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Enhanced Soil Degradation of Alachlor by Treatment with Ultraviolet Light and Ozone

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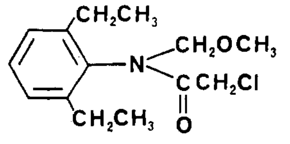
Photolytic ozonation followed by microbial degradation has been considered as a disposal option for agricultural pesticide wastewater. In an effort to better understand and ultimately to optimize the process with respect to alachlor, photolysis and ozonation have been examined separately. Alachlor is dechlorinated upon irradiation and forms a number of intermediates that retain the aromatic ring and carbonyl carbons as determined by labeling studies. These compounds include hydroxyalachlor, norchloralachlor, 2′,6′-diethylacetanilide, 2-hydroxy-2′,6′-diethyl-*N*-methylacetanilide, and a previously unreported lactam. In comparison, ozonation does not readily dechlorinate alachlor but rather oxidizes the alkyl side chain and opens the aromatic ring. Solutions that were subjected to photolysis or ozonation were placed in soil biometer flasks as was untreated alachlor, and the degradation was measured by the release of $^{14}CO_2$. Treated solutions showed rapid metabolism whereas less than 5% of the parent compound was mineralized after 35 days.

Alachlor [2-chloro-2′,6′-diethyl-*N*-(methoxymethyl)acetanilide] is a widely used herbicide that controls most annual grasses and certain broadleaf weeds. It is estimated that production in 1982 was 38 400 metric tons (Gianessi, 1986). Soil persistence studies indicated relatively rapid breakdown of alachlor. I.e., 30–40 days was required for 90% dissipation (Kearney et al., 1985); however, very little ring-labeled [^{14}C]alachlor was mineralized to $^{14}CO_2$ in soil (Chou and Tiedje, 1973). The soil fungus *Chaetomium globosum* reportedly converted alachlor to a number of ring-intact metabolites, including 2-chloro-2′,6′-diethylacetanilide, 2,6-diethyl-*N*-(methoxymethyl)aniline, 2,6-diethylaniline, and 1-(chloroacetyl)-2,3-dihydro-7-ethylindole (Tiedje and Hagedorn, 1975). In addition to microbial metabolism, alachlor is subject to photodecomposition on the soil surface. Residues of 67.5%, 54.1%, and 59.4% alachlor were measured on three soil surfaces exposed to sunlight (Fang, 1977). The major photoproducts reported in that study were 2-chloro-2′,6′-diethylacetanilide, 2,6-diethylaniline, 2′,6′-diethylacetanilide, monochloroacetic acid, 2,6-diethyl-*N*-(methoxymethyl)aniline, and 1-(chloroacetyl)-2,3-dihydro-7-ethylindole.



Alachlor

Despite the fact that alachlor is subject to both microbial metabolism and photodecomposition, residues have been detected in well water at certain locations (Cohen et al., 1986). Ultraviolet irradiation in conjunction with ozonation and followed by soil metabolism has been examined as a waste disposal method in an effort to reduce the risk of groundwater contamination from pesticide disposal (Kearney et al., 1984). In a recent survey of 11 major pesticides, formulated alachlor, in the concentration range 10–100 ppm, was shown to undergo rapid decomposition (Kearney et al., 1987).

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The efficiency of photolytic ozonation can be influenced by a number of factors. Some waste compounds possess a chromophore that absorbs in the UV region and can undergo phototransformations, further enhancing the degradation process. Also, in the presence of UV light or hydrogen peroxide, ozone can produce hydroxy radicals, which are more powerful oxidizers than ozone (Glaze, 1987; Peyton and Glaze, 1987). To better understand the combined use of irradiation and ozone as it applies to alachlor and to ultimately achieve optimization of the entire scheme, each process was studied separately. The objective of the current study was to examine the rates of alachlor degradation by UV irradiation and by ozone treatment, the types of products formed, and the effects of these treatments on the subsequent degradation in soil.

METHODS AND MATERIALS

Alachlor. Lasso EC (containing 480 g/L alachlor, Monsanto Agricultural Products, Co., St. Louis, MO) was received from the Farm Operations Branch at the USDA Beltsville Agricultural Research Center (BARC), Beltsville, MD. Analytical-grade alachlor was prepared by recrystallization of technical-grade alachlor (supplied by Monsanto Agricultural Products) from methanol. A purity of greater than 98% was achieved. Alachlor-*carbonyl*-^{14}C (specific activity 1 mCi/mmol) and alachlor-*U-ring*-^{14}C (specific activity 8.7 mCi/mmol) were received gratis from Monsanto Agricultural Products. The radioactive purity of each was determined to be greater than 98% by TLC/autoradiography (20 cm × 20 cm silica gel, 250 μm, developed with 5% methanol in toluene.)

Equipment and Instrumentation. Irradiation was carried out with use of a Hanovia-Conrad medium-pressure mercury vapor lamp equipped with a quartz water cooled immersion well and a 220-mL reactor with a sintered glass disk in the bottom for introducing nitrogen, oxygen, or ozone. The reactor was also fitted with a gas outlet line to measure the gas flow and a liquid sampling valve. Ozone was fed into the bottom of the reactor at the rate of 10–100 mg/min as determined by iodometric titration (Flamm, 1977). In some experiments ozonation was carried out in a 250-mL graduated cylinder with ozone introduced through a stainless steel airstone at the bottom of the vessel. Ozone was generated by a Griffin Ozone generator, Model GTC-1B, using oxygen feed.

HPLC data were obtained from one of the following: (1) two Waters Model 6000 pumps equipped with a Perkin-Elmer Model LC-95 UV–vis variable-wavelength detector and a Waters Model 720 system controller and 721 data module; (2) two Waters Model 6000 pumps equipped with a Waters Model 990 photodiode array detector and accompanying NEC APC-III controller and software; (3) a Gilson Model 42 HPLC system equipped with a Gilson Model 116 UV detector, an IBM PC/AT controller, and accompanying Gilson Windows software. NOVAPAK (C-18) 8 mm × 10 cm radial compression module columns were used with the Waters HPLC systems and an Axxiom C-18 4.6 mm × 25 cm steel jacketed column with the Gilson system. Preparative HPLC was carried out on the Gilson system with an Axxiom C-18 10 mm × 25 cm semipreparative column.

GC/MS spectra were obtained either on a Hewlett-Packard Model 5992A GC/MS equipped with a Hewlett-Packard Model 9825A data module, Hewlett-Packard Model 9885M disk drive, and Chrompak 11 m × 0.32 mm (i.d.) CPSil 19CB capillary column (film thickness 0.11 μm) or on a Kratos Model MS25RFA mass spectrometer. Probe work on the ozonated samples was conducted by William R. Lusby of the Insect and Nematode Hormone Laboratory at the USDA Beltsville Agricultural Research Center. These spectra were obtained on a Finnigan-MAT Model 4510 mass spectrometer equipped with a direct-exposure probe. Samples of ca. 100 ng were placed onto the probe tip, and a current increasing from 0 to 1000 mA was applied at a rate of 20 mA/s. Electron impact spectra were collected at a source temperature of 150 °C, while chemical ionization data were obtained at 60 °C. Methane (wet) provided a reagent gas ionic distribution of 40:100:48:17 (CH_5^+:H_3O^+:$C_2H_5^+$:$C_3H_5^+$) while ammonia provided a distribution of 35:37:100:49 [NH_4^+:$(NH_3)_2H^+$:$(NH_3)_3H^+$:$(NH_3)_4H^+$]. Determination of the number of exchangeable hydrogens was accomplished by use of deuterioammonia chemical ionization with a reagent gas ionic distribution similar to that of ammonia for analogous ions. NMR spectra were obtained on a General Electric QE-300 spectrometer, and IR spectra were obtained on a Nicolet Model 60SX FT/IR spectrophotometer.

Irradiation of Alachlor. A 60-mg portion of analytical-grade alachlor was dissolved in 250 mL of ultrapure water (18 MΩ) to afford a solution of 240 ppm, which was then irradiated with an oxygen feed. Ozone formation was not detected under these conditions as determined by iodometric titration. The reaction was also run with a solution of ca. 100 ppm formulated alachlor. Subsequent HPLC analysis was carried out in 45% acetonitrile in pH 2 phosphoric acid buffer. In a similar reaction a 240 ppm solution of analytical alachlor was added to the reactor, spiked with 0.5 μCi of either ring-labeled or carbonyl-labeled alachlor, and irradiated in the presence of oxygen. Samples of 10 mL were removed periodically, extracted three times with ethyl acetate, dried over sodium sulfate, and concentrated initially in vacuo to approximately 2 mL and then with nitrogen to 500 μL. Samples of 100 μL were spotted on a TLC plate (20 cm × 20 cm silica gel, 250-μm thickness) and developed with 5% methanol in toluene. These plates were analyzed by autoradiography using DEF-5 direct-contact X-ray film (Eastman Kodak Co., Rochester, NY). These experiments were also carried out with ca. 100 ppm formulated alachlor.

Isolation of Intermediates from Irradiated Alachlor. A 1-g portion of analytical alachlor was dissolved in 4 L of ultrapure water. The solution was divided into 200-mL batches, purged with nitrogen for 10 min, and irradiated for 6 min under continuous nitrogen flow. The batches were combined and redivided into 500-mL portions, which were extracted three times with 75 mL of diethyl ether. The ether extracts were dried over sodium sulfate and concentrated in vacuo. The mixture was separated by flash column chromatography (silica gel column 7 mm × 300 mm, 40–63-μm particle size) using a gradient of 25% ether in hexane (2 L) to 100% ether. Fractions were analyzed by HPLC as above and the structures determined by comparison with standards, GC/MS, NMR, and/or IR.

Ozonation of Alachlor. Ozonation was carried out in the same manner as in the irradiation of alachlor, except that ozone was fed into the reactor and no light was used. Acetonitrile (45%) in pH 2 phosphoric acid buffer was used in the HPLC analysis. Labeling experiments were conducted in a manner similar to that used in the photolysis of alachlor. In addition these experiments were carried out with ca. 100 ppm formulated alachlor.

Isolation of Products from Ozonated Alachlor. A 120-mg portion of analytical alachlor were dissolved in 500 mL of ultrapure water. The solution was ozonated as above for 30 min, concentrated in vacuo, and separated

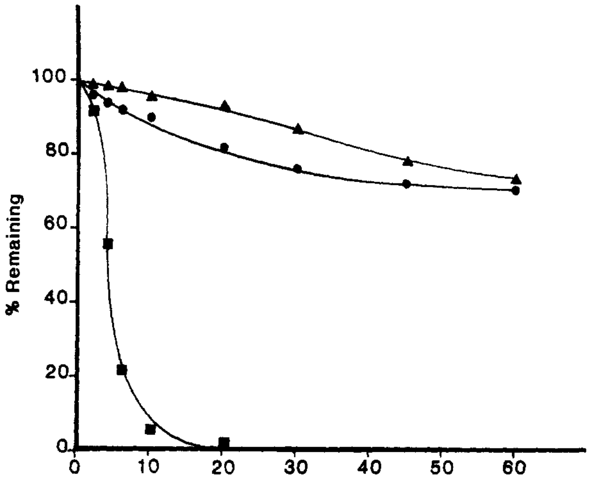


Figure 1. Treatment of analytical-grade alachlor (240 ppm) with ultraviolet light in the presence of oxygen: (●) label remaining using alachlor-*carbonyl*-^{14}C; (▲) label remaining using alachlor-*U-ring*-^{14}C; (■) parent compound as determined by HPLC analysis.

by preparative HPLC using an acetonitrile/water step gradient (0–2 min, 6.5 mL/min, 20% acetonitrile; 10–12 min, 7.5 mL/min, 70% acetonitrile; 16 min, 6.5 mL/min, 20% acetonitrile). The fractions were analyzed by HPLC as above. Structural analyses were carried by a variety of methods including probe MS, NMR, and IR.

Degradation of Treated Material on Soil. A 5-mL sample of formulated 100 ppm alachlor containing 0.1 μCi of alachlor-*carbonyl*-^{14}C or alachlor-*U-ring*-^{14}C was added to 50 g of 30% dry sand/70% Sassafras silt loam in duplicate biometer flasks (Bartha and Pramer, 1965). Collected Sassafras silt loam had the following characteristics: 14% organic matter, pH 4.2; moisture content of 36% with a field capacity of 57% (at 0.33 bar water potential); sand, silt, and clay contents of 56, 20, and 24%, respectively. Duplicate flasks were also amended with 5 mL of formulated alachlor previously subjected to either UV irradiation or ozonation for 60 min. Mineralization was determined by trapping $^{14}CO_2$ in 10 mL of 0.1 N KOH added to the side arm of the flask. On sampling, the 10 mL of base solution was removed, two 1-mL subsamples were added to 10-mL Beckman Ready-Solv HP (Beckman Instruments, Inc., Fullerton, CA), and ^{14}C was determined by liquid scintillation counting. Fresh base (10 mL) was added to the side arm after each sampling.

RESULTS

Treatment of Alachlor with Ultraviolet Light. When irradiation of analytical-grade alachlor in purified water was carried out in the presence of oxygen, all of the alachlor was depleted within 25 min. The reaction appeared to be first order and the $t_{1/2}$ was determined to be 1.6 min (Figure 1). The pH of this reaction was followed, and after 60 min the pH had fallen from 6.6 to 2.5, indicating the formation of acid. The reaction was repeated twice on solutions of analytical-grade alachlor independently spiked with alachlor-*U-ring*-^{14}C (0.5 μCi) and alachlor-*carbonyl*-^{14}C (0.5 μCi). After 60 min, 71% and 70% of the ring and carbonyl label, respectively, were retained in the reaction mixtures (Figure 1). Samples were removed from these reactions at 0, 4, 10, 30, and 60 min, extracted with ethyl acetate, and analyzed by TLC. No differences were observed between the autoradiograms of these two labeled substrates at any of the time intervals. There were virtually no differences between photolysis of analytical-grade alachlor and formulated alachlor as can be seen when Figures 1 and 2 are compared. The $t_{1/2}$ for formulated alachlor was 3.7 min, which is slightly longer than that of the analytical-grade substrate. The rate of disappearance of label was the same whether carbonyl- or ring-labeled alachlor was used.

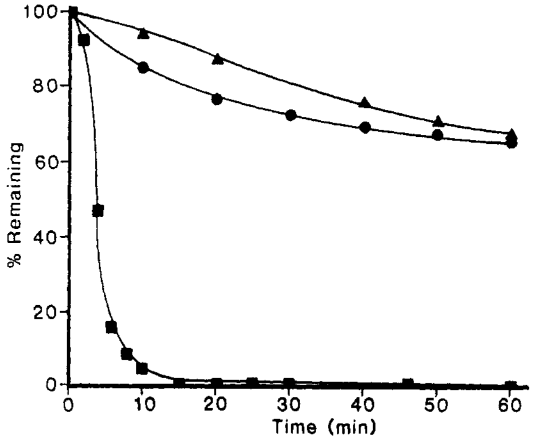
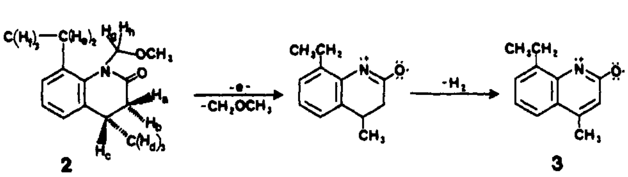


Figure 2. Treatment of formulated alachlor (Lasso EC ca. 100 ppm) with ultraviolet light in the presence of oxygen: (▲) label remaining using alachlor-*carbonyl*-^{14}C; (●) label remaining using alachlor-*U-ring*-^{14}C; (■) parent compound as determined by HPLC analysis.

Scheme I



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The rate of disappearance of alachlor using ultraviolet light in the presence of nitrogen was the same as when oxygen was used. The same intermediates were formed; however, their breakdown was much slower in nitrogen. To ascertain the structures of these compounds, the reaction was run with nitrogen and terminated early. Five major products were identified. Hydroxyalachlor (1) is the major product, and its identity was further established by ^1H NMR. The second most abundant product (2) was fully characterized. The mass spectrum of 2 showed a parent peak at *m/z* 233 and ion peaks at *m/z* 201, 188, and 146, which correspond to loss of a methoxy, loss of CH_2OCH_3, and loss of CH_2CO and CH_2OCH_3, respectively. The base peak was observed at *m/z* 186, which can be rationalized as the loss of molecular hydrogen from *m/z* 188 to give the aromatized intermediate 3 (Scheme I). The IR spectrum indicated the presence of an amide at 1691.4 cm^{-1}. The NMR spectrum showed a multiplet at 7.06–7.02 ppm corresponding to the three aromatic protons, a set of doublets at 5.41 and 4.87 ppm (J = 10 Hz), a singlet at 3.35 ppm, a multiplet at 3.09–2.96 ppm, and a quartet at 2.75 ppm (J = 7.5 Hz), which correspond to H_g and H_h, the methoxy protons, H_c, and H_e, respectively. H_a and H_b appear as a doublet of doublets at 2.66 and 2.40 ppm (J_{ab} = 4.4 Hz, J_{bc} = 8 Hz). The methyl protons H_d and H_f are observed at 1.31 ppm (d, J_{cd} = 7.0 Hz) and at 1.25 ppm (t, J_{ef} = 7.5 Hz). Three other compounds were also identified by GC/MS and/or comparison with authentic sample using HPLC: norchloralachlor (4), 2′,6′-diethylacetanilide (5), and 2-hydroxy-2′,6′-diethyl-*N*-methylacetanilide (6).

Treatment of Alachlor with Ozone. Alachlor was also treated with ozone alone. The reaction with ozone was in general slower than the photolysis just described. The

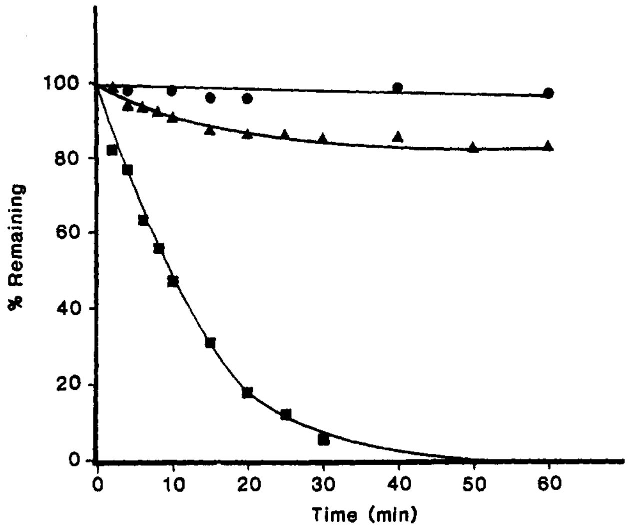


Figure 3. Treatment of analytical-grade alachlor (240 ppm) with ozone: (●) label remaining using alachlor-*carbonyl*-^{14}C: (▲) label remaining using alachlor-*U-ring*-^{14}C; (■) parent compound as determined by HPLC analysis.

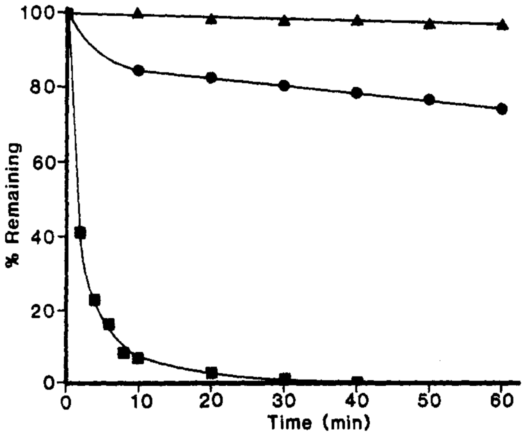


Figure 4. Treatment of formulated alachlor (Lasso EC ca. 100 ppm) with ozone: (▲) label remaining using alachlor-*carbonyl*-^{14}C; (●) label remaining using alachlor-*U-ring*-^{14}C; (■) parent compound as determined by HPLC analysis.

$t_{1/2}$ for ozonation of analytical-grade alachlor was determined to be 8.6 min, and all of the parent material was not depleted until 50 min. The $t_{1/2}$ for formulated alachlor was 1.9 min and total consumption of parent material observed at 30 min. The pH of the reaction mixture decreased from 6.6 to 4.5. The reactions were also monitored by HPLC, and none of the photolysis products were observed. As in the photolysis experiments, ozonolysis was carried out on both carbonyl- and ring-labeled alachlor. After 60 min, 97% of the carbonyl label remained in the reaction mixture whereas only 83% was left when the experiment was carried out using ring label (Figure 3). Samples were removed at 0, 30, and 60 min, extracted, and analyzed by TLC, and some differences were observed between the two labels in the autoradiogram. Formulated alachlor gave similar results (Figure 4).

Several compounds have been isolated, and their structural identification is in progress. In general, NMR and mass spectral data indicate that chlorine was retained and that ring opening and oxidation of the ethyl side chain had occurred.

Soil Studies. A series of soil degradation studies were conducted on the treated material. Solutions of alachlor with carbonyl or ring label were irradiated for 60 min and then placed in biometer flasks, and the release of $^{14}CO_2$ was monitored. Untreated material was used as a control, and after 35 days virtually none had been mineralized. The irradiated material, however, was rapidly degraded in the first few days and $^{14}CO_2$ evolution plateaued shortly thereafter, remaining at 55%. Carbonyl- and ring-labeled material gave exactly the same result (Figure 5).

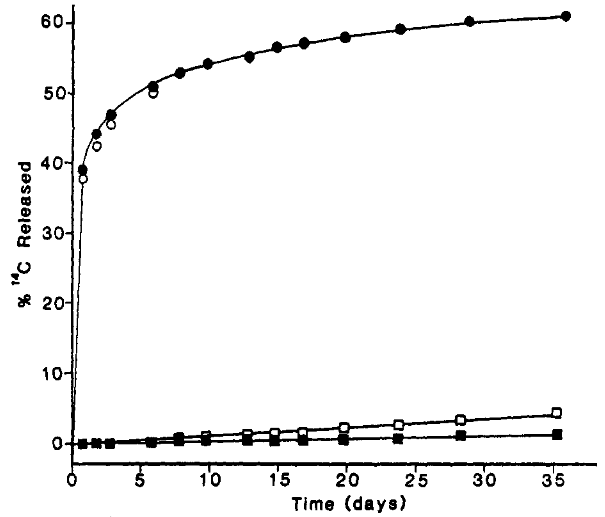


Figure 5. Soil degradation of photolyzed alachlor: (○) alachlor-*carbonyl*-^{14}C; (●) alachlor-*U-ring*-^{14}C; (□) untreated alachlor-*carbonyl*-^{14}C; (■) untreated alachlor-*U-ring*-^{14}C.

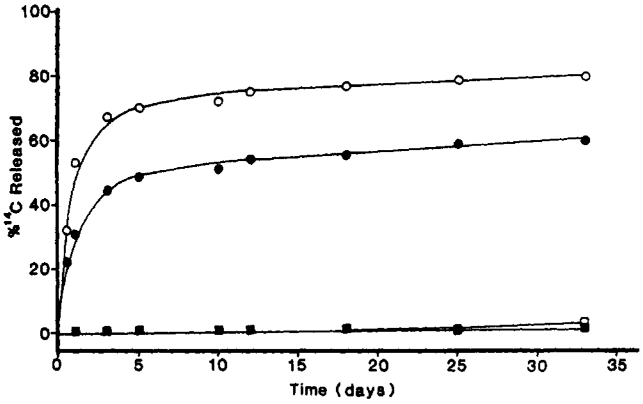


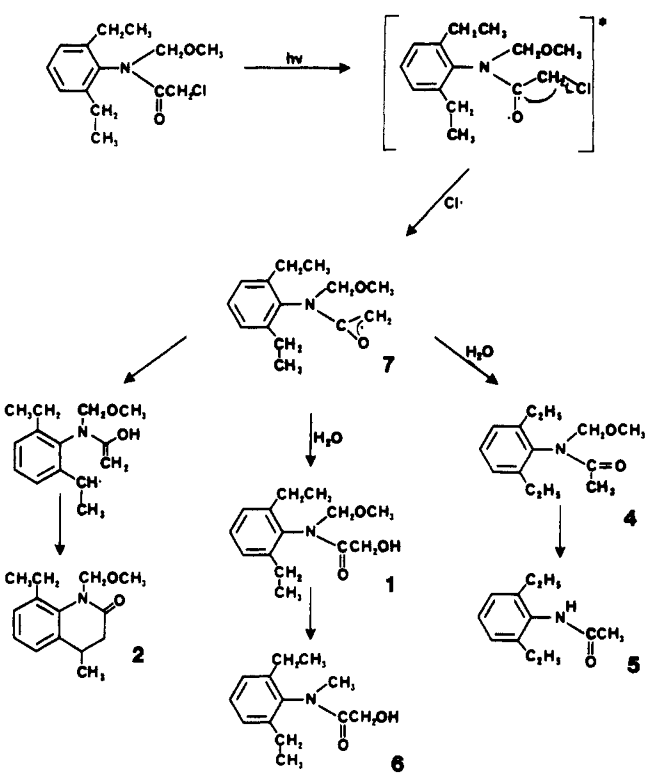
Figure 6. Soil degradation of ozonated alachlor: (○) alachlor-*carbonyl*-^{14}C; (●) alachlor-*U-ring*-^{14}C; (□) untreated alachlor-*carbonyl*-^{14}C; (■) untreated alachlor-*U-ring*-^{14}C.

Soil degradation studies were also conducted on alachlor treated with ozone for 60 min. Again, untreated material was not mineralized, as was expected. Ozonated material was rapidly metabolized, although differences were observed between the two labels. More $^{14}CO_2$ was produced from carbonyl-labeled alachlor (80% $^{14}CO_2$ release) than was produced from the corresponding ring-labeled substrate (60% $^{14}CO_2$ release) (Figure 6).

DISCUSSION AND CONCLUSION

Ultraviolet irradiation and ozonation of alachlor proceed by different pathways. Ozone does not appear to remove the chlorine readily whereas dechlorination is presumably the first step in photolysis. Absorption of a photon by the carbonyl of alachlor is followed by loss of chlorine at the α-carbon, affording intermediate 7 (Scheme II). Reaction with water would give either hydroxyalachlor or norchloroalachlor. Alternatively, intramolecular hydrogen abstraction can occur, whereupon collapse of the resultant radical and loss of a hydrogen would give lactam 2. Secondary reactions involving loss of the methoxy or the methoxymethyl can easily be rationalized. A number of

Scheme II



other minor products were observed but not isolated or identified; however, from the autoradiogram, it is clear that neither the carbonyl nor the ring carbons were removed during in the first few steps. Further photodegradation does occur, and after 1 h of irradiation only four very polar compounds were observed. Isolation and identification of these final products have proven to be complicated and are the subject of another study.

Ozonation, although somewhat slower than UV irradiation, appears to add another facet to decomposition. Ring cleavage, which probably enhances the degradation of alachlor, has been observed in ozonolysis. A good indication that ring cleavage does occur is that, after 1 h of treatment with ozone, none of the carbonyl label was depleted but nearly 30% of the ring label was lost. Additional evidence for ring cleavage was found in the NMR spectrum of one of the compounds where no aromatic protons were detected.

The addition of oxygen, the removal of chlorine, and the opening of the aromatic ring in these processes gave rise to compounds that were more biolabile than the parent material, as was demonstrated by results from soil experiments. The degradation of unaltered alachlor was very slow under these conditions, but the products of ozonolysis or photolysis were metabolized very rapidly. Although complete conversion of the products to CO_2 was not observed, it can be argued that much of the remaining label was incorporated into the biomass of the soil microorganisms.

In this study, we have examined separately the effects of aqueous photolysis and ozonation on alachlor and have found that each has an important role in the overall degradation scheme. Our work is continuing in an effort to optimize the combined use of photolytic ozonation with microbial metabolism which, we believe, will provide an efficient and economical pesticide waste treatment process to the agricultural community.

Registry No. Alachlor, 15972-60-8; **1**, 56681-55-1; **2**, 116149-24-7; **4**, 74886-79-6; **5**, 16665-89-7; **6**, 116149-23-6.

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Metal Complexes of Glyphosate

Vaseetha Subramaniam and Patrick E. Hoggard*

Insoluble complexes of glyphosate with iron(III), copper(II), calcium, and magnesium ions are formed at near-neutral pH. This suggests a mechanism for the inactivation of glyphosate in contaminated groundwater.

Glyphosate (*N*-(Phosphonomethyl)glycine, trade name (Monsanto) Roundup) is a nonselective, broad-spectrum, postemergent herbicide. Part of its appeal is due to its relatively rapid degradation by microorganisms in soils to nonphytotoxic products (Hoagland and Duke, 1982). These products can even include beneficial phosphorus- and nitrogen-containing species (Rueppel et al., 1977). Its

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