cochromatography with synthetically prepared carfentrazone metabolite standards. Typical retention times (t_R) of nonradiolabeled standards (UV 246 nm) under method A chromatographic conditions were as follows: parent CF-E (**1**), 40.6 min; CF-ClPAc (**2**), 26.5 min; CF-CAc (**3**), 33.6 min; CF-PAc (**4**), 34.8 min; CF-BAc (**5**), 16.8 min; and 3-OH-CF-BAc (**6**), 9.9 min.

TLC. All extracts generated were also analyzed by normal phase TLC as a qualitative method to confirm the identity of the degradation products established by HPLC. Samples in appropriate solvents (5−20 μL) were applied using micropipets to precoated TLC plates (Merck Silica kieselgel 60 or 60-F254, 20 × 20 cm, 0.25 mm). Plates were developed using a solvent

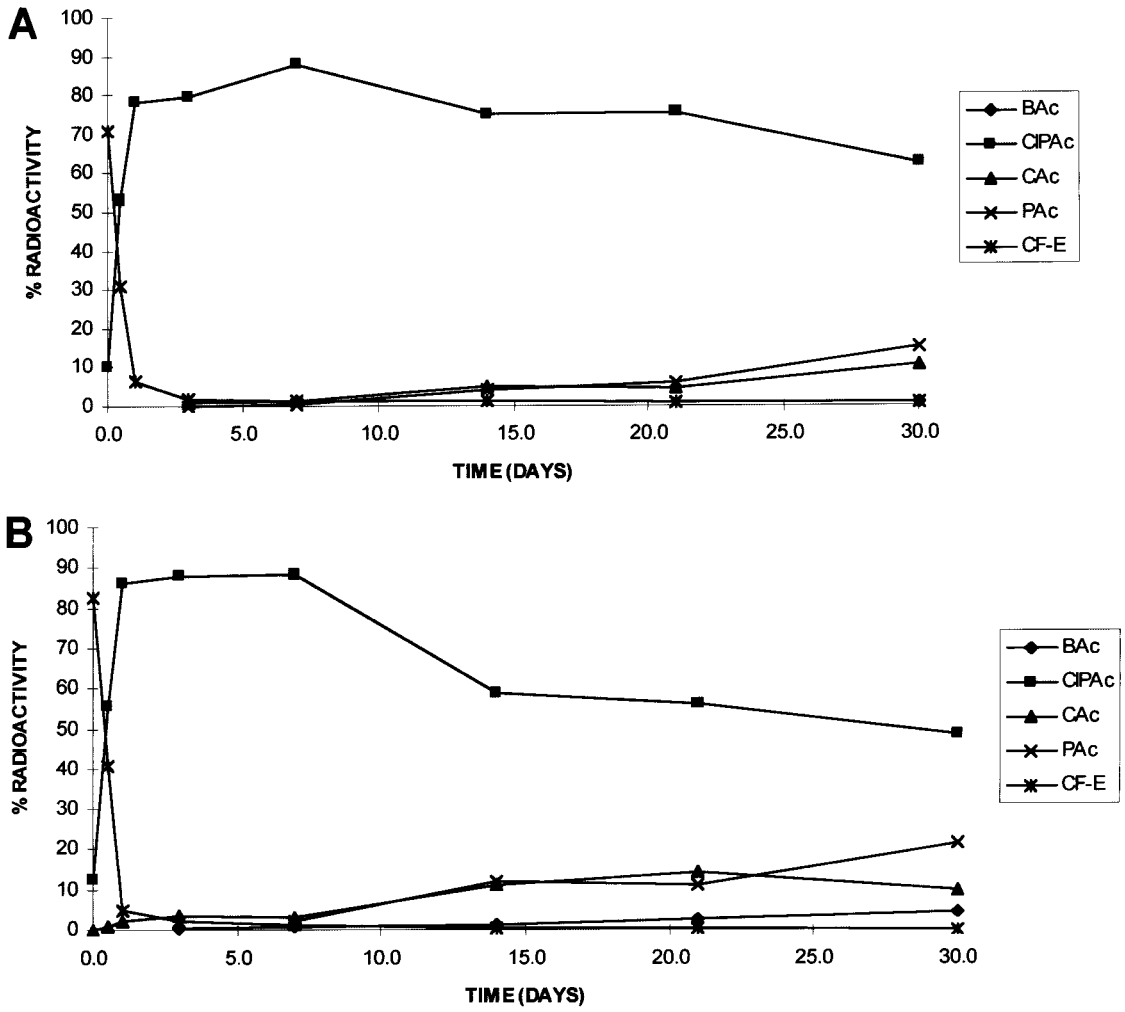

Figure 4. Degradation profile of carfentrazone-ethyl in total aquatic silty clay loam sediment: (A) [*phenyl*-^{14}C]CF-E; (B) [*triazole*-^{14}C]CF-E.

system of hexane/ethyl acetate/glacial acetic acid (30:90:1, v/v). The R_f values of radiolabeled metabolic products were compared with those of unlabeled standards, which were also included on each TLC plate. Visualization of standards was done under UV light (λ_{254} nm). Typical R_f values for unlabeled standards under the conditions described above were as follows: parent CF-E (**1**), 0.78; CF-ClPAc (**2**), 0.34; CF-CAc (**3**), 0.54; CF-PAc (**4**), 0.54; CF-BAc (**5**), 0.24; and 3-OH-CF-BAc (**6**), 0.15. Extracts were analyzed using an AMBIS Radioanalytical Imaging System to locate radioactive spots. The system consisted of an AMBIS TLC Imaging Scanner (model 4000) equipped with a complete data system.

Mass Spectral Analysis. Liquid chromatography−mass spectrometry (LC-MS) was performed using a Micromass Quattro II tandem mass spectrometer interfaced with a Hewlett-Packard LC system (HP 1100, variable wavelength UV detector) and equipped with a Raytest Ramona 2000 radioisotope detector. The mass spectrometer was operated in the electrospray (ES) ionization mode. Daughter (product ion) mass spectrometry analysis was performed at 12−18 eV collision energy. Subsamples of the degradation products (100 μL injections) were analyzed under chromatographic conditions that consisted of a Zorbax Eclipse XDB-C8 (4.6 × 150 mm, 3.5 μm) or a Zorbax Rx-C8 (4.6 × 250 mm, 5 μm) column with a flow rate of 1.0 mL/min and UV detection at 254 nm. The mobile phases consisted of 10 mM ammonium acetate, pH 4 (A) and methanol (B). For LC-MS analysis, HPLC gradient method B was utilized as follows: 0−3 min (isocratic at 90% A and 10% B); 3−15 min (linear to 65% A and 35% B); 15−20 min (linear to 60% A and 40% B); 20−24 min (linear to 55% A and 45% B); 24−26 min (isocratic at 55% A and 45% B); 26−35 min (linear to 50% A and 50%B); 35−37 (linear to 25% A and 75% B); 37−39 min (linear to 100% B); 39−41 min (isocratic at 100% B); 41−42 min (linear to 90% A and 10% B); 42−50 min (isocratic at 90% A and 10% B). All LC-MS analyses were performed at FMC Corp., Princeton, NJ.

RESULTS AND DISCUSSION

Degradation of CF-E under aerobic aquatic conditions was investigated in an effort to assess its overall environmental fate. The test matrices (sediment and water) used in this study were collected from two locations that represent typical use areas for the test compound. The ^{14}C-labeled test substance used was labeled at either of two sites (phenyl or triazole) to ensure the detection of any cleavage products formed. Analysis of the incubation extracts from either aquatic sediment indicated that CF-E was rapidly hydrolyzed to CF-ClPAc with a half-life value of <2 days. Separate analysis of the water and soil layers indicated that no significant differences in the distribution of radioactivity or mass balance values were observed between the two sediments or the two radiolabeled positions. A graphical representation of the mass balance and distribution of radioactivity of representative sediment (clay loam) is shown in Figure 2. The overall mass balance ranged from 87 to 100% of the applied radioactivity, >90% in most cases. Immediately following dosing (zero time), the majority of radioactivity was contained in the aqueous layer, averaging 86.8 and 87.8%, for silty clay

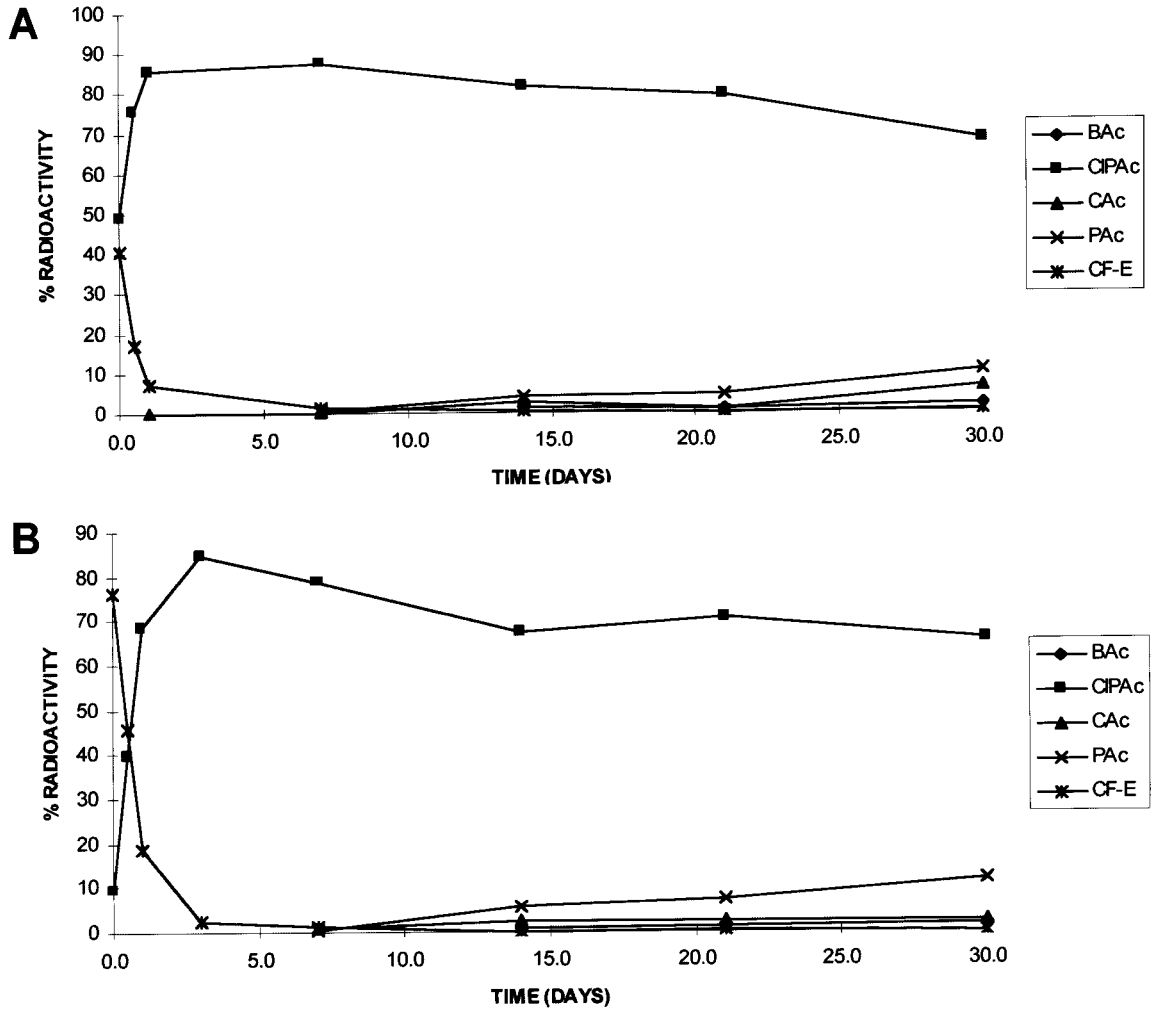

Figure 5. Degradation profile of carfentrazone-ethyl in total aquatic clay loam sediment: (A) [*phenyl*-^{14}C]CF-E; (B) [*triazole*-^{14}C]CF-E.

loam and clay loam sediments, respectively. A steady slow transfer of the radioactivity from the surface water into the sediment layer occurred over the course of the incubation. This was evidenced by the increased level of radioactivity in the sediment from an average (two sediments) of 5% at zero time to ~16% after 30 days. In addition, the average radioactivity remaining (post-extraction) in the sediment (bound residue) increased from <1% at zero time to ~4% after 30 days. The evolved ^{14}C-labeled volatile products (including $^{14}CO_2$) remained consistently low (<1%) throughout the incubation. The latter result indicates that little or no mineralization had occurred.

Quantitative analysis of the degradation products formed during this study was based primarily on the reversed phase HPLC analysis of both the surface water and the extract of the sediment layers. Initial identification of the degradation products was achieved by comparison with synthetic reference standards. A mixed solution of standards was routinely injected prior to HPLC analysis of the radiolabeled samples. A typical HPLC-UV chromatogram for the reference standards is shown in Figure 3. For any given sample, the degradation profile was typically similar for both the aqueous and sediment layers. A combined total percent of each degradation product formed, in all treatment groups over the duration of the study, is shown in Figures 4 and 5.

Surface Water Layer. Direct chromatographic analysis of the radiolabeled water layer samples was compared to that of the synthetic reference standards. The results indicated the presence of several degradation products of which CF-ClPAc (**2**) was the major product amounting to a combined average of 83% of the total radioactivity in the aqueous and sediment layers (clay loam sediment) after 7 days. The levels of this degradation product declined to an average of 67% after 30 days. Similar levels were observed for the silty clay loam sediment. Other metabolites formed included CF-CAc (**3**) and CF-PAc (**4**) in addition to a small percentage of CF-BAc (**5**), which was formed in the latter stages of the incubation. A representative 30-day water layer radiochromatogram is shown in Figure 6A. In addition, a summary of the formation of all degradation products in the surface water layer (as percent of applied radioactivity) for both sediments is presented in Table 1.

Sediment Layer. A degradation profile similar to that of the surface water was also observed for sediment samples except for the presence of trace amounts of 3-OH-CF-BAc (**6**), which were detected in later samplings (clay loam). Again, a rapid conversion of CF-E into the parent acid (**2**) was observed with increasing amounts of **3**, **4**, and **5** forming over time. Because of their close retention times, liquid scintillation quantitative analysis of **3** and **4** was facilitated by

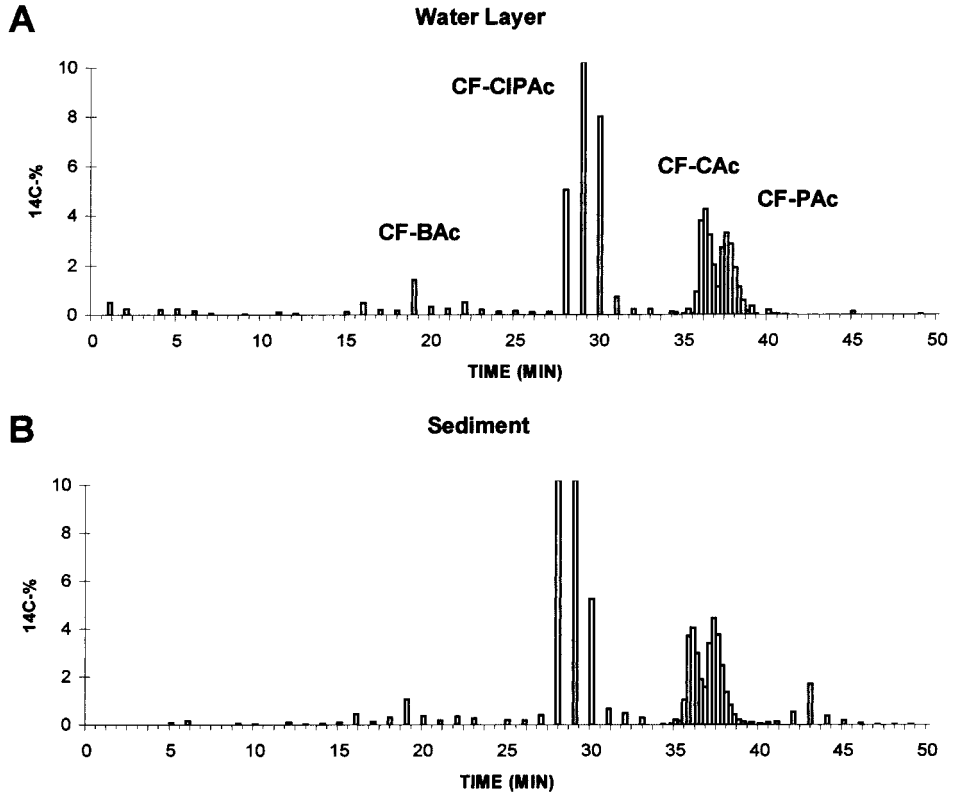

Figure 6. HPLC radiochromatograms of water (A) and sediment (B) layers of the silty clay loam treated with [*phenyl*-^{14}C]CF-E after 30 days of incubation.

collection of 15-s HPLC fractions. Representative 30-day sediment layer radiochromatograms are shown in Figure 6B.

Half-Life of [^{14}C]CF-E. On the basis of first-order kinetics for the degradation of [^{14}C]carfentrazone-ethyl, half-life ($t_{1/2}$) calculations were derived from

$$t_{1/2} = \ln 2/k = 0.693/k \quad (1)$$

where k is a first-order rate constant, determined as the slope value from test substance decline curves for each label and sediment. The decline curves were generated by plotting ln CF-E (as percent of total radioactivity) versus time (days). The CF-E half-life values, as determined from eq 1 and regression plots, were as follows: 1.40 days (phenyl label, silty clay loam); 1.36 days (triazole label, silty clay loam); 1.69 days (phenyl label, clay loam); and 1.25 days (triazole label, clay loam). Similar half-life determinations for [^{14}C]CF-E in the water layer only were also performed and amounted to 1.04, 1.22, 1.50, and 1.10 days for the above labels and sediments, respectively. When exponential regression analysis (maximized R^2 value) was applied for curve fitting, the half-life values were not significantly changed. The half-life results from this study, as well as the general degradation profile discussed below, are in good agreement with similar water/sediment studies involving application of CF-E to flooded rice fields recently reported by Ngim and Crosby (*13*).

Major Degradation Products and Their Identification. The overall metabolite profiles were qualitatively similar for both aquatic sediments used in this study. Furthermore, no significant differences were observed for the two labels (triazole and phenyl) utilized, indicating no apparent cleavage of the carfentrazone

Table 1. Summary of Percent CF-E and Degradation Products Formed in the Water Layer

time (days)	% CF-BAc	% CF-ClPAc	% CF-CAc	% CF-PAc	% CF-E
(A) [*phenyl*-^{14}C]CF-E Silty Clay Loam Sediment					
0	0.0	9.2	0.0	0.0	68.6
0.2	0.0	50.2	0.0	0.0	29.0
1.0	0.0	73.2	0.0	0.0	5.6
3.0	0.0	72.1	1.0	0.0	1.2
7.0	0.0	77.7	1.0	0.2	0.4
14.0	0.0	63.7	4.6	3.2	0.6
21.0	0.0	64.0	4.1	4.7	0.0
30.0	1.0	52.8	9.0	12.0	0.0
(B) [*triazole*-^{14}C]CF-E Silty Clay Loam Sediment					
0	0.0	8.4	0.0	0.0	81.2
0.2	0.0	51.7	1.0	0.0	38.8
1.0	0.0	79.4	2.1	0.0	3.8
3.0	0.5	78.9	2.9	0.0	1.3
7.0	0.7	79.6	2.5	2.3	0.9
14.0	0.9	40.9	8.8	7.3	0.0
21.0	2.4	45.1	11.3	8.5	0.0
30.0	3.6	40.2	8.8	15.7	0.0
(C) [*phenyl*-^{14}C]CF-E Clay Loam Sediment					
0	0.0	46.2	0.0	0.0	38.6
0.2	0.0	72.7	0.0	0.0	14.4
1.0	0.0	79.8	0.0	0.0	5.9
3.0	n/a	n/a	n/a	n/a	n/a
7.0	0.0	75.8	0.0	0.0	0.8
14.0	1.1	68.6	2.4	3.0	0.0
21.0	0.9	68.6	0.9	3.3	0.0
30.0	1.4	58.7	5.6	8.0	0.0
(D) [*triazole*-^{14}C]CF-E Clay Loam Sediment					
0	0.0	7.6	0.0	0.0	73.9
0.2	0.0	37.8	0.0	0.0	43.3
1.0	0.0	63.3	0.0	0.0	17.2
3.0	0.0	73.9	0.0	0.0	2.0
7.0	0.0	65.9	0.7	0.0	0.8
14.0	1.0	53.6	2.1	3.8	0.0
21.0	1.1	60.9	2.2	5.5	0.0
30.0	1.3	52.4	2.1	8.5	0.0

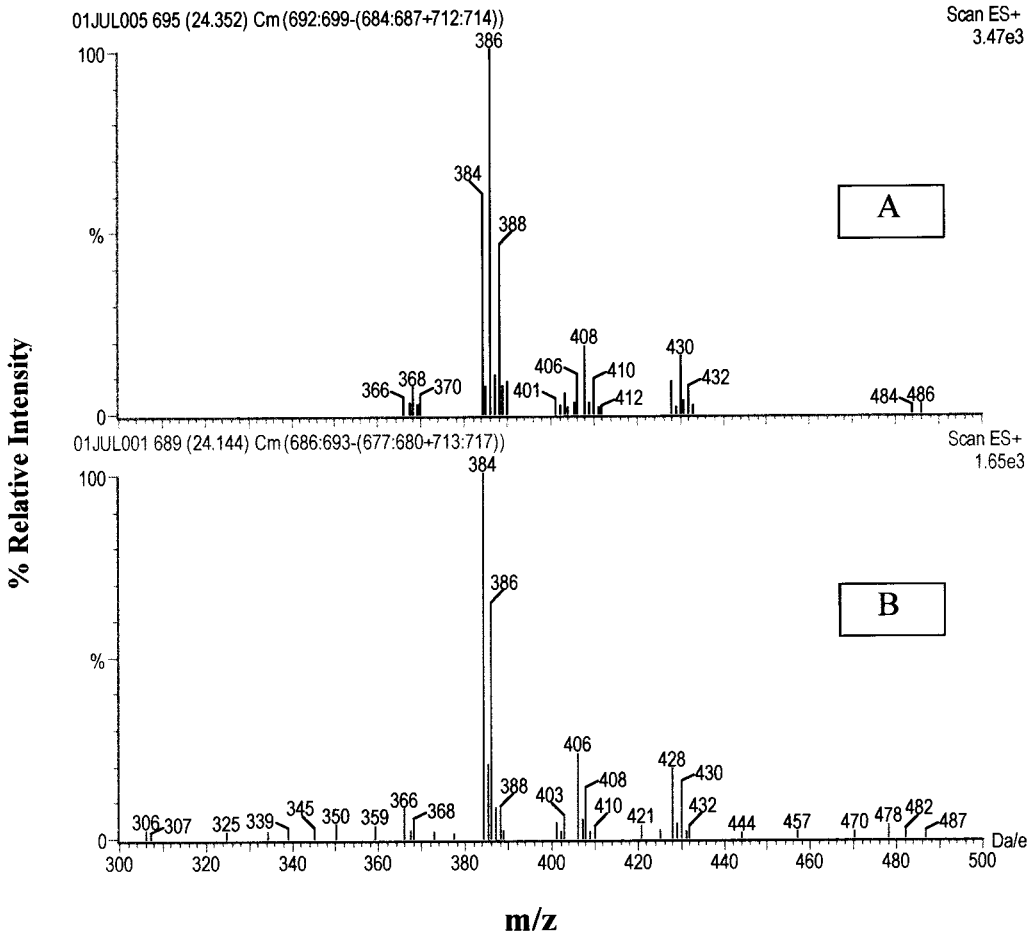

Figure 7. Full-scan LC-ESI mass spectra of [14C]CF-ClPAc degradation product (A) and reference standard (B).

molecule. The degradation products formed were initially identified through chromatographic comparison (radio-HPLC and -TLC) with available reference standards. Confirmation of the identity of the major degradation products was done using LC-MS analysis performed on a 30-day water layer extract (triazole label, silty clay loam sediment). Tandem (daughter ion) mass spectral analysis (MS/MS) was also performed on all of the products formed and further supports their identity. Individual degradation products are discussed below.

*CF-ClPAc (**2**).* This hydrolytic product is the major component formed in both aquatic sediments. Unambiguous confirmation of the identity of **2** was achieved by HPLC/electrospray ionization MS (LC/ESI-MS). The ES positive ionization spectrum of the radioactive peak corresponding to this degradation product (Figure 7A) gave the expected molecular ion peak at *m/z* 384 [M + 1] and +2 isotope at *m/z* 386 (due to the ^{37}Cl isotope). The higher intensity of the 386 fragment compared to 384 is due to the ^{14}C isotope enhancement. The MS/MS fragmentation (daughter ion spectrum) of **2** further supports the structure. The full-scan mass spectrum and the fragmentation pattern of standard CF-ClPAc were comparable to that of the product formed. A comparison of mass spectral scans of the ^{14}C-labeled degradation product and that of the standard is shown in Figure 7.

*CF-CAc (**3**).* The identity of **3** was also unambiguously established using LC-MS/MS techniques as described above. A molecular ion peak at *m/z* 348 (M + 1) was clearly present in the full-scan ES positive ionization spectrum of this degradation product. A prominent fragment at *m/z* 350, due to the characteristic ^{37}Cl contribution plus ^{14}C isotopic effect, further supports the identity of the product.

*CF-PAc (**4**).* A steady increase of the levels of this degradation product was observed throughout the incubation period, reaching 10−12% (clay loam) and 15−22% (silty clay loam) of the total radioactivity applied after 30 days. Similar to the other degradation products, the identity of this product was confirmed by the presence of a matching molecular ion peak at *m/z* 350 (M + 1) and a +2 isotopic fragment at *m/z* 352.

*CF-BAc (**5**).* The average combined levels (surface water plus sediment) of this degradation product in incubations corresponding to the various treatment groups were consistently <5% of the total radioactivity, the lowest of all significant products formed. Support for the identity of this product was also provided from LC-MS positive ionization analysis. A molecular ion peak at *m/z* 322 (M + 1) was evident in the mass spectrum obtained for this product. A similar matching mass spectrum was also obtained for the CF-BAc reference standard.

*3-OH-CF-BAc (**6**).* Only traces (<1%) of this metabolite were detected in selected clay loam extracts. Identification was based solely on similarity of the HPLC retention times of a reference standard and the product.

Proposed Degradation Pathway for CF-E in Aqueous Sediment. As illustrated in Figure 8, the primary degradative pathway of CF-E in aqueous sedi-

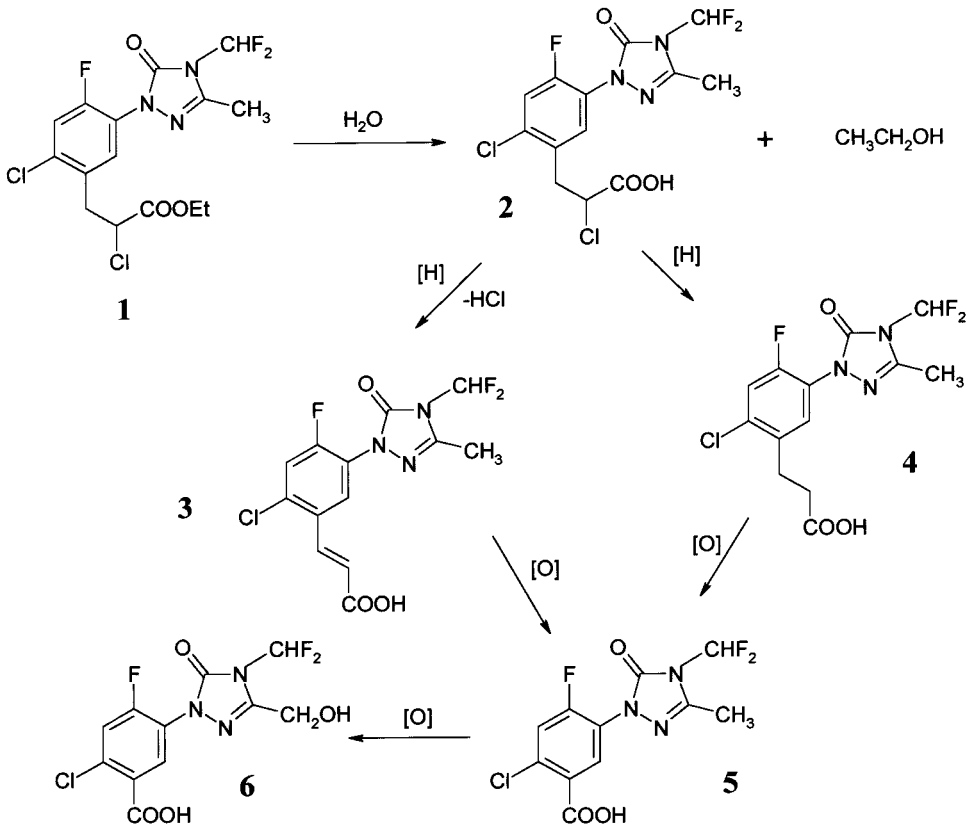

Figure 8. Proposed degradation pathway of carfentrazone-ethyl in aquatic sediment.

ments under aerobic conditions involves initial hydrolysis of the ester moiety resulting in the formation of the parent acid, CF-ClPAc **(2)**. Further metabolism of the free acid occurs either via dehydrochlorination to give CF-CAc **(3)** or through reductive dechlorination to form CF-PAc (**4**). Similar dehydrochlorination conversions caused by the reducing environment in saturated soils have been reported previously (*14*). Oxidation of the aromatic side chain of either **3** or **4** (β-oxidation) could account for the formation of CF-BAc (**5**). A monooxygenase-mediated oxidation of the exocyclic, allylic methyl group of the latter leads to the formation of 3-OH-CF-BAc (**6**). Only trace amounts (<1%) of the hydroxylated acid were detected throughout the incubations.

In conclusion, this study clearly indicates that CF-E is rapidly converted, under aerobic aquatic conditions, to a cascade of acidic degradation products. Half-life values at ~25 °C averaged 1.3−1.7 days in either silty clay loam or clay loam aquatic sediments. Half-lives of [^{14}C]CF-E measured in the water layer only were similar (1.0−1.5 days). The major products formed included CF-ClPAc, which was formed in high levels and then declined over time, resulting in the formation of increasing amounts of CF-CAc, CF-PAc, and CF-BAc. No significant differences in the degradation profiles were observed between the two labels (phenyl and triazole) or the two aquatic sediments used. Bound and volatile ^{14}C residues were formed in negligible amounts, indicating little or no incorporation into sediment components or mineralization.

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LITERATURE CITED

(1) Carfentrazone-ethyl, Pesticide Tolerance. *Fed. Regist.* **2000**, *65* (154), 48620.

(2) Carfentrazone-ethyl herbicide. In *The Pesticide Manual*, 11th ed.; Tomlin, C. D. S., Ed.; British Crop Protection Councl: Bear Farm, U.K., 1997; p 191.

(3) Van Saun, W. A.; Bahr, J. T.; Bourdouxhe, L. J.; Gargantiel, F. J.; Hotzman, F. W.; Shires, S. W.; Sladen, N. A.; Tutt, S. F.; Wilson, K. R. F8426—a new, rapidly acting, low rate herbicide for the post-emergence selective control of broad-leaved weeds in cereals. *Brighton Crop Prot. Conf.* **1993**, *1*, 19−28.

(4) Dayan, F. E.; Duke, S. O.; Weete, J. D.; Hancock, H. G. Selectivity and mode of action of carfentrazone-ethyl, a novel phenyl triazolinone herbicide. *Pestic. Sci.* **1997**, *51*, 65.

(5) Genot, B.; Hullebroeck, M. L. Carfentrazone-ethyl + mecoprop-p (platform S): a new herbicide for the control of cleavers and other broad-leaved weeds in wheat and barley. *Meded.-Fac. Landbouwkd. Toegepastte Biol. Wet. (Univ. Gent)* **1998**, *63* (3a), 751.

(6) Shires, S. W.; Bourdouxhe, L. A.; Crossman, A. R.; Genot, B.; Laffranque, J. P.; LeBlanc, J. Carfentrazone-ethyl: a new herbicide for the rapid control of key cereal broad-leaf weeds. *Brighton Crop Prot. Conf.* **1997**, *1*, 117−122.

(7) *Carfentrazone-ethyl. Product Profile*; FMC Agricultural Products Group: Philadelphia, PA, 2000.

(8) ElNaggar, S. F.; Creekmore, R. W.; Fang, X.; Patel, B. C.; McLaughlin, T. Metabolism of carfentrazone-ethyl in wheat and soybean. *Abstracts*, 220th National Meeting of the American Chemical Society, Washington, DC; ACS: Washington, DC, 2000; AGRO-115.

(9) Thompson, W. M.; Nissen, S. J. Absorption and fate of carfentrazone-ethyl in *Zea mays*, *Glycine max*, and *Abutilon theophrasti*. *Weed Sci.* **2000**, *48*, 15.

(10) Elmarakby, S. A.; Cook, R. F.; ElNaggar, S. F.; Fang, X.; Froelich, L. W.; Ramsey, R.; Weintraub, R. A.; Willut, J. M. Metabolism and environmental fate of carfentrazone-ethyl, a new reduced risk herbicide. *Abstracts*, 219th National Meeting of the American Chemical Society, San Francisco, CA; ACS: Washington, DC, 2000; AGRO-099.

(11) Theodoridis, G.; Bahr, J. T.; Davidson, B. L.; Hart, S. E.; Hotzman, F. W.; Poss, K. M.; Tutt, S. F. Alkyl 3-[2,4-disubstituted-4,5-dihydro-3-methyl-5-oxo-1*H*-1,2,4-triazol-1-yl)phenyl] propenoate derivatives—Synthesis and structure activity relationship. In *Synthesis and Chemistry of Agrochemicals IV*; Baker, D. R., Fenyes, J. G., Basarab, G. S., Eds.; ACS: Washington, DC, 1995; p 90.

(12) Seeley, H. W.; VanDemark, P. J. The determination of microbial numbers. In *Microbes in Action*, 3rd ed.; W. H. Freeman: New York, 1981; p 49.

(13) Ngim, K. K.; Crosby, D. G. Fate and kinetics of carfentrazone-ethyl herbicide in California, USA, flooded rice fields. *Environ. Toxicol. Chem*. **2001**, *20*, 485.

(14) Haag, W.; Mill, T. Effect of surface sediments on hydrolysis of haloalkanes and epoxides. *Enivron. Sci. Technol.* **1988**, *22*, 658.

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