Photodegradation of Metolachlor in Water in the Presence of Soil Mineral and Organic Constituents[†]

Regi Mathew* and Shahamat U. Khan

Centre for Land and Biological Resources Research, Research Branch, Agriculture and Agri-Food Canada, Ottawa, Ontario, Canada K1A 0C6

Photodegradation of metolachlor [2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl)-acetamide] at 253.7 nm was carried out in water containing soil minerals (kaolinite, montmorillonite, and goethite) and fulvic acid under two different pH conditions. The rate of photolysis was dependent on the nature of the soil constituents and the initial pH of the medium. Based on the regression analysis, it was shown that the photodegradation followed the first-order kinetics with respect to the metolachlor concentration, and the half-life of the herbicide under UV irradiation was longer in the absence of soil constituents. Hydroxylation, dehalogenation, oxoquinoline formation, and demethylation were the main processes observed during the photolysis of metolachlor. More degradation products were formed in the presence of kaolinite, montmorillonite, and goethite than with fulvic acid and water alone. The major degradation product formed under UV irradiation in all the treatments was identified as 4-(2-ethyl-6-methylphenyl)-5-methyl-3-morpholine.

Keywords: *Photodegradation; metolachlor; soil minerals; fulvic acid; degradation products*

INTRODUCTION

Metolachlor [2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl)acetamide] is one of the most widely used herbicides for the control of grasses in many crops (Lebaron et al., 1988; Chesters et al., 1989). Although metolachlor is not registered as an aquatic herbicide, its residues carried from terrestrial applications are reported in surface waters and groundwater (Frank and Logan, 1988; Maguire and Tkacz, 1993; Richards and Baker, 1993). When it reaches the various aquatic systems without transformation/degradation to less toxic products, the herbicide may pose a threat to our environment. Generally, volatilization, hydrolysis, and photolysis are the major chemical transformation pathways of a pesticide in aqueous solution. Among these, photolysis is known to be the important degradation pathway for metolachlor in water under normal conditions (Kochany and Maguire, 1994).

Natural waters contain a variety of dissolved, colloidal, and suspended organic and mineral constituents from soil. Therefore, a part of the pesticides present in the aquatic systems will be associated with these materials. In addition, metolachlor is a soil-applied pesticide with a relatively high sorption affinity for soil and various soil organic and mineral constituents (Obrigawitch et al., 1981; Bouchard et al., 1982; Weber and Peter, 1982; Kozak et al., 1983; Peter and Weber, 1985; Wood et al., 1987). Hence, it is possible that a major part of the soil-applied metolachlor reaching the natural waters through leaching and surface runoff is adsorbed on the soil mineral and organic constituents.

Soil organic and inorganic materials may influence the photolysis of chemicals in water in different ways. They may reduce the photolysis by quenching the excited states of organic molecules or by shielding them from incident radiation (Oliver et al., 1979). These materials may accelerate the photodegradation by energy transfer reactions, by photoinduced oxidation, or by efficient light scattering (Miller and Zepp, 1979a;

Katagi, 1991; Larson et al., 1991; Kochany, 1992; Katagi 1993). It is possible that some of the degradation products thus formed in the presence of soil constituents may be nontoxic or less toxic to the aquatic organisms. Therefore, this experiment was undertaken to study the photodegradation of metolachlor in water in the presence of soil mineral and organic constituents at different pH values. Various degradation products formed under UV irradiation were also identified, and regression analysis was carried out to determine the order of reaction.

MATERIALS AND METHODS

Materials. Analytical standards of metolachlor and degradation products were gifts from Ciba-Geigy Co. (Greensboro, NC). All the organic solvents used in this study were of HPLC grade.

The organic constituent and soil minerals used in this study were as follows: (i) Fulvic acid originated from the B_h horizon of a Podzol soil in Prince Edward Island, Canada. Methods of extraction, purification, and functional group analysis were the same as those described by Schnitzer and Skinner (1968) and Gamble (1972). It contained 1.0% ash, 50.9% C, 3.3% H, 0.7% N, 0.3% S, and 44.7% O on a moisture- and ash-free basis. Functional group analysis showed the presence of COOH (5.0 mequiv/g), phenolic OH (3.3 mequiv/g), alcoholic OH (3.6 mequiv/g), C=O (0.6 mequiv/g), and OCH$_3$ (2.5 mequiv/g) groups. (ii) Montmorillonite mineral from Wyoming (4.4% Fe as Fe_2O_3 and 0.15% Ti as TiO_2). (iii) Kaolinite from Georgia (0.35% Fe as Fe_2O_3 and 1.26% Ti as TiO_2). (iv) Goethite from Biwabik, MN (2–5 μm size; 86.04% Fe as Fe_2O_3).

Adsorption Study. Adsorption of chemicals to clays during photolysis may interfere with the kinetics of photodegradation (Zepp and Schlotzhauer, 1981). Therefore, the extent of metolachlor adsorption on various soil constituents prior to photolysis was determined. Fulvic acid was dissolved, minerals were suspended in 10 mL of deionized water for 8 h, and metolachlor stock solution (300 mL) was added to the mineral (0.05% w/v) suspensions and fulvic acid (0.01% w/v) solution to get a final concentration of 30 μg of metolachlor/mL. The samples were shaken over a reciprocating shaker for 12 h in the dark. Metolachlor in water was also shaken for 12 h in the dark prior to the photolysis experiment. In one set of experiments, the initial pH of the medium before and after

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Table 1. Initial pH and Amount of Metolachlor Adsorbed (mg/100 mg of Adsorbate), Partition Coefficient (K_d, mL/g) of Adsorption, and Rate Constants (min), Half-Life (h), and Covariance of Metolachlor Photodegradation in Different Treatments

treatment	initial pH	amount adsorbed	K_d	photodegradation rate constant ($\times 10^{-3}$)	half-life	covariance[a]
water	5.35[b]			7.76	1.49	12.9
water	7.00			4.48	2.58	9.66
FA	3.46[b]	19.7 (1.44)[c]	0.071 (0.001)	9.05	1.28	69.1
FA	7.00	15.6 (0.28)	0.055 (0.01)	9.89	1.17	64.8
MON	5.47[b]	13.4 (0.17)	0.047 (0.001)	11.2	1.03	27.3
MON	7.00	8.68 (0.50)	0.030 (0.003)	8.09	1.43	23.2
KAO	5.54[b]	12.2 (0.31)	0.043 (0.002)	8.82	1.31	23.7
KAO	7.00	7.42 (0.25)	0.025 (0.001)	9.00	1.28	21.1
GEO	4.41[b]	1.96 (0.16)	0.007 (0.000)	9.69	1.19	31.8
GEO	7.00	0.74 (0.08)	0.002 (0.001)	8.46	1.37	19.4

[a] Covariance of the linearized form of metolachlor degraded. Abbreviations: FA, fulvic acid; MON, montmorillonite; KAO, kaolinite; GEO, goethite. [b] Unadjusted pH. [c] Standard error of mean.

shaking with metolachlor was adjusted to 7.00 ± 0.02, using 0.01 N NaOH or HCl. In the other set, the initial pH was not adjusted after adding metolachlor. Determination of metolachlor concentration in the solution at regular intervals showed that the amount of metolachlor adsorbed remained constant after 8–10 h of reaction. Therefore, at the end of 12 h of shaking, a 25-mL aliquot was taken from all the treatments and centrifuged at 14000g for 20 min, and the supernatant was used for determining the concentration of metolachlor. The amount of metolachlor adsorbed to each adsorbate is estimated by subtracting the final solution concentration from the initial concentration. The starting concentration in each treatment at the beginning of the photolysis study is the amount of metolachlor present after the adsorption. Partition coefficient of metolachlor adsorption is determined as the ratio of the amount adsorbed to the concentration in the equilibrium solution.

Photolysis Study. About 150 mL of metolachlor in deionized water and fulvic acid solution or mineral suspensions at the end of the adsorption study were transferred to a 200-mL pear-shaped necked flask and photolyzed under UV light for a period of 6 h. For photolysis, the light source used was a UV Pen Ray Lamp (Model II, SC-IL, 5.5 W, manufactured by Ultraviolet Products, Inc., San Gabriel, CA) with the 253.7-nm line comprising 92% of the total irradiation. The Pen Ray Lamp was inserted into the solution or suspension through the neck of the reaction flask, and the apparatus was placed in a dark room. The temperature of the irradiation solution was maintained at 22 ± 2 °C by circulating water. A magnetic stirrer was used to agitate the solutions or suspension during irradiation. The control experiment was conducted in a similar manner in the dark for all the treatments. An aliquot (15 mL) at 0, 15, 30, 60, 120, 240, and 360 min of irradiation was withdrawn for the determination of metolachlor using high-pressure liquid chromatography (HPLC) and for the identification of photodegradation products by gas chromatography–mass spectrometry (GC–MS). After 6 h of photodegradation, the amount of metolachlor remaining for further photodegradation was negligible. Therefore, photodegradation during the 6-h period was taken for treatment comparison. All experiments were carried out in duplicate.

High-Pressure Liquid Chromatography. Samples for the determination of metolachlor were obtained by centrifuging the minerals and fulvic acid from the photolyzed mixture (14000g, 15 min), and an aliquot (25 μL) of the supernatant was injected directly into a HPLC pump (Waters 501). The column was a Beckman Ultrasphere ODS 5 μm (25 cm long × 4.5 mm i.d.) and was preceded by a adsorbosphere C18 5μm guard column. Methanol–water (80/20 v/v) was used as the eluting solvent at a flow rate of 1 mL/min. Varian Model 9050 UV detector was used for measuring the absorbance at 220 nm. Under these conditions, the retention times for metolachlor, 4-(2-ethyl-6-methylphenyl)-5-methyl-3-morpholine), 8-ethyl-3-hydroxy-*N*-(2-methoxy-1-methylethyl)-2-oxo-1,2,3,4 tetrahydroquinoline, and 2-hydroxy-*N*-(2-ethyl-6-methyl-phenyl)-*N*-(2-methoxy-1-methylethyl)acetamide were 6.7, 4.6,

1.9, and 3.7 min, respectively. Furthermore, the lower limit of detection for metolachlor under the above HPLC conditions was 0.1 μg/mL, and for the metabolites it ranged from 0.1 to 0.8 μg/mL. The amount of these compounds was calculated on the basis of the peak areas obtained with standardized authentic samples analyzed under the same HPLC conditions.

Gas Chromatography. For the GC–MS analysis, an aliquot (3 mL) of the supernatant was taken to dryness under reduced pressure at room temperature, and the residue was dissolved in 50 μL of methanol. Electron impact (EI) mass spectra were recorded on a Finnigan MAT 4500 instrument coupled to an INCOS data system. A DB-5 column (12m × 0.32 mm i.d.; 1 μm film thickness) was used. The column temperature was programmed from 100 to 280 °C at a rate of 15 °C/min. The inlet temperature was 250 °C. The flow rate of helium carrier gas was 1 mL/min, and the inlet pressure was 10 psi. For the EI mass spectrum, the electron energy was set at 70 eV and a source temperature of 190 °C. The scan range was 30–500 amu. The identity of the photodegradation products was confirmed by comparing the HPLC retention times with those of the available authentic samples, by co-chromatography, and by GC–MS.

Statistical Analysis of Data. Based on R^2 values, the first-order kinetic equation was used to depict the photodegradation of metolachlor. The integrated form of the first-order kinetic equation (Atkins, 1994) is

$$[C_t] = [C_0]e^{-kt}$$

where t is time (min), $[C_0]$ is the metolachlor concentration at time 0, $[C_t]$ is the metolachlor concentration at time t, and k is the rate constant (min). Half-life ($t_{1/2}$) of photodegradation is determined from the rate constants (k).

Covariance analysis was used to measure the joint variation of UV irradiation and the presence of soil constituents on photodegradation. It was done on the linearized form (log transformation) of the metolachlor degraded at different times of UV irradiation for all the treatments.

RESULTS AND DISCUSSION

Adsorption. The extent of the adsorption of metolachlor varied with the nature of the adsorbate and the initial pH of the adsorbing medium (Table 1). Sorption was higher at the unadjusted pH values than at pH 7 in all the treatments. Among the various treatments, fulvic acid adsorbed the highest amount of metolachlor at both pH values, and adsorption on the goethite surface was relatively very small. The partition coefficient (K_d) was higher for fulvic acid treatments than others at both pH values (Table 1).

The higher K_d in the fulvic acid solution indicates that the added metolachlor was retained with greater affinity than when montmorillonite or kaolinite were present.
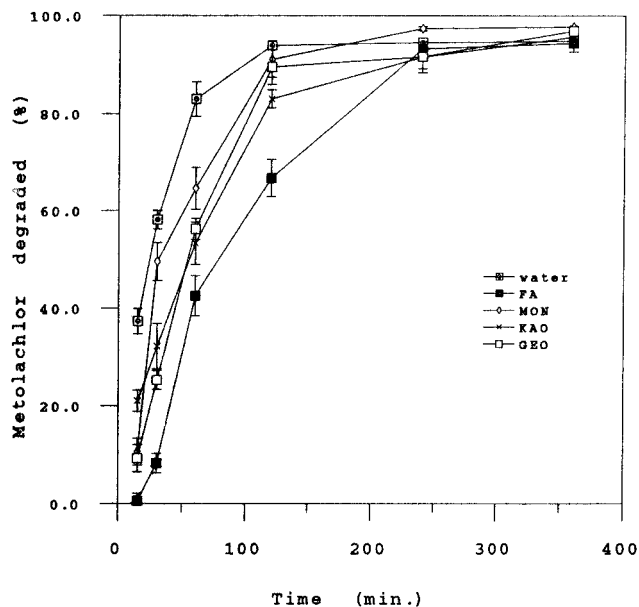
Figure 1. Influence of various treatments on the percentage of metolachlor photodegraded at different times of UV irradiation (pH not adjusted).

Figure 2. Influence of various treatments on the percentage of metolachlor photodegraded at different times of UV irradiation (pH 7).

Higher amount of metolachlor adsorbed from the montmorillonite suspension than from kaolinite suspension suggests that some of the metolachlor is also adsorbed on the interlayer surfaces of montmorillonite. Webber and Peter (1982) showed that the metolachlor is adsorbed to the Ca-saturated montmorillonite surfaces by coordination between the carbonyl oxygen atoms of metolachlor and the positively charged mineral surface. It is adsorbed by the fulvic acid involving hydrogen bonding and through charge transfer bonds between the aromatic nucleus of metolachlor and the aromatic rings at fulvic acid surface (Kozak et al., 1983). The number of positive sites in montmorillonite, kaolinite, and goethite surfaces is higher at lower pH (Bohn et al., 1979). This results in more binding between the carbonyls of metolachlor and the positive sites at clay surfaces at lower pH values. As a result, it is adsorbed more on the inorganic constituents at unadjusted pH values than at pH 7.

Photolysis. On exposure to UV light, a major part of the added metolachlor was photodegraded at both pH conditions in all the treatments (Figures 1 and 2). However, the rate of photolysis and the degradation products formed were dependent on the duration of UV irradiation, the initial pH of the medium, and the nature of the suspended/dissolved material. Regression analysis showed that in all the treatments the photolysis followed the first-order kinetics with respect to the herbicide concentration (Table 1).

Covariance analysis showed that the presence of soil constituents in water during UV irradiation has greater impact on the photodegradation of metolachlor than in their absence (Table 1). Among the soil constituents, FA treatment had the highest covariance at both pH conditions, indicating greater interaction than the inorganic constituents for photodegradation. The percentage of metolachlor degraded during the initial 15-min period was greater in water alone than in the presence of soil constituents at both pH conditions (Figures 1 and 2). However, with increasing time of UV irradiation, the effect of soil constituents on the photodegradation became more pronounced. After 6 h of photolysis, the amount of metolachlor degraded was
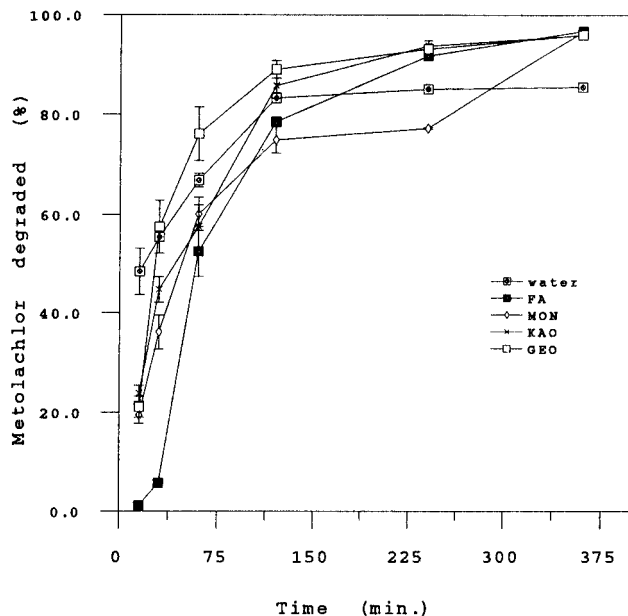
more in the presence of soil minerals and fulvic acid than with water alone at pH 7. When the original pH was not adjusted, the amount of metolachlor degraded in the 6-h period was more than 94% in all the treatments. The lowest degradation of metolachlor in the first 1-h period of UV irradiation occurred in the fulvic acid treatments at both pH conditions.

The rate of photodegradation of metolachlor in water alone, montmorillonite, and goethite treatment was higher when the initial pH was not adjusted (Table 1). Under both pH conditions, the half-lives of photodegradation was longer in the absence of soil constituents (Table 1). For example, the calculated half-life in water alone at pH 7 was 2.58 h, and at unadjusted pH condition, it was 1.49 h. The shortest half-life at pH 7 was in fulvic acid treatment (1.17 h), and at unadjusted pH, it was in montmorillonite treatment (1.03 h).

The loss of metolachlor from various treatments under UV irradiation was mainly attributed to photodegradation because of the following reasons: (1) transformation of metolachlor in the dark due to hydrolysis was negligible; (2) before starting the photolysis experiment, metolachlor was adsorbed to the soil constituents, and therefore the possibility of loss of pesticide from solution due to continuous adsorption to the soil constituents is ruled out. Metolachlor adsorbed on the clay surface as well as that present in the bulk water phase may affect the photolysis as shown for other pesticides (Miller and Zepp, 1979a; Katagi, 1990). However, no differentiation was made in this study to find the effect of adsorbed metolachlor and that present in the bulk solution on the photolysis rate and the nature of the photoproducts formed. The rate of photolysis in this study constituted that from the bulk solution and the metolachlor adsorbed on the surface of soil constituents.

The initial slow degradation of metolachlor (15 min) in the presence of soil constituents might be due to their light shielding effect (Oliver et al., 1979). Also, the 15 min of UV irradiation may not be enough for the intensive indirect photochemical reactions that occur in the presence of soil suspended sediments (Katagi, 1990). This initial light shielding effect was more with fulvic acid than with other inorganic constituents. However,

Table 2. Relative Distribution of Photoproducts (%) Formed at Different Times of UV Irradiation (Initial pH Not Adjusted)

photoproducts	water (%)	FA (%)	MON (%)	KAO (%)	GEO (%)
At 15 Minutes					
P1	18.8	−[a]	−	9.80	−
P2	37.5	100	100	76.5	31.9
P3	12.9	−	−	−	52.2
P4	−	−	−	−	−
P5	−	−	−	−	−
At 30 Minutes					
P1	18.2	−	3.1	9.5	−
P2	33.3	100	47.7	57.9	32.8
P3	6.1	−	4.6	4.2	36.0
P4	−	−	−	9.5	4.8
P5	−	−	−	−	12.8
At 60 Minutes					
P1	13.8	−	−	7.03	3.07
P2	53.8	94.4	50.0	59.4	26.6
P3	3.08	−	3.91	7.03	32.0
P4	−	−	4.69	−	4.78
P5	−	−	4.69	−	21.8
At 120 Minutes					
P1	3.2	−	−	−	1.66
P2	83.9	97.7	50.8	82.2	31.5
P3	6.5	−	2.09	5.93	36.5
P4	−	−	5.76	8.89	4.56
P5	−	2.31	12.1	−	24.5
At 240 Minutes					
P1	80.0	−	7.41	−	2.13
P2	20.0	96.9	49.7	53.0	28.6
P3	−	−	2.12	3.28	35.6
P4	−	−	8.99	9.84	4.86
P5	−	3.08	−	−	21.6
At 360 Minutes					
P1	25.6	−	4.9	22.6	2.26
P2	74.4	100	48.2	67.8	26.8
P3	−	−	−	−	40.4
P4	−	−	7.93	9.58	4.15
P5	−	−	−	−	18.9

[a] −, not detected

Table 3. Relative Distribution of Photoproducts (%) Formed at Different Times of UV Irradiation (Initial pH at 7)

photoproducts	water (%)	FA (%)	MON (%)	KAO (%)	GEO (%)
At 15 Minutes					
P1	−	−	−	7.58	−
P2	75.0	100	80.8	63.6	45.8
P3	25.0	−	19.2	9.09	35.4
P4	−	−	−	−	−
P5	−	−	−	−	−
At 30 Minutes					
P1	14.8	−	−	8.60	2.35
P2	70.4	91.4	92.7	67.7	38.8
P3	14.8	8.62	7.32	6.45	49.4
P4	−	−	−	−	−
P5	−	−	−	−	4.71
At 60 Minutes					
P1	−	−	−	4.86	1.33
P2	83.6	86.2	97.1	56.2	50.0
P3	−	4.62	2.94	3.24	30.0
P4	16.4	−	−	−	7.33
P5	−	9.23	−	24.9	7.33
At 120 Minutes					
P1	13.9	4.35	−	2.50	4.29
P2	86.1	95.7	89.7	54.7	53.4
P3	−	−	10.3	7.40	22.1
P4	−	−	−	7.88	4.29
P5	−	−	−	23.7	12.9
At 240 Minutes					
P1	−	6.66	−	−	4.14
P2	100	100	90.0	100	65.5
P3	−	−	3.33	−	−
P4	−	−	−	−	4.14
P5	−	−	−	−	26.2
At 360 Minutes					
P1	15.8	−	11.8	11.9	7.60
P2	84.4	100	85.3	80.4	40.0
P3	−	−	2.94	−	29.1
P4	−	−	−	7.70	5.70
P5	−	−	−	−	−

[a] −, not detected.

with increasing time of UV irradiation, the light shielding effect of fulvic acid decreased. When fulvic acid is UV irradiated, the solution turned colorless. Khan and Schnitzer (1978) found that irradiation of fulvic acid results in the destruction of the phenols that are the chromophores that give fulvic acid solutions their distinctive color. Therefore, once the phenolic hydroxyls are destroyed by UV irradiation in this experiment, more of the adsorbed metolachlor (metolachlor forms H bonds with the phenolic groups) is released into the bulk solution for further direct photodegradation. This results in a higher photodegradation of metolachlor with time in the presence of fulvic acid. While, as the time of UV irradiation increased, the light shielding effect of the suspended inorganic constituents was overcome by light scattering effect and/or by various photochemical reactions (Miller and Zepp, 1979b). This was clear from the increased photolysis of metolachlor in the presence of inorganic constituents after 15 min of UV irradiation. Iron and/or Ti present on the surfaces of montmorillonite, kaolinite, and goethite might have generated hydroxyl radicals and other active oxygen species that assisted in the increased rate of photodegradation of metolachlor (Fugihira et al., 1981; Katagi, 1989, 1990, 1992, 1993; Larson et al., 1991).

Photodegradation Products. The various photodegradation products identified were as follows: (1) 2-hydroxy-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl)acetamide, MW 265, [P1]; (2) 4-(2-ethyl-6-methylphenyl)-5-methyl-3-morpholine, MW 233, [P2]; (3) 8-ethyl-3-hydroxy-*N*-(2-methoxy-1-methylethyl)-2-oxo-1,2,3,4-tetrahydroquinoline, MW 263, [P3]; (4) 2-chloro-*N*-[2-(1-hydroxyethyl)-6-methylphenyl]-*N*-(2-hydroxy-1-methylethyl)acetamide, MW 285, [P4]; (5) 2-chloro-*N*-(2-ethyl-6-hydroxymethylphenyl)-*N*-(2-methoxy-1-methylethyl)acetamide, MW 299, [P5]. The number of photodegradation products formed were higher with inorganic constituents than with fulvic acid and water alone. In all the treatments, the major degradation product identified was P2. For example, after 6 h of photolysis, in water alone treatment, P2 constituted about 84% of the photodegradation products formed when the initial pH was 7, and it was 74% when the pH was not adjusted (Tables 2 and 3).

Hydroxylation, dehalogenation (dechlorination), oxoquinoline formation, and demethylation were the processes observed during the photodegradation of metolachlor in this study. P1, P2, and P3 were dechlorinated compounds. In P3, in addition to dehalogenation, oxoquinoline formation was observed. Formation of P1 and P2 was identified in earlier photolytic studies of metolachlor in water (Kochany and Maguire, 1994). P2 was also identified as a degradation product in bacterial cultures (Liu et al., 1989). P3 was identified as a fungal degradation product (McGahen and Tiedje, 1978). No dehalogenation occurred in the formation of P4 and P5. Benzylic hydroxylation occurred at methyl (P4) or at ethyl (P5) substituents. No change in *N*-alkyl and

N-chloroacetyl groups was found in P5. In P4, the methoxyl group of the *N*-alkyl substituent was demethylated, and a further hydroxylation of the ethyl group at the aromatic side chain occurred. P4 and P5 were identified as the degradation products in actinomycete cultures (Krause et al., 1985). The hydroxylated compounds have higher water solubility and are more easily degraded. Thus, hydroxylation occurring during photodegradation of metolachlor is associated with detoxification.

LITERATURE CITED

Atkins, P. W. The rates of chemical reactions. In *Physical Chemistry*; W. H. Freeman: New York, 1994; pp 870−872.

Bohn, H.; McNeal, B.; O'Connor, G. Anion and molecular retention. In *Soil Chemistry*; Wiley: New York, 1979; pp 171−187.

Bouchard, D. C.; Lavy, T. L.; Marx D. B. Fate of metribuzin, metolachlor and fluometuron in soil. *Weed Sci.* **1982**, *30*, 629−632.

Chesters, G.; Simsiman, G. V.; Levy, J.; Alhajjar, B. L.; Fathulla, R. N.; Harkin, J. M. Environmental fate of alachlor and metolachlor. In *Reviews of Environmental Contamination and Toxicology*; Ware, G. W., Ed.; Springer-Verlag: New York, 1989; Vol. 10, Chapter 1.

Frank, R.; Logan, L. Pesticides and industrial chemical residues at the mouth of the Grand, Saugeen and Thames Rivers, Ontario, Canada, 1981−1985. *Arch. Environ. Contam. Toxicol.* **1988**, *17*, 741−754.

Fujihira, M.; Satoh,Y.; Osa, T. Heterogeneous photocatalytic oxidation of aromatic compounds on TiO_2. *Nature* **1981**, *293*, 206−208.

Gamble, D. S. Potentiometric titration of fulvic acid: equivalence point calculations and acidic functional groups. *Can. J. Chem.* **1972**, *50*, 2680−2690.

Katagi, T. Molecular approaches to the photolysis of organophosphorus insecticide fenitrothion. *J. Agric. Food Chem.* **1989**, *37*, 1124−1128.

Katagi, T. Photoinduced oxidation of the organophosphorus fungicide tolclofos-methyl on clay minerals. *J. Agric. Food Chem.* **1990**, *38*, 1595−1600.

Katagi, T. Photodegradation of the pyrethroid insecticide esfenvalerate on soil, clay minerals and humic acid surfaces. *J. Agric. Food Chem.* **1991**, *39*, 1351−1356.

Katagi, T. Photodegradation of 3-phenoxybenzoic acid in water and on solid surfaces. *J. Agric. Food Chem.* **1992**, *40*, 1269−1274.

Katagi, T. Photodegradation of esfenvalerate in clay suspensions. *J. Agric. Food Chem.* **1993**, *41*, 2178−2183.

Khan, S. U.; Schnitzer, M. UV irradiation of atrazine in aqueous fulvic acid solution. *J. Environ. Sci. Health B13* **1978**, *3*, 299−310.

Kochany, J. Effects of iron(III) and manganese(II) ions on the aquatic photodegradation rate of bromoxynil (3,5-dibromo-4-hydroxybenzonitrile) herbicide. *Chemosphere* **1992**, *3*, 261−270.

Kochany, J.; Maguire, R. J. Sunlight photodegradation of metolachlor in water. *J. Agric. Food Chem.* **1994**, *42*, 406−412.

Kozak, J.; Weber, J. B.; Sheets, T. J. Adsorption of prometryn and metolachlor by selected soil organic matter fractions. *Soil Sci.* **1983**, *136*, 94−10.

Krause, A.; Hancock, W. G.; Minard, R. D.; Freyer, A. J.; Honeycutt, R. C.; Lebaron, H. M.; Paulson, D. L.; Liu, S, Y.; Bollag, J. M. Microbial transformation of the herbicide metolachlor by a soil actinomycete. *J. Agric. Food Chem.* **1985**, *33*, 584−589.

Larson, R. A.; Schlauch, B.; Marley, K. Ferric ion promoted photodecomposition of triazines. *J. Agric. Food Chem.* **1991**, *39*, 2057−2062.

Lebaron, H. M.; Mcfarland, J. E.; Simoneaux, B. J. Metolachlor. In *Herbicides: Chemistry, Degradation and Mode of Action*; Kearney, P. C., Kaufman, D. D., Eds.; Dekker: New York, 1988; Vol. 3, Chapter 7.

Liu, S. Y.; Zheng, Z.; Zhang, R.; Bollag, J. M. Sorption and metabolism of metolachlor by a bacterial community. *Appl. Environ. Microbiol.* **1989**, *55*, 733−740.

Maguire, R. J.; Tkacz, R. J. Occurrence of pesticides in the Yamasaka River, Quebec. *Arch. Environ. Contam. Toxicol.* **1993**, *25*, 220−226.

McGahen, L. L.; Tiedje, M. Metabolism of two new acylanilide herbicides, Antor herbicide (H-22234) and Dual (metolachlor) by the soil fungus *Chaetomium globosum*. *J. Agric. Food Chem.* **1978**, *26*, 414−419.

Miller, G. C.; Zepp, R, G. Photoreactivity of aquatic pollutants sorbed on suspended sediments. *Environ. Sci. Technol.* **1979a**, *13*, 860−863.

Miller, G. C.; Zepp, R. G. Effects of suspended sediments on photolysis rates of dissolved pollutants. *Water Res.* **1979b**, *13*, 453−459.

Obrigawitch, T.; Hons, F. M.; Abernathy, J. R.; Gipson, J. R. Adsorption, desorption and mobility of metolachlor in soils. *Weed Sci.* **1981**, *29*, 332−336.

Oliver, G. J.; Cosgrove, E. G.; Carey, J. H. Effect of suspended sediments on the photolysis of organics in water. *Environ. Sci. Technol.* **1979**, *13*, 1075−1077.

Peter, J. C.; Weber, J. B. Adsorption, mobility, and efficacy of alachlor and metolachlor as influenced by soil properties. *Weed Sci.* **1985**, *33*, 874−881.

Richards, R. P.; Baker, D. B. Pesticide concentration patterns in agricultural drainage networks in the Lake Erie basin. *Environ. Toxicol. Chem.* **1993**, *12*, 13−26.

Schnitzer, M.; Skinner, S. I. M. Alkali verses acid extraction of soil organic matter. *Soil Sci.* **1968**, *105*, 392−396.

Weber, J. B.; Peter, C. J. Adsorption, bioactivity and evaluation of soil tests for alachlor, acetochlor and metolachlor. *Weed Sci.* **1982**, *30*, 14−20.

Wood, L. S.; Scott, H. D.; Marx, D. B; Lavy, T. L. Variability in sorption coefficients of metolachlor on a captina silt loam. *J. Environ. Qual.* **1987**, *16*, 251−256.

Zepp, R. G.; Schlotzhauer, P. F. Effects of equilibrium time on photoreactivity of the pollutant DDE sorbed on natural sediments. *Chemosphere* **1981**, *10*, 453−460.