# Sunlight Photodegradation of Metolachlor in Water†

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The chemical and photochemical stability of the herbicide metolachlor [2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl)acetamide] was determined in organic-free water and lake water containing various solutes. Metolachlor was fairly stable in lake water in the dark, with <4% loss after 100 days. Sunlight photodegradation of metolachlor was faster than purely chemical degradation but was still a relatively slow process, with estimated near-surface half-lives in lake water of 22 calendar days in summer and 205 calendar days in winter at 40° N latitude. In 5 mg/L solutions of dissolved organic matter, the estimated half-lives were 2–3 times longer, depending upon the season. Four dechlorinated photoproducts were identified in lake water, accounting, after 40 days of sunlight irradiation, for 18% of the metolachlor originally present. These products resulted from dechlorination, hydroxylation, dehydrochlorination with subsequent morpholine ring formation, and N-dealkylation.

## INTRODUCTION

The herbicide metolachlor [2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl)acetamide] (see Figure 1) is a germination inhibitor used mainly for weed control of grasses (Chesters *et al.*, 1989). It is the most heavily used agricultural pesticide in Ontario. An estimated $7.2 \times 10^3$ metric tons of agricultural pesticides (active ingredient) of all types were used in Ontario in 1988 (Moxley, 1989). Twenty-four percent of this total was metolachlor ($1.7 \times 10^3$ metric tons), used mainly on crops such as soybeans, corn, and beans. Metolachlor used in Ontario more than doubled from 1983 to 1988 (McGee, 1984; Moxley, 1989), during which time the related herbicide alachlor was withdrawn from the Canadian market (Shapiro *et al.*, 1987).

In order that an assessment can be made of the hazards of metolachlor use to aquatic ecosystems, more information is required on its occurrence in water, its toxicity to aquatic organisms, and its persistence and fate.

There is relatively little information in the open literature on the occurrence of metolachlor in surface waters. Concentrations have been reported for the period 1979–1985 in the range 0.3–4.4 μg/L for various locations along the Mississippi Rover and 0.8–1.8 μg/L in the Sacramento River in California (Chesters *et al.*, 1989). Mean annual concentrations were up to 4.1 μg/L at the mouths of the Grand, Saugeen, and Thames Rivers in Ontario in 1981–1985 (Frank and Logan, 1988). The mean concentration in 34 Rhine River samples in Germany in 1985–1986 was 1.1 μg/L [range 0.1–3.2 μg/L (Oehmichen and Haberer, 1986)]. Mean concentrations in Upper Tuttle Creek Lake and Lower Tuttle Creek Lake, Kansas, in 1985 were 1.23 and 0.93 μg/L, respectively [four samples each (Arruda *et al.*, 1988)]. The mean concentration in 24 Yamaska River (Québec) basin samples in 1986–1987 was 1.7 μg/L [range nd–13.4 μg/L (Maguire and Tkacz, 1993)]. Time-weighted average concentrations for 7 Ohio rivers in the period 1983–1991 were in the range 0.15–1.80 μg/L [range nd–97 μg/L (Richards and Baker, 1993)].

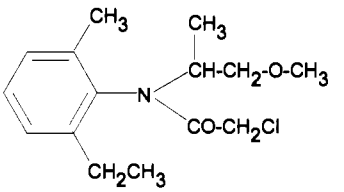


**Figure 1.** Chemical structure of metolachlor [2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl)acetamide].

There are few data on the acute and chronic toxicity of metolachlor to vertebrates and invertebrates and on effects on phytoplankton and aquatic vascular plants. The most sensitive fish species is rainbow trout (*Oncorhynchus mykiss*), with a 96-h $LC_{50}$ of 2 mg/L (Weed Science Society of America, 1983). The 48-h $LC_{50}$ for the water flea (*Daphnia magna*) was 25 mg/L (Mayer and Ellersieck, 1986). Until recently, the only chronic aquatic toxicity data were for fathead minnow (*Pimephales promelas*), for which a no-observed-effect concentration (NOEC) for reproduction of 780 μg/L was reported (U.S. Environmental Protection Agency, 1987). On the basis of available toxicological data, the U.S. Environmental Protection Agency (1987) set an advisory acute concentration value of 355 μg/L and an advisory chronic concentration value of 14.2 μg/L. The interim recommended Canadian water quality guideline for the protection of aquatic life is 8 μg/L (Kent *et al.*, 1991). The recent determination of a 96-h $EC_{50}$ value of 50 μg/L for metolachlor in the alga *Selenastrum capricornutum* (St-Laurent *et al.*, 1992) indicates that the guidelines may need to be lowered. Average metolachlor concentrations in water reported above were below presently recommended guidelines, but the maximum concentrations sometimes exceeded the guidelines.

There is little information in the open literature on the aquatic fate and persistence of metolachlor (U.S. Environmental Protection Agency, 1988; Kent *et al.*, 1991). Ripley *et al.* (1986) found that metolachlor was fairly resistant to hydrolysis at pH 2, 5.5, 8.5, and 10 at 38 °C. Less than 5% loss of compound was observed after 50 days, except at pH 10, where a 20% loss was observed. No products were identified. LeBaron *et al.* (1988) calculated hydrolysis half-lives at 20 °C to be >200 days at pH 1–9 and 97 days at pH 13, on the basis of rate studies at 30,

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50, and 70 °C. They also identified 2-hydroxy-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl)acetamide as a hydrolysis product under basic condtions at elevated temperature and showed that, under acidic conditions, metolachlor hydrolyzed to the transient compound 2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-hydroxy-1-methylethyl)acetamide, which was rapidly converted to 4-(2-ethyl-6-methylphenyl)-5-methyl-3-morpholinone. Slow photodegradation of metolachlor was found in aqueous solutions exposed to sunlight, 6–8% in 1 month (LeBaron *et al.*, 1988; Chesters *et al.*, 1989). The photoproducts 2-hydroxy-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl)acetamide and 4-(2-ethyl-6-methylphenyl)-5-methylmorpholine accounted for 2.3% of metolachlor applied; four unknown photoproducts accounted for 4.3%.

This study was undertaken primarily to determine the kinetics of sunlight photodegradation of metolachlor in natural water, the products of photodegradation, and the effects on the photodegradation rate of various solutes including dissolved organic matter (DOM) and iron and manganese ions, at typical environmental concentrations. DOM has been shown to affect the sunlight photodegradation of environmental contaminants [*e.g.*, Zafiriou *et al.* (1984)]. Ferric ion is a well-known oxidant, and ferric and manganese ions have been shown to catalyze the hydrolysis of esters and amides (Mabey and Mill, 1978; Mill and Mabey, 1988) and the photodegradation of the herbicide bromoxynil (Kochany, 1992).

## MATERIALS AND METHODS

**Materials.** The following analytical standards were obtained from Ciba-Geigy Canada Ltd. (Mississauga, ON): (1) metolachlor [2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl)acetamide]; (2) 4-(2-ethyl-6-methylphenyl)-5-methyl-3-morpholinone; (3) *N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl)oxalamide; (4) *N*-(2-ethyl-6-methylphenyl)-oxalamide; (5) 2-hydroxy-*N*-(2-ethyl-6-methylphenyl)acetamide; and (6) 2-hydroxy-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl)acetamide. Pesticide grade and high-performance liquid chromatography (HPLC) grade organic solvents were obtained from Caledon Laboratories (Georgetown, ON). Other chemicals were of reagent grade from various suppliers. The sodium sulfate used for drying organic extracts, and the disposable pipets, were heated to 500 °C for 24 h before use. All glassware was rinsed with pesticide grade solvents before use. Organic-free water for HPLC analyses and for photochemical experiments was prepared with a Milli-Q system from Millipore-Waters Co. (Mississauga, ON). The natural water used in some experiments was from the middle of Lake Ontario (pH 8.6, conductivity 300 μS, dissolved organic carbon 2.5 mg/L, dissolved inorganic carbon 21.9 mg/L). The DOM was isolated from a nearby creek and was determined by Brownlee *et al.* (1992) to be predominantly fulvic acid.

**Aqueous Stability.** The aqueous stability of metolachlor was characterized prior to photochemical experiments. The stability of metolachlor was tested in organic-free water and natural water at 20 °C in the dark over a 100-day period. Experiments with unsterile organic-free water and sterile organic-free water (containing 10 mg/L $HgCl_2$) were done over the pH range 4–9 at different concentrations of metolachlor (2.8–28 mg/L) and phosphate buffer (470–4800 mg/L, corresponding to 5–50 mM). The effects of $FeCl_3$ (0.2–1.6 mg/L) and $MnCl_2$ (0.1–1.3 mg/L) on stability were also studied at pH 4 and 7. Experiments with unsterile natural water and sterile natural water (containing 10 mg/L $HgCl_2$) were done at metolachlor concentrations of 1.4–28 mg/L. All experiments were done in duplicate. At 20, 30, 50, and 100 days metolachlor analyses were performed by HPLC-UV.

**Photodegradation.** The photochemical stability of metolachlor was tested under artificial light of wavelength 313 nm and in sunlight.

(*i*) *313-nm Light in Photoreactor.* Ultraviolet–visible (UV) spectra of metolachlor and available degradation products were measured with a Shimadzu UV-260 spectrophotometer. Preliminary experiments to compare the photodegradation rates of metolachlor under different conditions were done with a Rayonet photochemical reactor (Southern New England Ultraviolet Co., Stamford, CT). Air-saturated solutions of volume 50 mL were irradiated at 313 nm (16 Rayonet RPR 300-Å lamps) in a water-jacketed Pyrex reactor equipped with a magnetic stirrer. To filter out radiation around 313 nm, the water jacket of the reactor was filled with a chemical filter solution consisting of potassium chromate (0.27 g/L) and sodium carbonate (1 g/L) (Kochany *et al.*, 1990). Incident light was monitored with a chemical actinometer consisting of aqueous *p*-nitroacetophenone (PNAP) ($10^{-5}$ M) and pyridine ($1.41 \times 10^{-3}$ M) (Dulin and Mill, 1982). The effects of phosphate buffer, NaCl, $Na_2SO_4$, $NaNO_3$, DOM, and lake water on the photodegradation of metolachlor were examined over irradiation periods of 10–300 min. Periodically, samples of metolachlor solutions were withdrawn and analyzed by spectrophotometry and HPLC-UV. Actinometric solutions were analyzed by HPLC-UV.

(*ii*) *Sunlight.* Sunlight photodegradation experiments were done to obtain estimates for rate constants and half-lives in summer and winter at latitude 40° N, to determine the actual site-specific half-life during the period of irradiation (September 30 to November 30, 1992, at Burlington, ON, latitude 43° 17′ 50″, longitude 78° 48′ 00″), and to determine products of photodegradation. The experiments were done in Pyrex tubes containing 50 mL of air-saturated organic-free water, or lake water, or organic-free water containing 5 mg/L DOM. In all cases, the absorbance of solutions was <0.05 at λ between 290 and 330 nm. Appropriate dark control samples were wrapped in aluminum foil. All samples were placed outside during the daytime and brought indoors overnight and kept in the dark at room temperature. Incident solar radiation was estimated two ways, with the PNAP/pyridine chemical actinometric system described above and with a quantum sensor which measured radiation (einstein/$m^2$) in the wavelength range 400–700 nm (LI-190SA quantum sensor and LI-100 recording light meter from LI-COR Instruments, Lincoln, NE). Periodically, a subsample from a particular test tube containing metolachlor test solution was analyzed by spectrophotometry, HPLC-UV and HPLC–mass spectrometry (MS). The rest of the 50-mL sample was then extracted three times with 5 mL of hexane each time, and the test tube was thoroughly rinsed with hexane. The hexane extracts were combined, dried with $Na_2SO_4$, and concentrated to 1 mL, and the extract was analyzed by gas chromatography–mass spectrometry (GC–MS) for degradation products. In addition, some extracts were analyzed by gas chromatography–atomic emission spectrometry (GC–AES) to check for the presence of chlorine in the degradation products. Actinometric solutions were analyzed by HPLC-UV.

**Analysis.** Routine HPLC-UV analyses for metolachlor in the aqueous stability and photochemical experiments were done by direct aqueous injection (25 μL) into a Waters HPLC-UV system (U6K injector, 510 HPLC pump, and 481 spectrophotometric detector) with Hewlett-Packard 3392A integrator. The column was a 15 cm × 4.6 mm i.d. reversed-phased Supelcosil LC-8-DB column and was preceded by a Supelguard LC-8-DB guard column. The mobile phase was methanol/water (60/40 v/v), and the flow rate was 2 mL/min. Absorbance was monitored at wavelength 220 nm. Under these conditions, the retention times of metolachlor and photoproducts I, II, III, and IV identified in this study were 5.2, 2.4, 3.6, 1.4, and 1.8 min, respectively. The reaction of the PNAP/pyridine actinometric system was also followed by HPLC under the same conditions but at wavelength 250 nm.

HPLC–MS analyses were done by direct aqueous injection (20 μL by autosampler) into a Hewlett-Packard 1050 HPLC coupled to a 5989A MS engine by a thermospray LC/MS interface and controlled by a 59940A HPUX MS ChemStation. The HPLC column was a Hewlett-Packard ODS Hypersil 10 cm × 2.1 mm i.d. reversed-phase column. The mobile phase was methanol/0.1 M ammonium acetate (45:55 v/v), and the flow rate was 0.5 mL/min. The thermospray was configured in the positive ion mode with the filament on [equivalent to conventional chemical ionization yielding some fragmentation in addition to the usual protonated and deprotonated molecular ions (Yergey *et al.*, 1990)]

and the discharge off. The source and quadrupole temperatures were 250 and 100 °C, respectively. The full-scan mode (80–350 amu) was used with the electron multiplier at 2700 V and ionization potential of 70 eV. The retention times of metolachlor and photoproducts I and II under these conditions were 29.5, 16.2, and 18.1 min, respectively (photoproducts III and IV were not produced in large enough amounts to be determined by HPLC–MS).

GC–MS analyses were done with a Hewlett-Packard 5980-II GC, 7673 autosampler (1-μL injections), 5971A mass selective detector (MSD), and MS ChemStation. A 30 × 0.25 mm i.d. DB-5 column (0.25-μm film thickness) (Chromatographic Specialties, Brockville, ON) was used under the following temperature conditions: 1-min initial hold at 80 °C, 4°/min at 280 °C, 5-min final hold. The inlet temperature was 250 °C. The helium carrier gas flow rate was 1 mL/min, and the inlet pressure was 15 psig. The MSD was operated in electron impact mode with an ionization potential of 70 eV and a source temperature of 190 °C. The scan range was 50–500 amu. The retention times of metolachlor and photoproducts I, II, III, and IV under these conditions were 33.6, 32.3, 31.8, 30.0, and 28.2 min, respectively.

GC–AES analyses to check for chlorine in the degradation products were done with a Hewlett-Packard 5890-II GC, 7673 autosampler (1-μL injections), 5921A atomic emission detector (AED) and AED ChemStation. GC conditions were the same as for GC–MS. The temperature of the microwave-induced helium plasma was 3000 °C, and the power in the microwave cavity was 50 W. Chlorine was monitored at 479 nm.

## RESULTS AND DISCUSSION

**Aqueous Stability.** Metolachlor at 2.8–28 mg/L was fairly stable in organic-free water. Only minor losses of <5% were found after 100 days at pH 4, 7, and 9. There was no significant effect of phosphate buffer in the range 475–4750 mg/L (5–50 mM), of $FeCl_3$ in the range 0.2–1.6 mg/L, or of $MnCl_2$ in the range 0.1–1.3 mg/L, and there was no significant difference between results in sterile *vs* unsterile organic-free water. Metolachlor was also fairly stable in natural water, with less than 4% loss from sterile or unsterile natural water after 100 days. Products were not identified because there was so little degradation of metolachlor.

**Photodegradation.** The potential for sunlight photodegradation of metolachlor is indicated by the fact that it absorbs radiation weakly (extinction coefficient <750 L $mol^{-1}$ $cm^{-1}$) between 290 nm, which is the lower wavelength limit for sunlight radiation, and 330 nm. The molar extinction coefficients for metolachlor were the same in buffers of pH 4, 7, and 9 as in organic-free water.

(*i*) *Artificial Light in Photoreactor.* In the photoreactor experiments significant spectral changes in the irradiated solutions were evident above 240 nm, with an increase at $\lambda > 290$ nm. This indicates that the photoproducts absorb light more strongly than metolachlor and that they can also undergo photochemical transformation. First-order rate constants for the photodegradation of metolachlor under different conditions were obtained from plots of $\ln([\text{metolachlor}]_t/[\text{metolachlor}]_0)$ *vs* time, and quantum yields at 313 nm were obtained with (Leifer, 1988)

$$\phi_{313}^{\text{met}} = (k_{\text{met}}\epsilon_{313}^{\text{PNAP}}\phi_{313}^{\text{PNAP}})/(k_{\text{act}}\epsilon_{313}^{\text{met}}) \quad (1)$$

where met and PNAP refer to metolachlor and the actinometer, respectively, $\epsilon_{313}$ is the molar extinction coefficient at 313 nm, $\phi_{313}^{\text{PNAP}}$ is the quantum yield for the photodegradation of PNAP at 313 nm, and $k_{\text{met}}$ and $k_{\text{PNAP}}$ are the first-order rate constants for the photodegradation of metolachlor and PNAP, respectively. Table 1 shows rate constants, half-lives, and quantum yields at 313 nm for metolachlor in various solutions. The data show that metolachlor photodegradation rates are similar in organic-free water, buffers of pH 4 and 7, and $MnCl_2$ solution and faster in lake water (pH 8.6) and pH 9 buffer. The fact that both photodegradation rate and quantum yield were higher in alkaline solution suggested that photohydrolysis was an important process. Photodegradation rates of metolachlor were slower in $FeCl_3$ and DOM solutions than in distilled water. Further experiments indicated that $FeCl_3$ in the range 1.6–16 mg/L and DOM in the range 5–50 mg/L had a marked quenching effect on metolachlor photodegradation, probably by a light screening effect because both chemicals absorb light at 313 nm. Additional experiments demonstrated that 5–50 mg/L NaCl and 10–150 mg/L $Na_2SO_4$ had no effect on the photodegradation rate but that 5–75 mg/L $NaNO_3$ had a weak quenching effect. The quenching effect of DOM and $NaNO_3$, which are known to produce hydroxyl radicals and other reactive species upon sunlight irradiation (Zafiriou *et al.*, 1984; Cooper *et al.*, 1989), suggested that hydroxylation and/or oxidation may not be the main routes of photodegradation of metolachlor in water. However, two of the subsequently identified photoproducts were hydroxylated, albeit not on the benzene ring.

**Table 1. First-Order Rate Constants, Half-Lives, and Quantum Yields for Metolachlor Photodegradation at 313 nm[a]**

| solution | rate constant, $s^{-1}$ | half-life, min | $\phi_{313}$ |
|---|---|---|---|
| organic-free water | $(1.5 \pm 0.1) \times 10^{-4}$ | 77 ± 8 | $2.8 \times 10^{-5}$ |
| lake water | $(1.9 \pm 0.2) \times 10^{-4}$ | 61 ± 7 | $3.5 \times 10^{-5}$ |
| pH 4 buffer | $(1.3 \pm 0.1) \times 10^{-4}$ | 88 ± 9 | $2.3 \times 10^{-5}$ |
| pH 7 buffer | $(1.6 \pm 0.2) \times 10^{-4}$ | 72 ± 8 | $3.0 \times 10^{-5}$ |
| pH 9 buffer | $(2.2 \pm 0.2) \times 10^{-4}$ | 53 ± 5 | $4.1 \times 10^{-5}$ |
| 1.6 mg/L $FeCl_3$ | $(1.1 \pm 0.1) \times 10^{-4}$ | 105 ± 12 | $2.1 \times 10^{-5}$ |
| 0.1 mg/L $MnCl_2$ | $(1.4 \pm 0.1) \times 10^{-4}$ | 82 ± 9 | $2.6 \times 10^{-5}$ |
| 5 mg/L DOM | $(0.8 \pm 0.1) \times 10^{-4}$ | 144 ± 15 | $1.5 \times 10^{-5}$ |

[a] Metolachlor concentration was 2.8 mg/L. Buffer concentrations were 475 mg/L. All solutions were air-saturated.

(*ii*) *Sunlight.* Sunlight quantum yields for the photodegradation of metolachlor were calculated two ways, by comparison with actinometric data and by using incident light data obtained with a quantum meter. The actinometric method used was that of Leifer (1988). This procedure is applicable to the direct photoreaction of chemicals in a homogeneous solution with absorbance ≤0.05 in reaction cells at all wavelengths >290 nm and at shallow depths (<0.5 m). Consequently, this method was also valid for the photodegradation of metolachlor in lake water and 5 mg/L DOM. The sunlight quantum yield for metolachlor by the quantum meter method was calculated from measured incident solar radiation values and reaction rates according to the method of Leifer (1988). With the knowledge of the sunlight quantum yield for metolachlor by either technique, the "direct photoreaction rate constant in a natural water body" (Leifer, 1988) and the corresponding half-life can be calculated.

Table 2 shows the reaction rates and quantum yields calculated by both methods for the sunlight photodegradation of metolachlor in organic-free water, lake water, and water with 5 mg/L DOM. There is reasonable agreement between rates and quantum yields calculated by the two methods. Reaction rates and sunlight quantum yields may be higher by actinometry than by the quantum meter method because of different geometries of the sample tubes and the light sensor. It is assumed that the results by actinometry are more reliable than results by the quantum meter method because in the actinometric procedure sunlight irradiation of metolachlor and actinometric solutions was done in tubes of identical geometry. Consequently, actinometric results were used in the calculation of the rate constants and half-lives for sunlight photodegradation of metolachlor in organic-free water,

**Table 2. Reaction Rates and Quantum Yields for Sunlight Photodegradation of Metolachlor[a]**

| solution | reaction rate (mol/L)/(einstein/m²) | | quantum yield (mol/einstein) | |
|---|---|---|---|---|
| | actinometry | quantum meter | actinometry | quantum meter |
| organic-free water | $(1.2 \pm 0.2) \times 10^{-7}$ | $(0.9 \pm 0.1) \times 10^{-7}$ | $(9.6 \pm 1.2) \times 10^{-3}$ | $(5.6 \pm 0.7) \times 10^{-3}$ |
| lake water | $(0.9 \pm 0.1) \times 10^{-7}$ | $(0.6 \pm 0.1) \times 10^{-7}$ | $(6.8 \pm 0.8) \times 10^{-3}$ | $(4.1 \pm 0.5) \times 10^{-3}$ |
| DOM (5 mg/L) | $(0.7 \pm 0.1) \times 10^{-7}$ | $(0.5 \pm 0.1) \times 10^{-7}$ | $(3.4 \pm 0.4) \times 10^{-3}$ | $(0.6 \pm 0.1) \times 10^{-3}$ |

[a] All solutions were air-saturated.

**Table 3. Calculated Rate Constants and Half-Lives of the Sunlight Photodegradation of Metolachlor in Water[a]**

| solution | rate constant, days⁻¹ | | half-life, days | |
|---|---|---|---|---|
| | summer | winter | summer | winter |
| organic-free water | $(9.6 \pm 1.0) \times 10^{-2}$ | $(1.3 \pm 0.2) \times 10^{-2}$ | $8 \pm 1$ | $54 \pm 6$ |
| lake water | $(6.8 \pm 0.7) \times 10^{-2}$ | $(9.0 \pm 1.0) \times 10^{-3}$ | $11 \pm 2$ | $77 \pm 9$ |
| 5 mg/L DOM | $(3.4 \pm 0.4) \times 10^{-2}$ | $(3.0 \pm 1.0) \times 10^{-3}$ | $22 \pm 3$ | $231 \pm 25$ |

[a] Calculated from the actinometry data in Table 2, spectral data for metolachlor, and solar irradiance data for latitude 40° N in summer and winter (Leifer, 1988). Half-lives are for continuous insolation; half-lives in calender days are obtained by multiplication by the ratio [24/(average number of hours of daylight at that season)].

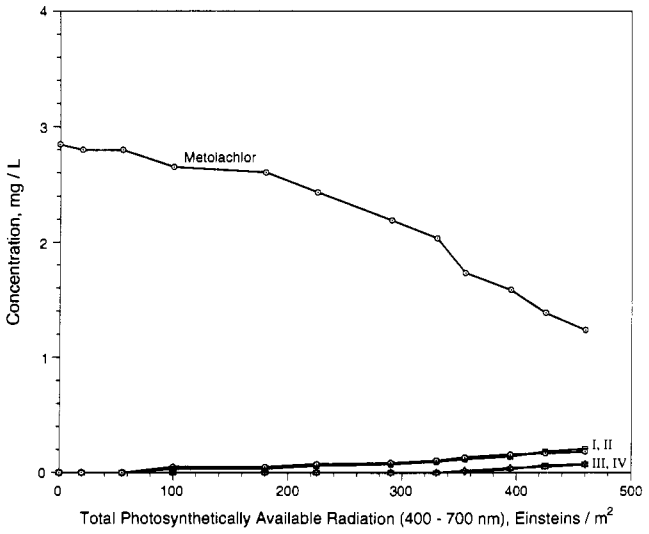


**Figure 2.** Sunlight photodegradation of metolachlor in lake water. Concentrations were determined by HPLC-UV, with the assumption that the extinction coefficient of photoproduct II at 220 nm was the same as that of photoproduct I. The structures of photoproducts I–IV are shown in Figure 3.

lake water, and a 5 mg/L DOM solution in summer and winter at 40° N; the results are shown in Table 3. In near-surface lake water in summer, metolachlor was calculated to degrade fairly slowly in sunlight, with a half-life of 11 days of continuous insolation or 22 calendar days (assumed 12 h of sunlight per day). In winter, the calculated half-life was 77 days of continuous isolation or 205 calendar days (assumed 9 h of sunlight per day). Furthermore, DOM retarded the photodegradation by a factor of 2–3 depending upon the season.

Figure 2 shows the time course of the sunlight photodegradation of metolachlor in lake water at Burlington, ON, at approximately 43° N. Incident radiation was monitored by quantum meter. In the fall of 1992, the "half-life" of about 425 einstein/m² corresponded to about 35 calendar days.

*(iii) Sunlight Photoproducts.* Figure 2 also shows that four photoproducts were found in the course of the sunlight photodegradation of metolachlor in lake water. At the end of the irradiation period, the sum of their concentrations accounted for 18% of the metolachlor originally present, and the metolachlor remaining accounted for a further 44%, leaving 38% unaccounted for. GC–AES spectra indicated that none of these photoproducts contained chlorine. The identities of three of the photoproducts (I, III, and IV) were confirmed by mass spectra, while the identification of photoproduct II was tentative. The structures of the photoproducts are shown in Figure 3.

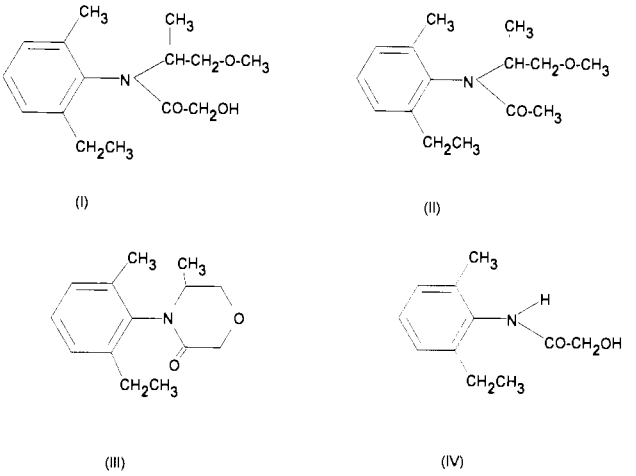


**Figure 3.** Chemical structures of four sunlight photodegradation products of metolachlor: I [2-hydroxy-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl)acetamide]; II [*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl)acetamide]; III [4-(2-ethyl-6-methylphenyl)-5-methyl-3-morpholinone]; IV [2-hydroxy-*N*-(2-ethyl-6-methylphenyl)acetamide]. The structures of I, III, and IV were confirmed by mass spectra, while the identification of II is tentative.

Photoproduct I [2-hydroxy-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl)acetamide] ($C_{15}H_{23}NO_3$, MW 265) was tentatively identified by HPLC-UV, HPLC–MS, and GS–MSD retention time matching with a known standard. The identification was confirmed by matching the electron impact GC–MSD and HPLC–MS thermospray filament-on mass spectra for compound I with those of a known standard (see Figure 4). The electron impact GC–MSD spectrum (Figure 4a) showed prominent peaks at *m/z* 220, 193, and 162. The ion at *m/z* 220 is likely due to loss of a $CH_2OCH_3$ fragment from the molecular ion, while the ion at *m/z* 193 probably results from cleavage of the 2-methoxy-1-methylethyl fragment with concurrent hydrogen migration. The ion at *m/z* 162 probably results from cleavage of the $COCH_2OH$ fragment from the *m/z* 220 ion, with concurrent hydrogen migration. The HPLC–MS thermospray filament-on mass spectrum (Figure 4b) showed a strong M–H ion at *m/z* 264 and ions at *m/z* 238 and 206. The ion at *m/z* 206 may be due to the loss of a $C(O)CH_2O$ fragment from the deprotonated molecular ion.

Photoproduct II was tentatively identified as *N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl)acetamide ($C_{15}H_{23}NO_2$, MW 249). There was no available standard with which to match HPLC and GC retention times. However, its electron impact GC–MS spectrum was similar to that reported by McGahen (1982), with the base peak at *m/z* 162, and the only other significant ion (30% relative intensity) at *m/z* 204. Support for this

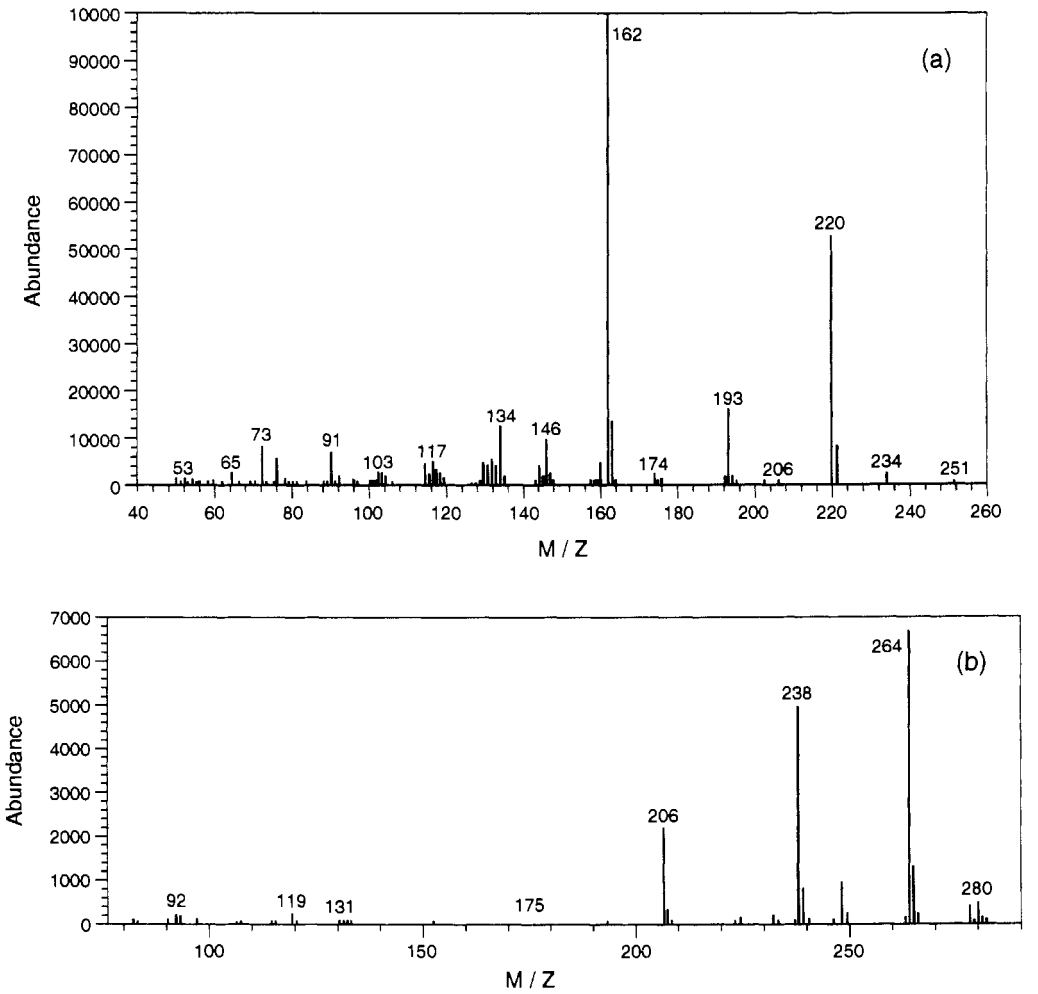


**Figure 4.** GC–MSD electron impact mass spectrum (a) and HPLC–MS thermospray filament-on mass spectrum (b) for photoproduct I [2-hydroxy-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl)acetamide].

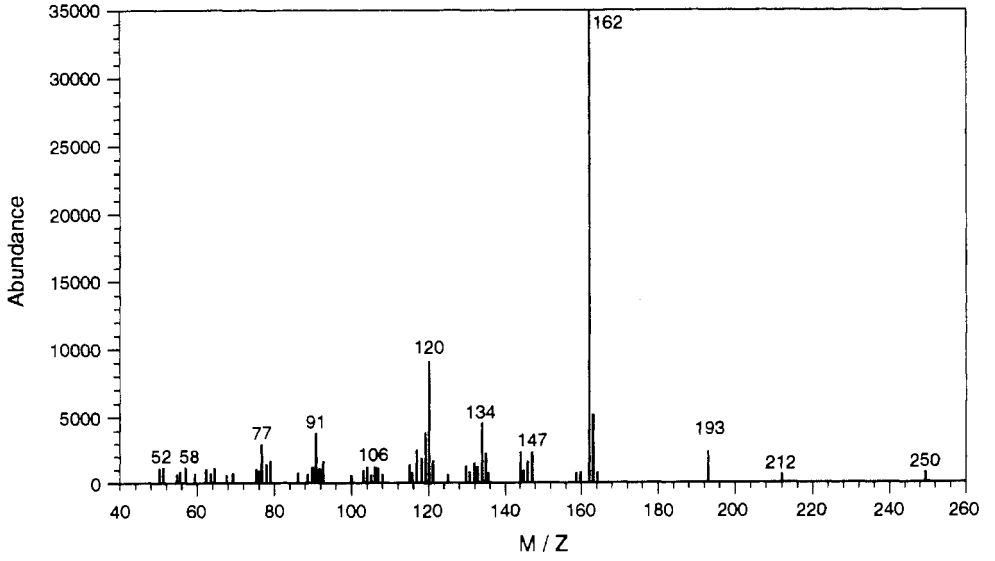


**Figure 5.** GC–MSD electron impact mass spectrum for photoproduct IV [2-hydroxy-*N*-(2-ethyl-6-methylphenyl)acetamide].

structure was provided by the HPLC–MS thermospray filament-on mass spectrum. The only significant ion in the latter spectrum was the base peak at *m/z* 248, which may be the M–H ion.

Photoproduct III [4-(2-ethyl-6-methylphenyl)-5-methyl-3-morpholinone] ($C_{14}H_{19}NO_2$, MW 233) was tentatively identified by HPLC–UV and GC–MSD retention time matching with a known standard. The identification was confirmed by matching the electron impact GC–MS spectrum for photoproduct III with that of a known standard. The mass spectrum was the same as that reported by Liu *et al.* (1989). There was not enough compound to obtain a satisfactory HPLC–MS thermospray filament-on mass spectrum.

Photoproduct IV [2-hydroxy-*N*-(2-ethyl-6-methylphenyl)acetamide] ($C_{11}H_{15}NO_2$, MW 193) was tentatively

identified by HPLC–UV and GC–MSD retention time matching with a known standard. The identification was confirmed by matching the electron impact GC–MS spectrum for photoproduct IV with that of a known standard (see Figure 5). The ion at $m/z$ 162 may result from loss of a $CH_2OH$ fragment from the molecular ion at $m/z$ 193, while the ion at $m/z$ 134 likely results from loss of a CO fragment from the $m/z$ 162 ion. The ion at $m/z$ 120 may result from loss of nitrogen from the ion at $m/z$ 134, with concurrent hydrogen migration. There was not enough compound to obtain a satisfactory HPLC–MS thermospray filament-on mass spectrum.

Many degradation products have been identified in studies of the metabolism of metolachlor by microorganisms (McGahen and Tiedje, 1978; Leavitt and Penner, 1979; McGahen, 1982; Krause *et al.*, 1985; Saxena *et al.*, 1987; Liu *et al.*, 1988, 1989), fish (Cruz *et al.*, 1993), and rodents (Kimmel *et al.*, 1986), but relatively few sunlight photoproducts have been identified. In an earlier photodegradation study, the two identified products 2-hydroxy-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl)acetamide and 4-(2-ethyl-6-methylphenyl)-5-methylmorpholine accounted for 2.3% of metolachlor applied, and four unknown photoproducts accounted for 4.3% (LeBaron *et al.*, 1988; Chesters *et al.*, 1989). Four sunlight photodegradation products of metolachlor were identified in the present study, accounting for 18% of the original metolachlor. Photoproduct I [2-hydroxy-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl)-acetamide] has been identified before as a sunlight photoproduct (LeBaron *et al.*, 1988; Chesters *et al.*, 1989) and as a product of basic hydrolysis at high temperature (LeBaron *et al.*, 1988). Photoproduct II [*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl)acetamide] has been identified as a product of anaerobic degradation in a eutrophic lake sediment (McGahen, 1982). Photoproduct III [4-(2-ethyl-6-methylphenyl)-5-methyl-3-morpholinone] has been identified as an acidic hydrolysis product at high temperature (LeBaron *et al.*, 1988) and as a degradation product in a bacterial culture (Liu *et al.*, 1989). Photoproduct IV [2-hydroxy-*N*-(2-ethyl-6-methylphenyl)acetamide] has apparently not been identified before in degradation or metabolism studies. It appears that photodegradation of metolachlor is at least partially a detoxification process, since photoproducts I, III, and IV have recently been shown to be less toxic than parent metolachlor to the algae *Scenedesmus quadricauda* and *Anabaena cylindrica* in 96-h growth assays and less toxic to the duckweed *Lemna gibba* in 7-day growth assays (K. E. Day, National Water Research Institute, personal communication, 1993).

In summary, this study confirms and extends earlier findings that metolachlor in natural water is moderately persistent with regard to hydrolysis and sunlight photolysis. Purely chemical degradation of metolachlor in lake water was a slow process, with <4% loss after 100 days at 20 °C. Sunlight photodegradation of metolachlor was faster than purely chemical degradation but was still a relatively slow process, with estimated near-surface half-lives in lake water of 22 calendar days in summer and 205 calendar days in winter at 40° N latitude. DOM retarded the photodegradation by a factor of 2–3 depending upon the season. Further work is planned on the kinetics, mechanism, and products of biological degradation of metolachlor in natural waters of different trophic status.

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