Photodegradation of Metolachlor: Isolation, Identification, and Quantification of Monochloroacetic Acid

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The photolysis of metolachlor [2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl)acetamide] in a sunlight simulator under actinic radiation was investigated. The focus of the study was to determine the extent of monochloroacetic acid (MCA) production. MCA was concentrated and derivatized from photolysate as the *n*-propyl ester using propanol and sulfuric acid and then identified as the ester using GC/MS and GC/ECD. On the basis of regression analysis, it was shown that the direct photodegradation of ~10 μM metolachlor followed pseudo-first-order kinetics with respect to the metolachlor concentration, and the half-life of the herbicide (~74 h) was independent of the pH of the medium. Photolysis in synthetic field water (SFW) resulted in a significant reduction of photolysis time ($t_{1/2} \sim 9$ h). Direct photolysis experiments indicate a $5.19 \pm 0.81\%$ (n=3) conversion of metolachlor to MCA, while photolysis in synthetic field water and in a Don River water sample resulted in $29.8 \pm 4.6\%$ ($n = 3$) and $12.6 \pm 4.1\%$ ($n = 3$) conversion, respectively; MCA was shown to be hydrolytically stable over the time course of the photoreaction. The photodegradation of alachlor, butachlor and a model chloroacetanilide, 2-chloro-*N*-methylacetanilide, in SFW were also investigated.

Keywords: *Chloroacetanilide; herbicide; monochloroacetic acid; photolysis*

INTRODUCTION

Chloroacetanilides have been under development for use in agriculture since 1952 (Chesters et al., 1989). They are used in Canada and in the United States as preemergence herbicides to control annual grass weeds and broadleaf weeds in corn, peanuts, soybeans, and beans. This class of herbicides includes metolachlor [2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl)acetamide], alachlor [2-chloro-*N*-(2,6-diethylphenyl)-*N*-(methoxymethyl)acetamide], and butachlor [2-chloro-*N*-(2,6-diethylphenyl)-*N*-(butoxymethyl)acetamide] introduced in 1976, 1969, and 1971, respectively (Hamm, 1974). The structure, as the name implies, has been developed around the acetanilide moiety; however, the difference is manifested mainly in the methoxyalkyl side chain. This moiety regulates selectivity, water solubility, and other such herbicidal properties (Matolesy et al., 1988). Specifically, chloroacetanilides are detoxified by conjugation with glutathione to the chloroacetyl side chain via glutathione S-transferase (GST) (Lange et al., 1998). Selectivity comes about since corn and other such tolerant species are capable of rapid conjugation while target weeds have reduced GST activity.

Alachlor was withdrawn from general use in Ontario in 1985 (Chesters et al., 1989), resulting in an increase in use of metolachlor. By 1988, metolachlor became the most widely used herbicide in Ontario, with usage exceeding 1.33×10^6 kg by 1993 (Ontario Ministry of Agriculture, 1993). Estimated United States annual use of alachlor according to Chesters et al. (1989) was approximately 37×10^6 kg, while use of metolachlor was estimated at 22×10^6 kg.

Contamination of surface water due to pesticide use occurs mainly due to runoff, usually within a few weeks of application. Studies across the United States and Canada have confirmed that chloroacetanilide herbicides do infiltrate ground and surface waters (Chesters et al., 1989; Kent et al., 1990; Capel et al., 1995; Clark et al., 1999; Kolpin and Nations, 1996; Zacharias et al., 1999; Hatfield et al., 1999). A study of 149 drainage basins across Midwestern United States reported that alachlor and metolachlor are among those herbicides most frequently detected, often in the part-per-billion level (Jaynes et al., 1999). Similarly in Ontario, mean annual concentrations of metolachlor reached 4.1 μg/L at the mouths of the Grand, Saugeen, and Thames Rivers from 1981 to 1985 (Kochany and Maguire, 1994).

Once in an aqueous environment, a pesticide is subject to volatilization, hydrolysis, or photolysis. The volatility of the chloroacetanilides is expected to be low due to low values of Henry's Law constant, K_H ($<10^{-5}$, Kent et al., 1990). Alachlor and metolachlor each possess a long hydrolysis half-life (Chiron et al., 1995). Photolysis becomes the most important abiotic degradation pathway for metolachlor under normal conditions in an aqueous environment.

Past investigations regarding the photodegradation of chloroacetanilide herbicides have focused on identifying products resulting from hydroxylation, dehalogenation, oxoquinoline formation, and demethylation of the parent compound (Mathew and Khan, 1996), showing that such products are identifiable with little sample preparation using LC/MS or GC/MS. Photoproducts that are not easily identifiable, however, have often been reported as "unidentified polar products" (Chiron et al., 1995, Kochany and Maguire, 1994; Somich et al., 1988). Studies quantifying photoproducts have only been able to account for 62% (Kochany et al., 1994) and 40% (Chiron et al., 1995) of the degraded parent chloroacetanilide, leaving a significant portion of products unidentified and unaccounted for.

Monochloroacetic acid (MCA) is a polar product that has been identified as a product of chloroacetanilide degradation. Pignatello and Sun (1995) reported MCA as a significant photoproduct of metolachlor resulting from the photoassisted Fenton Reaction during the investigation of a potential pesticide waste management strategy. Mangiapan et al. (1997) identified MCA as a product of the biodegradation of alachlor incubated in river water for 28 days. Both studies, while valuable, do not provide any information regarding the possibility that direct or indirect photodegradation of chloroacetanilide herbicides could be a source of monochloroacetic acid in the environment.

The presence of haloacetic acids in the environment such as MCA is widespread (Scott and Alaee, 1998); therefore, identification of potential sources is of interest. The chlorination of drinking water (Hirvonen et al., 1996; Wu and Chadik 1998; Kristiansen et al., 1996) is one possible source for haloacetic acids in the environment. Concerns regarding levels of MCA in particular exist since MCA has proven to be highly phytotoxic; the 48 h effective concentration, 10% (EC10) for the green algae *Scenedesmus subspicatus* is 7 μg/L (Kuhn and Pattard, 1990).

The main objective of this investigation was to use a representative chloroacetanilide herbicide, metolachlor, to investigate the potential for the production of MCA as a photoproduct in various matrixes. Further, we hoped to quantify MCA and determine possible conditions leading to maximum production of the acid. Once the conditions producing significant acid were realized, the photolysis of alachlor, butachlor, and a model chloroacetanilide were used to investigate structural factors that may play a role in the production of MCA.

MATERIALS AND METHODS

Chemicals. Metolachlor, alachlor, and butachlor were obtained from Chem-Service (West Chester, PA). Monochloroacetic acid was of ACS grade obtained from Fischer Scientific (Fair Lawn, NJ). High-performance liquid chromatography (HPLC) grade acetonitrile was obtained from J. T. Baker (Phillipsburg, NJ). HPLC grade water was obtained from Caledon Laboratories (Georgetown, ON). Acetonitrile and water were passed through a 0.45 μm filter before use. Organic-free water used for photochemical experiments was 18 MΩ deionized water. Sodium nitrate and sodium bicarbonate used to prepare synthetic field water (SFW) were of reagent grade. Dissolved organic carbon (DOC) used was prepared by pre-aging a humic acid stock solution in a homemade photosimulator for 8 days. Methylaniline and chloroacetyl chloride were purchased from Aldrich Chemical Co. (Milwaukee, WI).

Synthesis. The propyl ester of MCA was synthesized by refluxing 1 g of MCA, 10 mL of 1-propanol, and 0.5 mL of concentrated sulfuric acid for 2 h. The ester was identified using GC/MS (*m/z* (abundance) [suggested pathway]): 109 (4), 107 (12) [$M^+ - C_2H_5$], 97 (14), 95 (45) [$M^+ - C_3H_5$], 79 (32), 77 (100) [$M^+ - OC_3H_7$], 57 (17).

The model chloroacetanilide, 2-chloro-*N*-methylacetanilide, was synthesized by the method of Biechler et al. (1957): A 5 g sample of chloroacetyl chloride was dissolved in 25 mL anhydrous diethyl ether. Dropwise, 3.7 g of methylaniline was added to the solution. The ether layer was washed with water and evaporated. White crystals were obtained upon recrystallization from ethanol–water. The model was identified using GC/MS and ^{1}H NMR (Varian 400 MHz spectrometer with CDCl$_3$ as solvent). GC/MS: 185 (17), 183 (43) [M^+], 134 (42) [$M^+ - CH_2Cl$], 107 (46), 106 (100) [$M^+ - C(O)CH_2Cl$], 92 (13), 90 (43), 79 (16), 77 (68) [$M^+ - CH_3NC(O)CH_2Cl$]. ^{1}H NMR (δ, chemical shift in ppm, s = singlet, m = multiplet): δ 7.6–7.2 (m, 5H, H Ar), 3.85 (s, 2H, CH$_2$), 3.30 (s, 3H, CH$_3$).

Aqueous Stability. The aqueous stability of monochloroacetic acid was characterized before photochemical experiments. MCA (13 mg/L) solutions were adjusted to pH 7 and pH 9 daily using 0.1 N HCl or 0.1 N NaOH and stored in the dark for a 12 day period. Each pH treatment was done in duplicate. At various times MCA levels were analyzed using ion chromatography.

Photodegradation. The photochemical stability of four chloroacetanilides was tested using a Suntest CPS Photosimulator equipped with a xenon arc lamp and a water-cooled tray. Irradiance was set to maximum, 765 W/m^2 $\pm$ 10%, and included wavelengths from 290 to 800 nm to mimic the intensity distribution of natural light. It has been shown that the behavior of our photosimulator shows similar irradiance to the sunlight in July in Toronto around midday. For each photolysis experiment, three 80–100 mL samples of 7–12 μM chloroacetanilide (consistent concentration within each experiment) were placed in quartz test tubes inside the photoreactor and sealed with rubber stoppers and Teflon tape. Tubes were removed throughout the course of the run, so that three time points in addition to the zero time point were analyzed for each set of photolysis conditions. Samples were stored in bottles wrapped in aluminum foil in the fridge (4 °C) until analysis. Plots of ln C/C_0 (C represents the concentration of the parent chloroacetanilide at time t and C_0 is the initial concentration) vs time for each experiment provided pseudo-first-order kinetic data including rate constants and half-lives.

Direct Photolysis Experiments. Metolachlor was degraded in deionized water adjusted to pH 7 and pH 9. The pH was monitored and adjusted regularly using 0.1 N HCl and 0.1 N NaOH.

Indirect Photolysis Conditions. Indirect photolysis of metolachlor was examined using two different matrixes chosen for the potential to yield high concentrations of carbonate radical upon irradiation. Metolachlor was degraded in the photosimulator in a solution of 3 mM H$_2$O$_2$ and 0.092 M HCO$_3{}^-$ (pH = 8.23) (Larson and Zepp, 1988). Metolachlor, alachlor, butachlor, and 2-chloro-*N*-methylacetanilide were irradiated in a synthetic field water (SFW) matrix in order to mimic possible environmental sample constituents. SFW consisted of 4.9 mM HCO$_3{}^-$, 0.5 mg of C/L DOC, and 0.81 mM NO$_3{}^-$ (pH = 8.30). Metolachlor was also irradiated in a sample of Don River water (pH = 8.42). The Don River water sample consisted of 3.7 mM HCO$_3{}^-$, 5.77 mg of C/L of DOC, and 0.44 mM NO$_3{}^-$. The H$_2$O$_2$/HCO$_3{}^-$ and SFW treatments were carried out three and four times, respectively. All other treatments were performed once.

Analysis. Routine HPLC–UV analyses to monitor the photodegradation of the parent chloroacetanilide compound were done by direct aqueous injection into a Waters 600S system with a 486 Variable Wavelength Detector set at 220 nm. The column was a 25 cm × 4.6 mm i.d. reversed-phase Alltech Econosil C18, 5U and was preceded by an Alltech All-Guard Cartridge system with an Econosil C18 10U guard cartridge. Various mixtures of acetonitrile and water were used as the mobile phase. The flow rate was 1.0 mL/min for all experiments. Calibration was performed daily using external standards and linear regression analysis.

The aqueous stability of MCA was investigated using ion chromatography including a PE Series 200 pump, Alltech ERIS 1000 HP autosuppressor, and a Waters 712 WISP autosampler. The column was a 25 cm × 4 mm i.d. Dionex IonPac anion exchange column. The mobile phase and flow rate were 2.1 mM Na$_2$CO$_3$:0.6 mM NaHCO$_3$ and 1 mL/min, respectively. Calibration was preformed daily using external standards and linear regression analysis.

The production of MCA was monitored using a PE Autosystem XL gas chromatograph with electron capture detection (ECD). A Simplicity 1701 column (30 m × 0.32 mm i.d., 0.25 μm film thickness) was used to elute the propyl ester of the acid using the following temperature program: hold for 8 min at 45 °C, ramp at 30 °C/min to 250 °C. The injector and detector temperatures were 220 and 300 °C, respectively. The carrier gas was hydrogen and had a setpoint of 14 psi; the makeup gas was nitrogen at a flow rate of 30 mL/min. The injection mode was splitless, and the injection volume was 2.0

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μL. Calibration was performed daily using external standards and linear regression analysis.

A PE Autosystem XL gas chromatograph coupled to a PE TurboMass mass spectrometer was used for GC/MS analyses in the electron impact (EI) mode. Full scan EI spectra were obtained at 70 eV, from *m/z* 50−450 for the propyl ester of MCA and for the model chloroacetanilide 2-chloro-*N*-methylaniline. Single ion monitoring (SIM) EI spectra were obtained for the determination of *N*-methylaniline in the photolysate of the model compound by monitoring masses 106 and 77. An MDN-5 column (30 m × 0.25 mm, 0.25 μm film thickness) was programmed as follows. MCA propyl ester: 45 °C held for 8 min, 30 °C/min to 250 °C. 2-Chloro-*N*-methylaniline: 60 °C held for 2 min, 10 °C/min to 250 °C. *N*-Methylaniline: 70 °C held for 1 min 10 °C/min to 180 °C, 30 °C/min to 250 °C. The injector temperature and setpoint were 220 °C and 8 psi, respectively. The injection mode was splitless, and the injection volume was 1.0 or 2.0 μL.

Photolysate Analysis. Prior to GC/ECD analysis, samples had to be concentrated, derivatized, and extracted in order to analyze monochloroacetic acid as its respective ester. For direct photolysis experiments, the method of Reimann et al. (1996) was used. The method had originally been used for the analysis of MCA in rainwater. A known volume of the photolysate (80−100 mL) was passed through a 3 mL, 500 mg strong anion exchange (SAX) cartridge from either Supelco (Bellefonte, PA) or Varian (Harbor City, CA) via a Vacmaster vacuum manifold (Mid Glamorgan, U.K.). Cartridges were preconditioned with 5 mL of 10% NaCl and washed with 3 mL of 1-propanol once the photolysate had passed. Elution of the acid was achieved via centrifugation for 2 min using 2 mL of 1-propanol acidified with 12.5 μL/mL of concentrated H_2SO_4. To derivatize MCA, a further 190 μL of concentrated H_2SO_4 was added followed by heating in sealed vials at 70 °C for 2 h. The mixture was then made aqueous by adding 18 mL of 20% NaCl. Extraction with 2 × 0.5 mL of pentane followed by a wash of the pentane layer with 9 mL of 20% NaCl completed the sample preparation for GC/ECD analysis. Comparison of the derivatized acid with the synthesized ester on GC/ECD and GC/MS confirmed that the ester was made using this method. Solutions of MCA in deionized water were treated using the method in order to obtain standards for all photolysis treatments.

Low recoveries were found in all matrixes, excluding the deionized water treatments, using the method established by Reimann et al. Method development to improve recovery included sample pretreatment and variation in the SAX capacity and sample volume. The following variations in the method were tested: (1) acidify to pH 5 using concentrated HCl and degas the photolysate under vacuum prior to sample concentration on the SAX cartridges, (2) acidify, degas, and reduce sample volume to 50 mL and use 2500 mg capacity SAX cartridges, and (3) acidify, degas, and reduce sample volume to 40 mL. Spike and recovery experiments were used to test the efficiency of each variation in the method. All spikes were 25−30 μg/L in MCA in the matrix of interest. Data for these experiments are given in Table 2. Results indicated that the most effective modifications were achieved using variation (3). Poor recoveries persisted for the H_2O_2/HCO_3^- matrix; however, they did reach acceptable levels for the SFW matrix. The presence of the complementary compound to MCA production from the photolysis of the model compound (2-chloro-*N*-methylacetanilide) was also investigated. The remaining photolysate (around 50 mL) was passed through 500 mg capacity C18 solid-phase extraction (SPE) cartridges (Supelco, Bellefonte PA). Ethyl acetate (1 mL) was used to elute the cartridge via centrifugation. After drying, the ethyl acetate was examined for *N*-methylaniline using GC/MS.

RESULTS AND DISCUSSION

Aqueous Stability. Over a 12 day period there was no significant decrease in the original MCA present. MCA was considered hydrolytically stable within the time course of all photolysis treatments.

Table 1. Pseudo-First-Order Kinetic Data for the Photolysis of Chloroacetanilides under Various Treatments

treatment	chloroacetanilide	rate constant (h^{-1})	half-life (h)	$(R^2)^a$
pH 7	metolachlor	0.00946	73.3	0.999
pH 9	metolachlor	0.00942	73.6	0.915
H_2O_2/HCO_3^-	metolachlor	0.288 ± 0.033 ($n = 3$)	2.41 ± 0.13 ($n = 3$)	0.989
Don River water	metolachlor	0.0588	12.4	0.998
synthetic field water (SFW)	metolachlor	0.0895 ± 0.014 ($n = 4$)	7.74 ± 1.2 ($n = 4$)	0.979
SFW	alachlor	0.0780	8.89	0.999
SFW	butachlor	0.0618	7.96	0.969
SFW	2-chloro-*N*-methyl-acetamide	0.0870	11.2	0.982

[a] Coefficient of determination.

Photodegradation of Chloroacetanilides. All treatments were undertaken to elucidate those environmental conditions that may provide a large yield of MCA as a product of chloroacetanilide photodegradation. Regression analysis showed that in all treatments, the photolysis followed pseudo-first-order kinetics with respect to the herbicide concentration (Table 1). In deionized water, the photodegradation of metolachlor appeared to be independent of the pH, indicating similar degradation mechanisms. Introduction of naturally occurring species such as nitrate, bicarbonate, hydrogen peroxide, and dissolved organic carbon within the same pH range had a significant kinetic effect. The half-life of metolachlor in H_2O_2/HCO_3^- treatment decreased by approximately a factor of 30. Dark control experiments show no degradation of the parent compound. In SFW, the half-life of metolachlor decreased by close to a factor of 9 compared to the deionized water treatments.

Sample Preparation. The method of Reimann et al. (1996) proved reliable for the determination of MCA in the deionized water treatments. Several variations of the method were attempted in order to obtain acceptable recoveries for the SFW and H_2O_2/HCO_3^- treatments. Low recoveries seen for the unmodified derivatization method are believed to be a result of the high levels of carbonate/bicarbonate anions in these two treatments. That is, the anions competed with MCA for active sites on the SAX cartridges. To remedy the competition, each modification was designed to provide more sites on the cartridges for the eluting species. Recovery results and descriptions of each modification are shown in Table 2. Reducing the pH to 5 and degassing the samples should have driven off most of the carbonate as CO_2; however, persistent low recovery following modification number could be attributed to competition on the SAX cartridge between MCA and Cl^- (from the HCl used for acidification).

The second modification of the method was also unsuccessful in improving the recovery of MCA from photolysate matrixes, possibly due to problems with eluting MCA off the larger capacity cartridge. That is, we found that while they surely provide more sites for the eluting species, the recovery of 2 mL acidified propanol from the 2500 mg cartridges was not quantitative. Returning to the use of the smaller cartridges and reducing the volume of photolysate extracted (modification number 3) did provide acceptable recoveries (>80%) for the SFW matrix; however, so far, we have been unsuccessful in determining a method that will provide acceptable recoveries for the H_2O_2/HCO_3^- matrix.

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Table 2. Results from Spike and Recovery Experiments Conducted for Method Development of Monochloroacetic Acid (MCA) Extraction Procedure (Frank et al., 1996) from Photolysate of Chloroacetanilides

|	method description	treatment	recovery (%)	std dev (range when $n = 2$)	N
unmodified		pH 7/pH 9	81.7	16	3
modified (1):	acidify (pH 5) and degas photolysate	SFW	33.6	2.0	3
		H_2O_2/HCO_3^-	negligible		2
modified (2):	acidify (pH5) and degas photolysate large capacity (2500 mg) SAX cartridge reduce sample volume to 50 mL	SFW	18.2	3.1	5
		H_2O_2/HCO_3^-	31.2	1.3	2
modified (3):	acidify (pH 5) and degas photolysate reduce sample volume to 40 mL	SFW	82.0	5.9	3
		H_2O_2/HCO_3^-	37.5	8.4	2

Table 3. Monochloroacetic Acid (MCA) Production Data from the Photolysis of Chloroacetanilides under Various Photolysis Treatments

chloroacetanilide	treatment	MCA[a]	std dev	n[a]
metolachlor	pH 7	5.66	0.83	3
metolachlor	pH 9	4.38	0.73	3
metolachlor	Don River water	12.6	4.1	3
metolachlor	synthetic field water (SFW)	29.3	4.2	3
alachlor	SFW	50.5	18.2	2
butachlor	SFW	38.9	14.7	3
2-chloro-*N*-methyl-acetamide	SFW	46.8	3.4	3

[a] MCA was calculated as the percent of the degraded parent chloroacetanilide at each of three time points (n indicates the number of time points) over the course of the photolysis treatment.

MCA Analysis. Comparison of the standard curves of each of the derivatized acid and the synthesized ester indicated that the derivatization efficiency of the method was not 100%. Preparing standards according to the same method as photolysate samples accounts for any discrepancy. Table 3 shows the results from the determination of MCA in each photolysis treatment. MCA, as a percent of the parent chloroacetanilide degraded at each of three time points, was calculated and expressed as an average ± one standard deviation.

Direct Photodegradation Experiments. It was found that in pH 7 and pH 9 deionized water, MCA was a minor photoproduct of metolachlor. It is probable that the mechanism for the production of MCA in pH 7 and pH 9 deionized water treatment proceeds via a photoinduced base catalyzed anilide hydrolysis mechanism. The hydrolysis of chloroacetanilides such as metolachlor and alachlor under nonphotolytic conditions does not proceed to a significant extent (Chiron et al., 1995). Hydrolysis studies of anilides conducted by Biechler and Taft (1957) suggest that a significant activation energy requirement exists for the decomposition of the tetrahedral intermediate formed upon addition of hydroxide ion to the carbonyl of the anilide. Under photolytic conditions, however, MCA is produced, thus providing evidence that hydrolysis does occur. Hydrolysis presumably occurs since the absorption of light has created an excited state intermediate that now possesses enough energy to undergo loss of the anilide moiety, disrupting the tetrahedral geometry (Figure 1). It follows that the similarity in production of MCA at pH 7 and pH 9 arises from the fact that the rate-determining step for the hydrolysis mechanism is the degradation of the tetrahedral intermediate (consistent with a high activation barrier), and not initial attack by the hydroxide anion. We have shown that within an environmentally relevant pH range, MCA has the potential to arise as a result of direct photolysis of metolachlor.
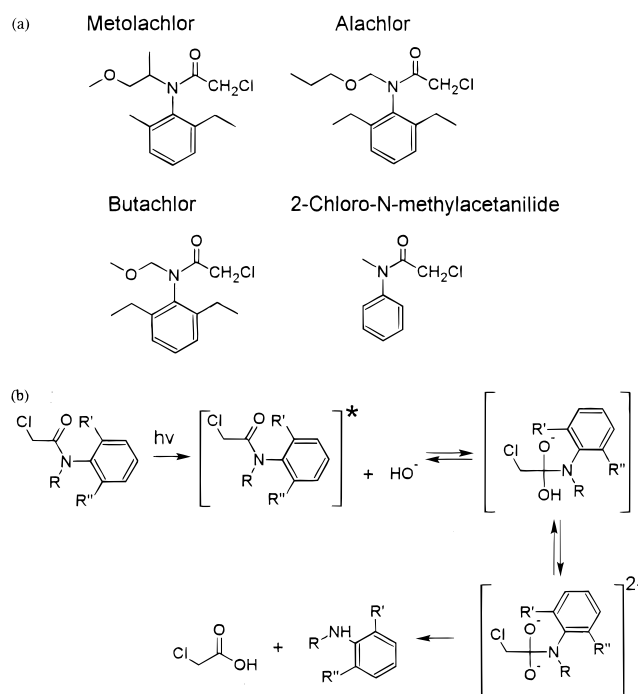
Figure 1. (a) Structures of the four chloroacetanilides investigated. (b) Photoinduced hydrolysis is the proposed mechanism for the production of monochloroacetic acid (MCA) from chloroacetanilides in deionized water at pH 7 and pH 9.

Indirect Photolysis Experiments. Naturally occurring species such as nitrate, bicarbonate, hydrogen peroxide, and dissolved organic carbon (DOC) are expected to have an effect on the mechanism and the yield of MCA. Each species has a specific contribution to the constitution of natural water. The role of nitrate in natural water has largely been shown as a primary source of the hydroxyl radical (Zepp et al., 1987). Zepp et al. (1987) have claimed that nitrate in naturally occurring water can range from <0.1 mM up to 10 times in extreme cases where a water body receives large inputs of groundwater rich in nitrate. Hydrogen peroxide also produces hydroxyl radicals upon irradiation but is considered secondary to nitrate in this regard largely based upon the low UV absorption and slow formation rate of H_2O_2 in the environment (Haag and Hoine, 1985).

Bicarbonate and dissolved organic carbon (DOC), the two remaining natural water constituents involved in this investigation, play slightly different roles than nitrate and hydrogen peroxide. Although DOC can produce radicals upon irradiation, bicarbonate and DOC can both act as scavengers of photoproduced radicals. Concentrations greater than 1 mM of carbonate or bicarbonate are considered high carbonate waters (Mo-
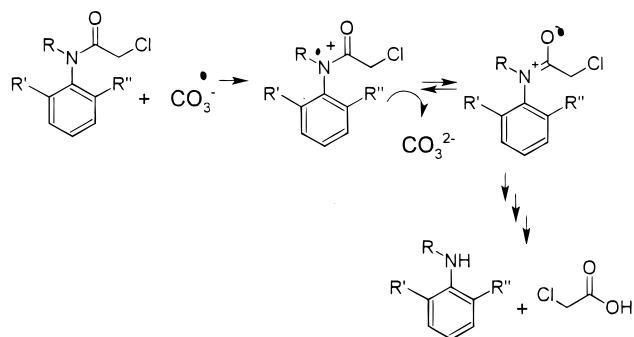
Figure 2. Proposed scheme for the production of monochloroacetic acid (MCA) from chloroacetanilides in the presence of a carbonate radical.

rel and Hering, 1993), while DOC typically exists in fresh water within the range 0.5−25 mg of C/L (Larson and Zepp, 1988).

It was our intention to examine the effect of indirect photolysis on the production of MCA from the parent chloroacetanilide. Two matrixes were chosen to suit this purpose. First, the H_2O_2/HCO_3^- solution was used to provide an extreme case of high carbonate radical in order to survey the effect of this secondary sunlight radical on the overall production of MCA from chloroacetanilides. Upon irradiation, 3 mM H_2O_2 produces hydroxyl radicals that are quickly scavenged by excess bicarbonate (0.092 M) to form the bicarbonate radical. The pH of the solution was 8.23−8.30, while the pK_a of the carbonate radical has been shown to lie between 7.0 and 8.2 (Eriksen and Lind, 1985), indicating that the carbonate radical will dominate in the photolysis matrix. Second, the purpose of using a SFW solution was to provide a matrix high in carbonate radical produced in this case by environmentally realistic concentrations of species likely to be present in a natural water sample. Upon irradiation, nitrate (0.5 mM) produces hydroxyl radicals that are scavenged by bicarbonate (3.6 mM) to produce the carbonate radical (pH of SFW matrix: 8.3). Table 3 shows that in SFW the production of MCA is a major pathway for the photodegradation of four chloroacetanilides; however, due to the difficulty of analyzing MCA in H_2O_2/HCO_3 we have not been able to accurately represent the amount of MCA produced in this particular matrix.

We were specifically interested in exposing chloroacetanilides to carbonate radical since Larson and Zepp (1988) and Elango et al. (1984) have postulated that the rate limiting step for the reaction of carbonate radicals with aniline type compounds is electron transfer from the aniline to the carbonate radical. Based on this premise, a scheme for the production of MCA from metolachlor has been proposed (Figure 2). It is entirely possible that carbonate radical is not the only species responsible for the initial electron transfer; in SFW and in natural water samples, carbonate radicals, hydroxyl radicals, and alkylperoxy radicals may all be present and capable of initiating the first step to the production of MCA.

Our proposal for the initial step in going from the chloroacetanilide to MCA has been supported elsewhere; Pignatello and Sun (1995) showed that MCA was a major photoproduct of metolachlor using the photoassisted Fenton reaction. While this type of system is not naturally occurring, the conditions used and results obtained help to provide insight as to the possible mechanism for the production of the acid. That is, the
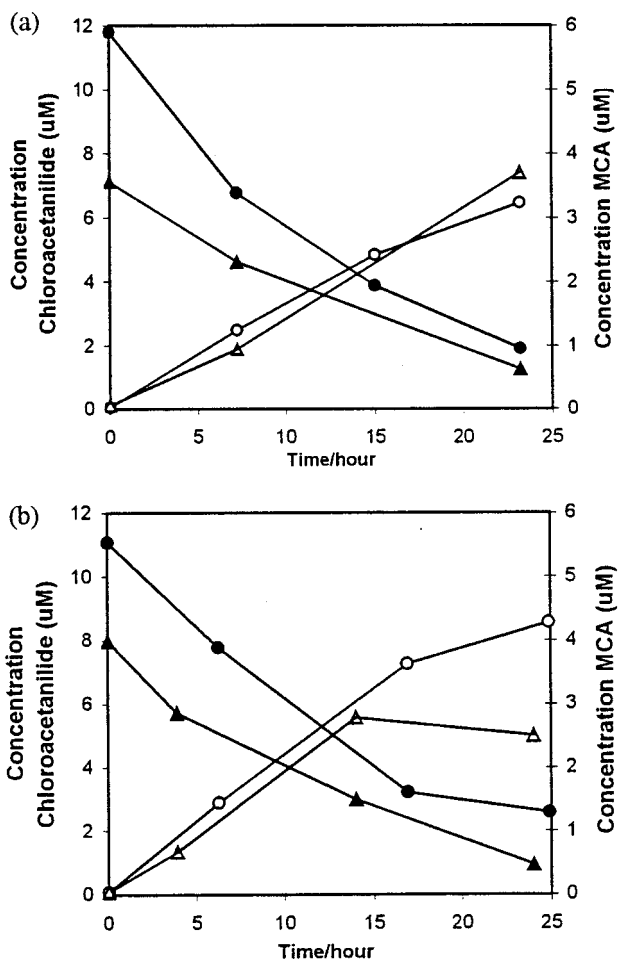
photodegradation of metolachlor was carried out using $Fe^{3+}/H_2O_2/UV$ and also using the same conditions without H_2O_2. In the absence of H_2O_2, MCA was plotted as a photoproduct and was shown to reach an approximate 40% yield. The reaction of metolachlor under these conditions was thought to be due to charge-transfer photolysis of $Fe^{3+}(aq)$, which is consistent with our hypothesis. That is, the photodegradation of metolachlor in SFW and using modified photo-Fenton conditions are believed to proceed via an initial photolytically induced electron transfer giving a consistently large yield of MCA throughout the course of the photodegradation.

Evidence to support the initial step of our mechanism is also provided in the work done by Chan et al., (1992) in an experiment investigating the degradation of atrazine by hydroxy radicals. They similarly propose that the fission of *N*-alkyl groups begins with one-electron oxidation and have conducted a number of experiments that strongly support this hypothesis.

Metolachlor was irradiated in a sample of Don River water. Table 3 shows that in a natural water sample, the production of MCA is intermediate to that in SFW and in deionized water. The results obtained are also consistent with the hypothesis; that is, the natural water sample contains less nitrate and bicarbonate and close to 10 times the amount of DOC. Reduced amounts of nitrate and bicarbonate ultimately result in lower concentrations of carbonate radical. As well, a large increase in DOC concentration may also decrease levels of radical species due to scavenging.

Structural Investigation. Having established that MCA is a major photoproduct of metolachlor in synthetic field water, we attempted to elucidate whether the structure of the chloroacetanilide would be a factor in the yield of MCA. The kinetic data from the photolysis of alachlor, butachlor, and a model chloroacetanilide (2-chloro-*N*-methylacetanilide), as well as the production data for MCA are given in Tables 1 and 3, respectively. Figure 3 allows the comparison of all four chloroacetanilides concerning parent degradation and MCA production. On the basis of the assumption that all SFW treatments showed similar precision, it appears that metolachlor, alachlor, and butachlor all photodegrade at comparable rates. Conversely, the photodegradation of the model chloroacetanilide (2-chloro-*N*-methylacetanilide) is slower, with a half-life approximately 39% greater than the average of the other three. Table 3 shows that among the four chloroacetanilides, MCA production varies from 29.3% to 50.5% of the parent chloroacetanilide. Only metolachlor and the model were significantly different from one another since the precision for alachlor and butachlor places them rather ambiguously.

It has been argued that the presence of electron donating substituents on the nitrogen atom of anilines results in a more rapid reaction with the carbonate radical (Larson and Zepp, 1988). In addition, the model compound lacks any type of side chain on the aryl ring, thus decreasing electron donation to the ring. Removal of alkyl side chains will reduce the occasion of several previously established photodegradation products formed from processes such as oxoquinoline formation, ring hydroxylation, and oxidation of aryl side chains (Somich et al., 1988; Schmidt et al., 1995; Moza et al., 1992; Pignatello and Sun, 1995). Since there are fewer overall degradation pathways available to the model and the

Figure 3. Absolute production of monochloroacetic acid and the photodegradation over time of chloroacetanilides. (a) The photodegradation of metolachlor and alachlor and the production of MCA from each: (●) metolachlor; (○) MCA from metolachlor; (▲) alachlor; (△) MCA from alachlor. (b) Photodegradation of butachlor and the model 2-chloro-*N*-methyl-acetanilide and the production of MCA from each: (●) model; (○) MCA from model; (▲) butachlor; (△) MCA from butachlor.

nitrogen atom of the model is less sterically hindered than that of metolachlor, it follows that the overall rate of photodegradation of the model compound is slower and leads to increased MCA production in comparison with metolachlor, alachlor, and butachlor.

To support the proposed mechanism for the degradation of chloroacetanilides, we thought it prudent to identify the complementary anilide product (refer to Figure 1b). The model was chosen for this analysis since it had the largest yield of MCA. *N*-Methylaniline was successfully identified in the photolysate of the model using GC/MS.

CONCLUSIONS

In this study, we have examined the photodegradation of four chloroacetanilides and found that monochloroacetic acid was a major photoproduct in each case following the photodegradation of the parent compound in synthetic field water. The significance of such a finding is that MCA is phytotoxic and, under the conditions of this experiment, is more persistent than the parent compound. The matrix in which the photolysis occurs influences the mechanism and extent of production of the acid. Certain structural features may

also play a role in the yield of MCA. This investigation supports the premise that photolysis of chloroacetanilide herbicides has the potential to be a significant source of MCA in the natural environment.

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