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Formation and Transport of the Sulfonic Acid Metabolites of Alachlor and Metolachlor in Soil

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Alachlor and metolachlor are dechlorinated and transformed into their corresponding ethane sulfonic acid (ESA) metabolites in soil. In a field-disappearance study, it was shown that alachlor ESA was formed at a faster rate and at concentrations 2−4 times higher than metolachlor ESA, conforming with the observed longer disappearance half-life of metolachlor (15.5 d) in the field as compared to alachlor (8 d). Runoff data also showed higher concentrations of alachlor ESA as compared to metolachlor ESA, even though they were applied at the same levels. Data from soil cores showed transport of the ESA compounds in soil to as far down as 75−90 cm below the surface, at concentrations ranging from less than 0.5 μg/L to about 50 μg/L. In contrast, no parent herbicide was detected at these depths. This observation correlates with the higher log K_{oc} values for alachlor (3.33) and metolachlor (3.01) relative to their corresponding ESA metabolites, alachlor ESA (2.26), and metolachlor ESA (2.29).

Introduction

The chloroacetanilide herbicides are among the most frequently used herbicides in the United States both for agricultural and noncrop applications (*1*). Included in this class of herbicides are acetochlor, alachlor, metolachlor, and propachlor; all are selective herbicides used to control specific annual grasses and broadleaf weeds. These herbicides and their metabolites may leach to groundwater where their degradation potential may be decreased substantially.

Alachlor [2-chloro-*N*-(2,6-diethylphenyl)-*N*-(methoxymethyl)acetamide] degrades to a more polar compound, alachlor ESA [2-(2,6-diethylphenyl)methoxymethylamino-2-oxo-ethanesulfonic acid], which has been found more frequently and at higher concentrations than the parent herbicide in groundwater from wells in the Midwestern United States (*2, 3*). Although recent toxicological studies on alachlor ESA indicate that this metabolite is not mutagenic and does not bioaccumulate at the levels commonly found in surface and groundwater (*4*), it is important to investigate the fate of alachlor ESA in the environment because it is relatively persistent and mobile (*5*).

The formation of the metolachlor ESA (2-[(2-ethyl-6-methylphenyl)(2-methoxy-1-methylethyl)amino]-2-oxo-ethanesulfonic acid) metabolite in soil has been recently reported in samples collected from a field plot where metolachlor [2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(methoxy-1-methylethyl)acetamide] was applied (*6*) and from groundwater samples in many agricultural areas (*7*). Alachlor and metolachlor are detoxified rapidly in nonsensitive plants via conjugation with glutathione and/or homoglutathione (*8, 9*). The glutathione conjugates degrade to the sulfonic acid derivatives, which have been reported as major soil metabolites of acetochlor (*10*), alachlor (*11*), and propachlor (*12*).

The environmental significance of herbicide metabolites is not well-known because of the difficulty in the analysis of polar ionic compounds, such as the sulfonic acids. In many pesticide metabolism studies, there has been some fraction of water-soluble metabolic products that are unaccounted for due to the difficulty of their extraction and analysis, thus limiting the available information on pesticide conversion products in many matrixes.

To understand thoroughly the behavior of pesticides in the environment, it is important to investigate the fate and transport of their degradation products under actual agricultural conditions. The specific objectives of this study were to (i) determine the relative rates of disappearance of alachlor and metolachlor in experimental field plots and (ii) determine the persistence and mobility of alachlor, metolachlor, and their sulfonic acid metabolites in soil.

Experimental Methods

Field-Disappearance Study. A field-disappearance study was conducted in 1993 and 1994 at the Kansas State University, Kansas River Valley Experimental Field, located on the Kansas River alluvial flood plain, near Topeka, KS. In 1993, two adjacent plots were used; plot 1 was 4.6 m × 30.5 m, whereas plot 2 was 4.6 m × 18.3 m. In 1994, two new plots (east of the 1993 field plots) were used; both plots were 3.1 m × 30.5 m. The field plots used in this study had less than 1% slope, and the water table was at a depth of approximately 5.5 m. The soil consisted of a Eudora silt-loam with a particle-size distribution of 44−62% silt, 26−50% sand, and 5−21% clay (*13*). The pH of the soil was in the range of 6.8−7.8. Soil samples were submitted to Huffman Laboratories (Golden, CO) for analysis of the organic carbon content. The organic carbon contents of the soil were 0.45, 0.22, and 0.19%, at 15, 45, and 76 cm, respectively.

Suction lysimeters (Soil-Moisture Equipment Corp., Santa Barbara, CA) 5 cm in diameter were installed in duplicate near the center of each plot at depths of 0.3, 0.6, 0.9, 1.2, and 1.5 m, following the procedure described by the manufacturer. Samples were collected whenever there was rain or at a 2-week interval during dry periods for about 3 months after application.

Each plot was equipped with a surface water runoff collection system. A 19-L plastic bucket was installed at the down-slope end of each plot so that the rim was even with the top of the soil. A float-activated bilge pump attached to a battery/solar panel system was placed about 0.6 cm from the bottom of each bucket. During surface water runoff, water was continuously pumped from the buckets into 1875-L galvanized metal troughs. The water level of the trough from each field plot was recorded.

Herbicide was applied in late May of each year using a boom sprayer at an application rate of 2.8 kg/ha. In the 1993 study, alachlor (Monsanto, St. Louis, MO) and metolachlor (Ciba Geigy, Greensboro, NC) were applied together in duplicate plots (plots 1 and 2). In the 1994 study, the two herbicides were applied to plot 1, whereas only metolachlor was applied to plot 2. The herbicides were incorporated by

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disking to a depth of 10 cm. After the herbicides were incorporated, corn (*Zea mays* L.) was planted in each plot.

Soil cores of 30.5−152.4 cm in depth from the surface were obtained using a 5 cm diameter, split-tube sampler (CME Co., St. Louis, MO) before and after herbicide application. These soil cores were collected near the lysimeters. Sampling of soil cores was continued at approximately 2-week intervals. Two soil cores were obtained per plot and were mixed as composites after they were divided into 15-cm intervals. The soil composites were placed in polypropylene bags and frozen at −10 °C until they were thawed for herbicide analysis.

Extraction Procedure for Soil. Approximately 15−20 g of soil was extracted in duplicate with 20 mL of a 75/25 (v/v) methanol/water mixture in a Teflon-lined, screw-capped test tube. This mixture was shaken to a slurry using a Vortex mixer (Daigger and Co. Inc., Wheeling, IL) and heated at 75 °C for 30 min. Then the soil mixture was allowed to equilibrate and cool to room temperature in a mechanical shaker for at least 1 h. Each sample then was centrifuged, and the clear supernatant was poured directly into a 40-mL vial. The extraction procedure was repeated on the same soil sample, and the second supernatant was combined with the first. The combined extracts were evaporated at 50 °C using a Turbovap (Zymark, Palo Alto, CA) until only 10 mL of water remained. The concentrate was transferred to a test tube for automated solid-phase extraction (SPE) using a C_{18} Sep-Pak cartridge (Waters, Milford, MA). The C_{18} cartridges were preconditioned sequentially with methanol (1 mL), ethyl acetate (1 mL), methanol (1 mL), and water (3 mL). Then the soil extracts were passed through the cartridge and eluted first with ethyl acetate (2.5 mL) followed by methanol (2.5 mL). This sequential elution separated the parent herbicides (eluted in ethyl acetate) from their more polar ESA metabolites (eluted in methanol) as described previously (*14*). An aliquot (about 5 g) of each soil sample was weighed and dried to correct for the percent moisture content of the soil. Blank soil samples spiked with 5 μg/kg alachlor or metolachlor were extracted to determine whether ESA or OXA (oxanilic acid derivative) can be formed during the extraction procedure at elevated temperature. Neither ESA nor OXA were detected in the spiked blank samples. The recovery of this extraction procedure ranged from 80 to 90% of the spiked concentrations.

ELISA Procedure for Alachlor and Metolachlor. The ethyl acetate fractions from the SPE of the soil samples were analyzed for alachlor and metolachlor using enzyme-linked immunosorbent assay (ELISA) obtained from Idetek/Quantix Systems (Sunnyvale, CA). First, the ethyl acetate was evaporated to dryness and then reconstituted with 5 mL of water. The ELISA procedure described in the kit insert was followed. Optical densities were read at 650 nm on a Vmax microplate reader with Softmax software (Molecular Devices, Menlo Park, CA). Concentrations of the analytes were calculated using four-parameter-fit data reduction. Samples with herbicide concentrations exceeding the linear working range were diluted and reanalyzed.

Analysis of alachlor ESA from the methanol fractions was performed by the SPE-ELISA method described by Aga et al. (*14*) using RaPID Alachlor ELISA (Ohmicron Corp, Newtown, PA).

High-Performance Liquid Chromatography (HPLC) Analysis. The HPLC analysis of the methanol extracts for the confirmation of ESA was performed in an HP model 1090 series II liquid chromatograph with a photodiode-array (PDA) detector (Hewlett-Packard, Palo Alto, CA). An HPLC method was developed and optimized for the separation of alachlor ESA and metolachlor ESA in the methanol fraction of the SPE eluant. The HPLC was equipped with a 4.6 mm × 250 mm reversed-phase column packed with 3-μm particle size, 120 A pore size, C_{18} Hypersil ODS (Keystone Scientific, Bellefonte, PA). The mobile phase was 5/35/60 acetonitrile/methanol/phosphate buffer (pH 7.0, 25 mM) at a flow rate of 1.2 mL/min. The ESA metabolites have rotational isomers at room temperature that make separation difficult because of the presence of two unresolved peaks. In this HPLC method, it was critical to maintain the oven temperature at 60 °C to obtain baseline separation of the ESA compounds. Since it was not relevant in this study to determine individual isomeric forms of each metabolites, the combined concentrations of the isomers were measured by raising the HPLC column temperature to 60 °C. The sample injection volume was 80 μL. ESA was monitored at a wavelength of 200 nm with a 4-nm bandwidth. The reference wavelength was set at 450 nm with a 80-nm bandwidth. The detection limit of this method is 0.5 μg/L using a 100-mL water sample for SPE. To confirm the identity of the ESA compounds, the ultraviolet spectra were scanned from 190 to 400 nm, and the spectra were matched to standard spectra in a customized automated library search. The concentration of alachlor ESA was further confirmed by SPE-ELISA (*14*). Immunoassay for metolachor ESA is not available; therefore, it was only analyzed by HPLC.

Gas Chromatography/Mass Spectrometry (GC/MS) Analysis. For the determination of herbicide concentrations in water samples by GC/MS, 100 mL of water was used for SPE as described previously (*15*). For soil analysis by GC/MS, the soil-extraction procedure just described was followed except that 250 ng of a surrogate compound (deuterated atrazine-d_5) was added to the soil prior to extraction. In addition, the ethyl acetate fraction of the soil extract was passed through an ion-exchange SPE resin to reduce the amount of natural organic acids in the extract, which cause rapid degradation of the GC/MS column. The ethyl acetate fractions from the SPE elution, which contained the parent herbicides, were evaporated to about 50−75 μL for analysis by GC/MS under selected-ion monitoring (SIM) mode.

Synthesis and Characterization of Alachlor and Metolachlor ESA. Alachlor ESA and metolachlor ESA were synthesized using the procedure described by Feng (*10*). Either alachlor or metolachlor was refluxed with excess (10 times more than the starting moles of the herbicide) sodium sulfite in 100 mL of 10% ethanol/water (10/90, v/v) for 3−6 h or until the mixture became homogeneous. Following acidification with sulfuric acid, the product was extracted into methylene chloride. The methylene chloride was evaporated, and the reaction products were dissolved in hot ethanol. The hot ethanol mixture was filtered and allowed to stand undisturbed for recrystallization of the ESA. The white crystals that formed were collected and washed several times with cold ethanol. The chemical structures of the white crystals were confirmed as alachlor ESA or metolachlor ESA by negative-ion, fast-atom bombardment (FAB) mass spectrometry (*6*) and by nuclear magnetic resonance spectroscopy (*16*).

Results and Discussion

Disappearance of Herbicides and Their Metabolites in Surface Runoff. The disappearance half-lives of the applied herbicides were determined from their concentrations in the surface water runoff. The chloroacetanilide herbicides were observed to decay exponentially, and the disappearance may be interpreted using first-order kinetics. The equation for a first-order reaction is

$$C = C_o e^{-kt} \quad (1)$$

where C is the concentration after time t, C_o is the initial concentration, and k is the rate constant (*17*). Thus, a plot of the logarithm of concentration against time gives a straight line with a slope proportional to the rate constant. The value

TABLE 1. Concentrations (μg/L) of Alachlor, Alachlor ESA, and Metolachlor in Surface Water Runoff during the 1993 Field-Disappearance Study

event date	days after application	alachlor	alachlor ESA	metolachlor
		Plot 1, 1993		
6/8/93	11	35.14	24.20	38.74
6/18/93	21	8.88	6.30	11.95
6/19/93	22	7.90	7.15	10.62
7/1/93	34	2.37	48.84	4.68
7/2/93	35	1.74	5.95	3.93
7/5/93	39	2.58	5.95	4.31
7/9/93	43	0.73	5.95	2.17
7/11/93	45	0.94	3.73	2.23
		Plot 2, 1993		
6/8/93	11	43.63	18.10	46.93
6/18/93	21	12.71	6.30	12.43
6/19/93	22	7.90	5.65	10.62
7/1/93	34	4.54	48.25	5.83
7/2/93	35	6.15	59.66	8.69
7/5/93	39	0.97	2.28	2.29
7/9/93	43	2.05	4.25	4.22

TABLE 2. Concentrations (μg/L) of Alachlor, Metolachlor and Their ESA Metabolites in Surface-Water Runoff during the 1994 Field-Disappearance Study[a]

event date	days after application	alachlor	alachlor ESA	metolachlor	metolachlor ESA
			Plot 1, 1994		
5/28/94	3	39.11	nd	18.04	nd
6/8/94	14	9.94	0.42	8.33	0.05
6/15/94	21	2.07	nd	7.69	nd
6/23/94	29	3.89	2.51	4.5	0.56
6/30/94	36	2.70	2.47	7.45	0.22
7/22/94	58	0.09	1.44	3.24	0.05
7/29/94	65	0.12	2.70	0.69	0.38
8/19/94	86	nd	1.59	nd	0.34
			Plot 2, 1994		
5/28/94	3	na	na	20.89	0.26
6/8/94	14	na	na	12.08	0.52
6/15/94	21	na	na	6.34	0.26
6/22/94	28	na	na	11.95	0.94
6/23/94	29	na	na	6.63	0.60
6/30/94	36	na	na	1.58	0.52
7/22/94	58	na	na	0.26	0.38
8/1/94	68	na	na	1.00	1.26
8/19/94	86	na	na	0.29	0.22

[a] nd, not detected; na, not applicable.

of the slope is taken as k and is used to calculate the half-life, $t_{1/2}$, which is the time needed for 50% disappearance. Therefore, eq 1 becomes

$$t_{1/2} = \frac{0.6932}{k} \quad (2)$$

In the field-disappearance study conducted in 1993, the average half-lives were 6.5 d for alachlor and 9 d for metolachlor (Table 1). Results of the 1994 study (Table 2) showed slightly longer half-lives for alachlor (8 d) and metolachlor (15.5 d). The differences in the observed half-lives between 1993 and 1994 may be attributed to the difference in the moisture conditions in the field during the two periods of study. The year 1993 was extremely wet, with an average total monthly precipitation of 6.86 cm between the months of June and September as compared to 4.22 cm in 1994. The cumulative rain during the period of study are shown in Figure 1.

Soil temperature and moisture content affect herbicide biodegradation by controlling microbial activity (*18*). The rate of herbicide degradation generally increases with increasing soil temperature within the range of mesophilic microbial activity (*19*). Water is required for microbial activity and affects the oxygen level in soil. Because the average monthly temperature was comparable during 1993 and 1994, ranging from 22 to 26 °C, the moisture content of the soil probably played a more important role in causing the differences in herbicide half-lives calculated for the two years. This hypothesis is consistent with previous reports showing a faster degradation of alachlor in soil with higher moisture content (*19, 20*).

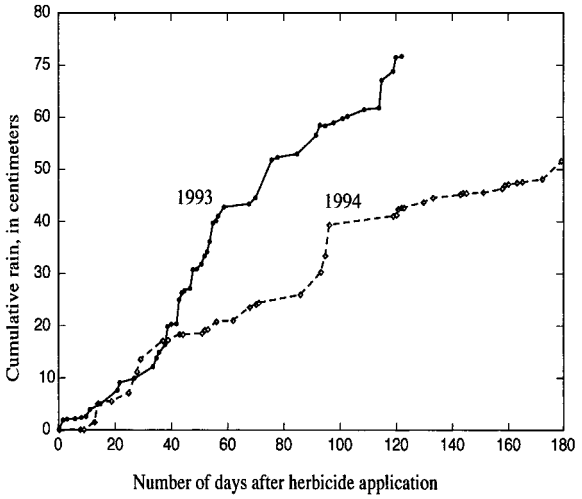

FIGURE 1. Cumulative rainfall in 1993 (herbicide application date, May 27) and 1994 (herbicide application date, May 25) at the Kansas River Valley Experimental Field during the field-disappearance study.

The runoff data for the ESA metabolites indicate that alachlor ESA (Tables 1 and 2) is present in the runoff water at relatively higher concentrations than metolachlor ESA (Table 2) even though the application rates for the parent herbicides were the same. This difference may be due to the relatively longer half-life of metolachlor as compared to alachlor; thus, the formation of metolachlor ESA could be slower. Also, it is possible that the degradation of metolachlor to several other polar metabolites is more significant than the metolachlor ESA formation (*21*).

In the 1993 study, only alachlor ESA was determined because the metolachlor ESA standard was not available at that time. The concentration of alachlor ESA reached a maximum of about 60 μg/L in runoff water from plot 2 at approximately 4 weeks after application (Table 1). During this time, the concentration of the parent herbicide was about 6 μg/L in the runoff water from plot 2. In the 1994 study, the concentrations of alachlor ESA in the runoff were significantly lower; the peak concentration was only 2.7 μg/L at about 9 weeks after application (Table 2). Again, this can be attributed to the more frequent rainfall that occurred during 1993. In contrast, the rain was less frequent and less in volume during the 1994 study. At lower intensity and frequency of precipitation, soluble metabolites are more likely to be moved into the subsurface soil by the infiltrating water before runoff begins. Analysis of post-harvest runoff samples collected at least 120 d after application showed no detectable concentrations of either parent herbicides (alachlor and metolachlor) or ESA metabolites in both years of field study.

Transport and Transformation of Chloroacetanilides in Soil. *Lysimeter Samples.* In the 1993 study, alachlor was detected in the 0.3-m lysimeter from day 1 (at 8.23 μg/L) to day 21 (at 0.07 μg/L) (Figure 2). However, no alachlor was observed after day 26 in the lysimeters deeper than 0.6 m. Unlike the parent herbicide, alachlor ESA was transported at least as deep as 1.5 m below ground surface, where the

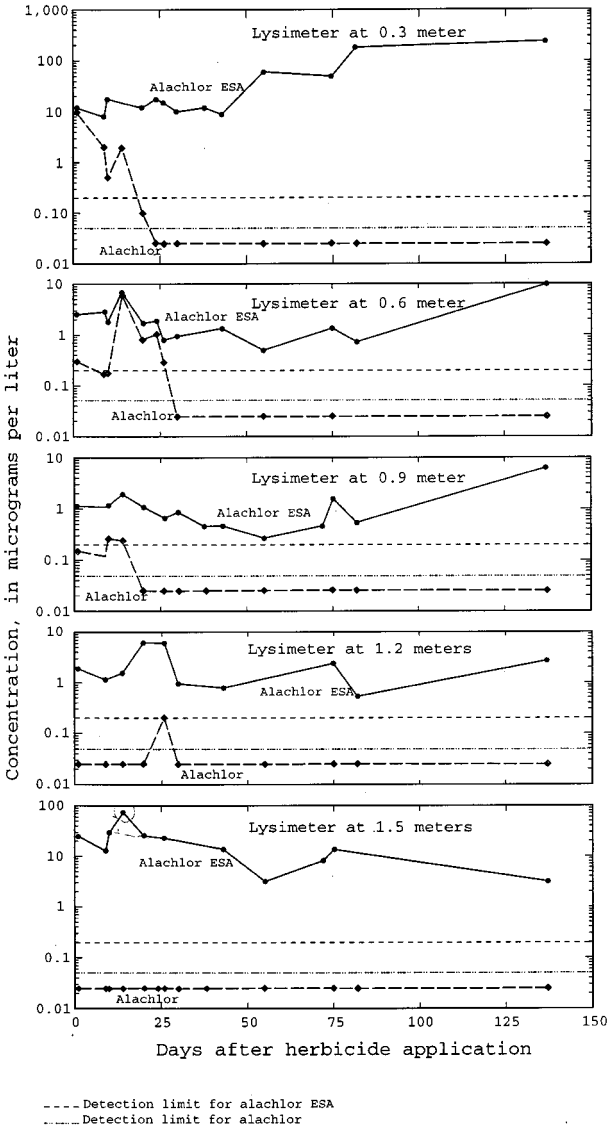

FIGURE 2. Concentration of alachlor and its metabolite, alachlor ESA, in the unsaturated zone; collected with lysimeters at 0.3-, 0.6-, 0.9-, 1.2-, and 1.5-m depths in 1993.

concentrations ranging from 3 to 73 μg/L. Alachlor ESA was observed at considerably higher concentrations than alachlor in the soil porewater collected from the lysimeters at various depths. A peak in the concentration of alachlor ESA was observed between 14 and 20 d after application in the 0.6-, 0.9-, 1.2-, and 1.5-m lysimeters. This period coincides with several rains of at least 1.25 cm/d.

It is interesting to note that the concentration of alachlor ESA increased substantially in the samples collected from the shallow lysimeters (0.3−0.9 m) between day 82 and day 136. Between these two sampling dates, corn was harvested from the field plots. It is possible that corn plants took up the ESA metabolite and then released it back to the soil after harvest, resulting in a considerable increase in ESA concentration in the soil. A previous study (*12*) reported that propachlor ESA metabolite produced in soil is taken up by soybean plants and that this metabolite is not present in plants grown and treated under hydroponic culture. This suggests that the final step in the formation of ESA derivatives occurs in soil and not in plants. On the other hand, this observed increase in alachlor ESA concentration may have been caused by the change in hydrology or soil disturbance that occurred after harvest. Metolachlor was measured in the 0.3-, 0.6-, and 0.9-m lysimeters up to day 30 at concentrations ranging from less than 0.05 to 4.84 μg/L, suggesting greater transport of metolachlor as compared to alachlor. Again, metolachlor ESA was not included in the analysis of the 1993 samples due to unavailability of the standard.

The unusually high concentration of alachlor ESA in the 1.5-m lysimeter on day 20 can be attributed from previous application of alachlor at least 2 yr prior to this study. A large storm occurred few days prior to sampling and resulted in a flush of stored alachlor ESA metabolites that were readily transported down to the deepest lysimeter by infiltrating stormwater. It is possible that the stored alachlor ESA in soil were quickly flushed downward due to its very high water solubility, such that the observed concentration in the 1.5-m lysimeter was much higher than those found in the shallow lysimeters.

Due to the relatively dry season in the 1994 study, limited water volumes were obtained from the lysimeters. Most of the samples obtained were from the 0.3-m-deep lysimeters, and the sample volumes were not enough for GC/MS and HPLC analysis. Therefore, no data from the 1994 lysimeters are presented here.

Soil Samples. Analysis of herbicides in soil cores complements the information provided by lysimeter samples. Whereas the data from lysimeter samples can be used to infer the rate of transport of compounds in solution, soil cores can account for the extractable herbicides adsorbed in soil particles in addition to those dissolved in the soil porewater. Therefore, for the study of alachlor and metolachlor transport, soil cores from several depths of the experimental plots also were analyzed. Unfortunately, the soil core samples collected during the 1993 study were not analyzed right away due to the lack of a reliable analytical method for soil during the earlier stage of the study. Significant microbial degradation during storage was suspected, and thus, analysis of these samples was not pursued further.

Results from the soil core samples collected from the 1994 field study suggest that alachlor ESA is formed at a faster rate in surface soil than metolachlor ESA. For example, on day 2, the concentration of alachlor ESA in the top 15 cm of soil from plot 1 was 43.5 μg/kg (Figure 3A), whereas metolachlor ESA was only 11.91 μg/kg (Figure 3B), despite the same application rate used for the parent herbicides. It can be calculated that on day 2 alachlor ESA was 3% of the parent compound and then increased to 10% and 20% on days 8 and 9, respectively. Metolachlor ESA started at 0.4% of the parent compound on day 2 and increased to 3 and 5% of the parent compounds on days 8 and 14, respectively. Apparently, metolachlor ESA forms more slowly than alachlor ESA, which is consistent with a previous study (*22*) of enzymatic and nonenzymatic glutathione conjugation of 2-chloroacetanilide herbicides. In the said study, the enzymatic activation of the conjugation reaction by the glutathione transferase was more significant for alachlor than for metolachlor.

Alachlor ESA and metolachlor ESA concentrations both increased progressively until they reached a peak concentration 9−10 weeks after application. The highest concentration of alachlor ESA detected in surface soil (0−15 cm) was 210 μg/kg, which is about 60% of the concentration of alachlor present in the same soil sample. At 9−10 weeks, the concentration of alachlor was less than 15% of the initial concentration applied. On the other hand, the highest concentration observed for metolachlor ESA in surface soil was 93 and 128 μg/kg in plots 1 and 2, respectively. This corresponds to about 26 and 34% of the metolachlor present in the same soil sample. Like alachlor, the concentration of metolachlor during this period was less than 15% of the initial concentration applied. To compare, the peak concentration

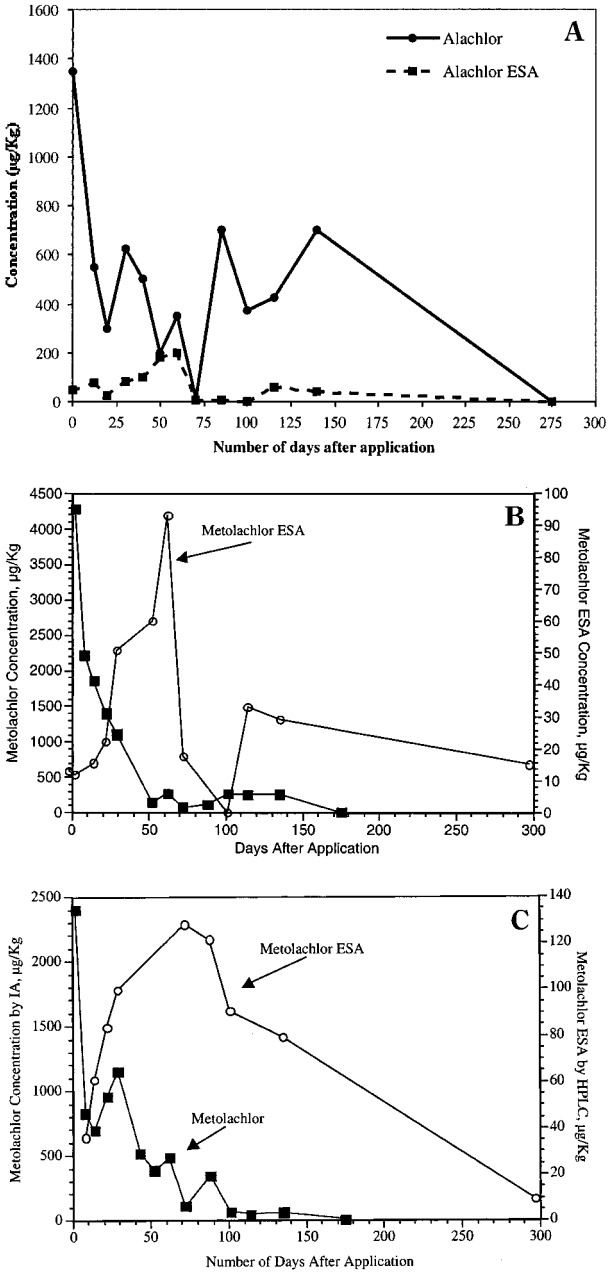

FIGURE 3. (A) Alachlor disappearance and alachlor ESA formation in the upper 15 cm of soil (plot 1, 1994). (B) Metolachlor disappearance and metolachlor ESA formation in the upper 15 cm of soil (plot 1, 1994). Note: The scale for metolachlor concentration is on the left *y*-axis, but the scale for metolachlor ESA is on the right *y*-axis. (C) Metolachlor disappearance and metolachlor ESA formation in the upper 15 cm of soil (plot 2, 1994)). Note: The scale for metolachlor concentration is on the left *y*-axis, but the scale for metolachlor ESA is on the right *y*-axis.

of alachlor ESA was approximately 15% and that of metolachlor ESA was 8% of the initial concentration applied.

In addition to water solubility, herbicide adsorption in soil plays an important role in determining the susceptibility to loss by leaching or runoff. Thus, it is helpful to compare the soil organic carbon partition coefficients (K_{oc}) of these herbicides and their ESA metabolites. As a matter of fact, the disappearance half-lives of alachlor (26−40 d) and metolachlor (27−30 d) in surface soil are longer than in the surface runoff, suggesting that soil adsorption may play a more important role than water solubility in the rate of disappearance of alachlor and metolachlor in soil. There is no apparent statistical difference between the alachlor and metolachlor soil half-lives due to the significant spatial variability in the herbicide concentrations in soil. In addition, the experimentally determined values of log K_{oc} for alachlor and metolachlor were 3.33 and 3.01, respectively (*23*). The difference in these log K_{oc} values is small, which may also explain the very similar disappearance half-lives of these two herbicides in surface soil.

In general, the infiltration rate of metolachlor in soil was greater than alachlor. For example, metolachlor was detected in soil at a depth of 30−45 cm at a concentration of 80 μg/kg on day 8, which increased to 142 μg/kg on day 14. On the other hand, the concentration of alachlor was only 3.6 μg/kg on day 8 and 13.3 μg/kg on day 14 at the same depth. This observation is consistent with the higher water solubility of metolachlor (530 ppm at 20 °C) relative to that of alachlor (242 ppm at 25 °C) and the slightly higher log K_{oc} of alachlor as compared to metolachlor.

The concentrations of alachlor ESA in soil were almost always higher than metolachlor ESA by about 2−3 times at all depths. Results of this study showed that the two ESA metabolites were transported at higher concentrations and to greater depths as compared to their parent herbicides. For example, as high as 140 μg/kg of alachlor ESA and 122 μg/kg of metolachlor ESA were observed in soils at the 60−75-cm depth on day 43. Neither alachlor nor metolachlor exceeded 3.0 μg/kg at depths lower than 45 cm. Moreover, alachlor ESA (13.3 μg/kg) and metolachlor ESA (18.7 μg/kg) were observed at a depth of 75−90 cm on day 297 but not the parent herbicides. These results are not surprising considering that the ESA derivatives have higher water solubility and much lower K_{oc} than the parent herbicides. The experimentally determined values of log K_{oc} are 2.26 and 2.29 for alachlor ESA and metolachlor ESA (*23*), respectively. This field study correlates with a recent study showing that the concentrations of ESA and OXA metabolites of alachlor and metolachlor are often much higher than the parent herbicides in groundwater, tile drain, and stream runoff (*24*).

Acknowledgments

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