

## Photodegradation of Acetochlor and Butachlor in Waters Containing Humic Acid and Inorganic Ion

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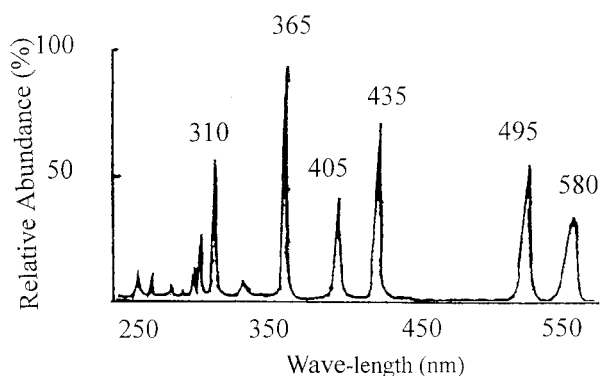
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Acetochlor [2-chloro-N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl) acetamide] and butachlor [2-chloro-N-(2,6-diethylphenyl)-N-(butoxymethyl) acetamide] are the two of three most heavily used herbicides in China. The total mass of them have been above  $1.5 \times 10^7$  kg (Wang 1999). Acetochlor was conditionally registered in March 1994 (USEPA 1994) and has been classified as a B-2 carcinogen by the USEPA. Use of acetochlor has been increasing and already is substantial. By 1996, acetochlor applications had reached 13.5 million kg (USDA, 1995). There is little information in open literature on the occurrence of acetochlor and butachlor. Acetochlor and butachlor are chloracetamide herbicides having chemical structure and properties similar to those of alachlor and metolachlor. The USEPA (1990) has set the maximum contaminant level of alachlor in drinking water at 2 µg/L. Chloracetamide herbicides degradation products are generally of lower molecular weight and more oxidized than the parent compounds, therefore they may be consequently more water soluble, more mobile, and have a greater potential to leach (Baker et al. 1993; Koplin et al. 1995). Somich et al. (1988) reported that alachlor was dechlorinated upon UV irradiation and formed a number of intermediates that retained the aromatic ring and carbonyl carbons. Jacobsen (1991) reported that degradation, in particular, cleavage of alachlor's N-methoxymethyl group, contributes to detoxification. But other published data have indicated that at least one of the residues, 2, 6-diethylaniline, is a promutagen (Kimmel et al. 1986).

Kolpin et al. (1996) reported results from sampling conducted during 1994. Maximum concentration of acetochlor found in 1994 were 2.5 µg/L (rain) and 1.2 µg/L (streams). Kalkhoff et al. (1998) reported the median value of the summed concentrations of acetochlor, alachlor, and metolachlor was less than 0.05 µg/L in groundwater and 0.13 µg/L in surface water. Indirect photolysis of acetochlor was studied by Brekken and Brezonik (1998). Summer-time half-lives of 1–20 days for acetochlor were estimated for the Blue Earth River (southern Minnesota).

Ferric and manganese ions have been shown to catalyze the photodegradation of the herbicides triazines (Larson et al. 1991) and bromoxynil (Kochany 1992). Hydroxyl radicals can be produced in water under photocatalyst of hydrogen



**Figure 1.** The emission spectrogram of light source

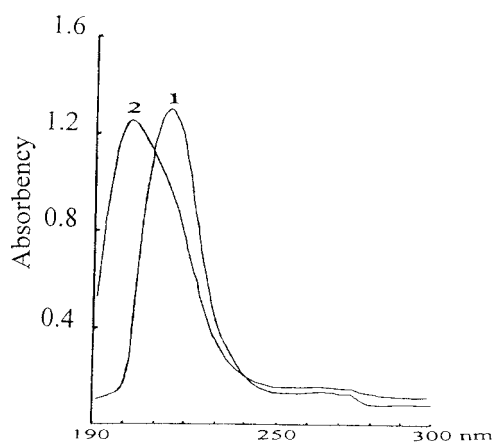
peroxide, nitrate, nitrite, dissolved organic matter (DOM) and ferric ions. It can be inferred that indirect photodegradation of acetochlor and butachlor may occur due to react with hydroxyl radicals. But Kochany and Maguire (1994) reported that DOM,  $\text{FeCl}_3$  and  $\text{MnCl}_2$  retarded the sunlight photodegradation of metolachlor.

We investigated the photodegradation rates of acetochlor and butachlor in de-ionized water, river water, and paddy water. The effects of humic acids (HA), pH, nitrite, hydrogen peroxide, ferric and manganese ions were also examined.

## MATERIALS AND METHODS

Acetochlor and butachlor of 99.5% (analytical reference standard) were obtained from Monsanto Company (St. Louis, MO, USA). Methanol of analytical-reagent grade was purified by redistillation. Paddy water, from Beijing Haidian rice field, and river water, from Jingmi canal which irrigated Beijing Haidian rice field, were filtered with a microporous funnel (4G). Ferric sulfate ( $\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ , Fe: 21.0-23.0%), manganese sulfate ( $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ ), sodium nitrite ( $\text{NaNO}_2$ ), and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) were of reagent grade from Beijing Chemical Reagents Company (Beijing, China). A stock solution of humic acid sodium (HA) was prepared. After 0.5g of humic acid was dissolved in 100mL of 0.1 M NaOH at 60 °C in water bath, the humic acid sodium was adjusted at pH8. The stock solution of humic acid sodium was diluted to 2, 5, 10, 20 mg/L.

A LC-6A High Performance Liquid Chromatography (HPLC) was equipped with a shimadzu spectro-photometric detector. The stainless steel column used (25 cm  $\times$  4.6 mm I.D.) was packed with DuPont ODS chemically bonded phase, particle size 10  $\mu\text{m}$ . The detection wavelength of 215 nm was selected in all measurements for both acetochlor and butachlor. The mobile phase was methanol – water (80/20, v/v) at a flow rate of 1.0 mL/min. The retention times of acetochlor and butachlor are 6.9 and 11.0 min, respectively.



**Figure 2.** Acetochlor adsorption spectrogram. 1. In methanol solution; 2. In water solution.

**Table 1.** Photodegradation of acetochlor and butachlor in water solution

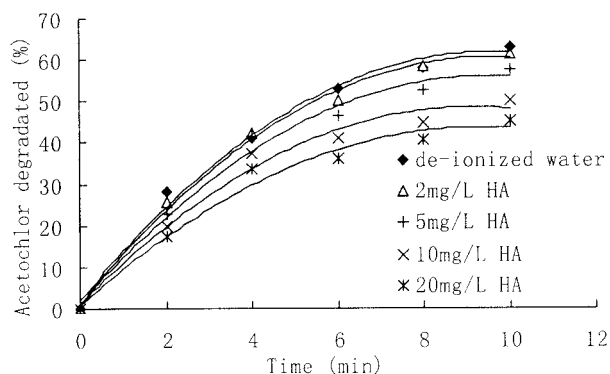
Herbicides	Water	k	t <sub>1/2</sub> (min)
Acetochlor	De-ionized water	0.0973	7.12
Acetochlor	River water	0.0685	10.11
Acetochlor	Paddy water	0.0604	11.47
Butachlor	De-ionized water	0.0919	7.54
Butachlor	River water	0.0656	10.56
Butachlor	Paddy water	0.0567	12.22

A 100-W medium pressure quartz mercury vapor lamp (produced by Beijing Electric Light Source Institute) was used as UV irradiation source. The lamp was immersed inside a quartz glass immersion well through which cold tap water flowed to keep the lamp cool. The emission spectrum of light source is showed in Figure 1. The light intensity is 658  $\mu\text{W}/\text{cm}^2$  (measured by ZDZ-1 UV irradiation photometer, 254 nm).

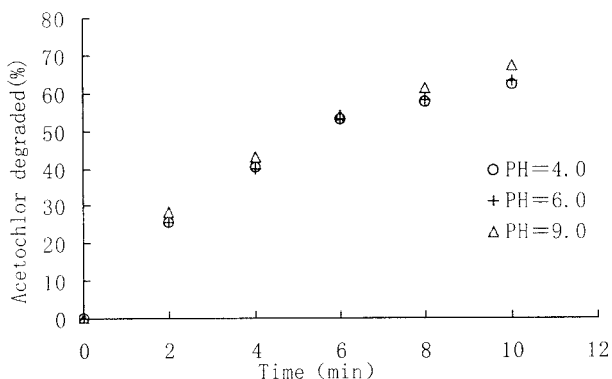
Ten mL of samples were added into a quartz test tube and irradiated with a 100-W medium pressure quartz mercury vapor lamp. Samples were removed every 2 min and analyzed by HPLC.

## RESULTS AND DISCUSSION

Acetochlor and butachlor were scanned using a Shimadzu DU-650 spectrophotometer. Acetochlor's main adsorption wave-length is less than 280nm (Figure 2). Butachlor adsorption spectrogram was similar to acetochlor. Photodegradation of acetochlor and butachlor appeared to be caused by adsorption of ultraviolet light less than 280nm wave-length.



**Figure 3.** Influence of HA on photodegradation of acetochlor



**Figure 4.** Influence of pH on photodegradation of acetochlor

Ten mL of 20mg/L acetochlor and butachlor in de-ionized water, river water and paddy water was irradiated. The logarithm of the ratio of the initial concentration to the concentration at a given time (t) vs time was plotted and the (pseudo-first-order) rate constant (k) determined by calculating the slope of the line obtained.  $t_{1/2}$  was half-life time. The calculated results were showed in Table 1. The half-lives of 20mg/L acetochlor and butachlor were 7.12 and 7.54 min in de-ionized water, 10.11 and 10.56 min in river water, 11.47 and 12.22 min in paddy water respectively. The photodegradation rate of acetochlor was a little faster than that of butachlor. The photodegradation rates of acetochlor and butachlor have an order of in de-ionized water greater than in river water and greater in paddy water. The possible explanation was that river water and paddy water had a higher concentration of DOM and inorganic ions, which can adsorb light energy and impede light transmitting. Our experiment demonstrated that DOM had a quenching effect on photodegradation of acetochlor.

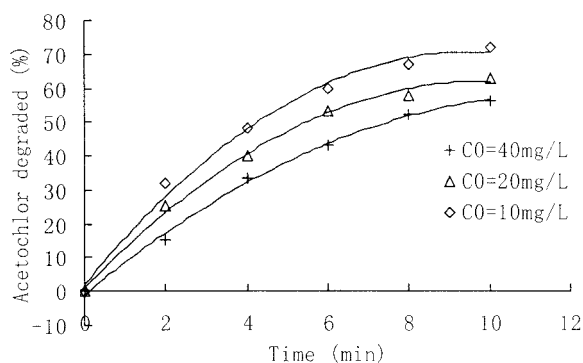
**Table 2.** Photodegradation of acetochlor (20 mg/L)

treatment	k	t <sub>1/2</sub> (min)
2mg/L HA	0.0949	7.30
5 mg/L HA	0.0831	8.34
10 mg/L HA	0.0663	10.45
20 mg/L HA	0.0575	12.05
10 mg/L H <sub>2</sub> O <sub>2</sub>	0.1251	5.54
Air-saturated	0.1002	6.92
10mg/L Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·xH <sub>2</sub> O	0.0764	9.07
10mg/LMgSO <sub>4</sub> · H <sub>2</sub> O	0.0741	9.35
10mg/L NaNO <sub>2</sub>	0.0742	9.34

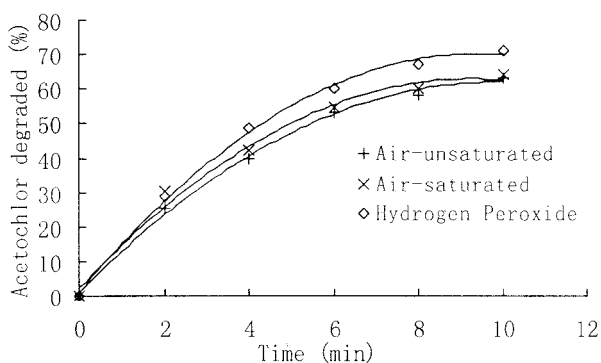
In our experiment, we had studied the effect of HA as DOM on the photodegradation of acetochlor that indicated HA had a quenching effect on photodegradation of acetochlor. Probably both HA and acetochlor completed to adsorb less than 280nm wave-length ultraviolet. The results are demonstrated in Figure 3. Although DOM are known to produce hydroxyl radicals and other reactive species upon irradiation (Cooper et al. 1989; Brezonik 1994), the quenching effect of HA suggested that hydroxylation may not be a control step of photodegradation rate of acetochlor in water. Two mg/L of HA had little effect on photodegradation of acetochlor. Quenching effect was more significant in higher concentration of HA (from 5mg/L to 20mg/L). The half-lives of 20 mg/L acetochlor in 2, 5, 10, 20 mg/L HA solutions were 7.30, 8.34, 10.45, 12.05 min (Table 2).

The pH 4 and pH 9 phosphate buffer solutions were prepared with 1 g/L of KH<sub>2</sub>PO<sub>4</sub> solution adjusted by adding appropriate H<sub>3</sub>PO<sub>4</sub> or KOH concentration solution. The pH of de-ionized water was 6.0. The half-lives of 20 mg/L acetochlor in de-ionized water, pH 4 and pH 9 buffer solutions were 7.12, 7.16, and 6.38 min, respectively. Alkaline solution promoted photodegradation of acetochlor (Figure 4). When 100 mg/L of acetochlor in de-ionized water was irradiated, after 40 min, almost all of the acetochlor was depleted. The pH had fallen from 6.7 to 3.6, indicating the formation of acid. Alkaline solution could remove H<sup>+</sup> formed by photodegradation and promoted the reaction to develop in a positive direction.

Ten mL of 10, 20, 40 mg/L of acetochlor solution was added into various quartz tubes and was simultaneously irradiated with A 100-W medium pressure quartz mercury vapor lamp. The acetochlor residues were detected by HPLC every 2 min. The half-lives of 10, 20, 40 mg/L acetochlor in de-ionized water were 5.54, 7.12, 8.06 min, respectively. The photodegradation rate of acetochlor was faster in lower concentration of acetochlor solution (Figure 5). The possible explanation was that photodegradation rate of acetochlor was positively correlated with light



**Figure 5.** Influence of concentration on photodegradation of acetochlor



**Figure 6.** Influence of O<sub>2</sub>, hydrogen peroxide on photodegradation of acetochlor

energy absorbed by acetochlor molecule. Because light energy is fixed in a unit volume, acetochlor molecules can accept more light energy in lower concentration of acetochlor.

The half-life of 20 mg/L acetochlor in the air-saturated solution was 6.92 min. Comparing to the air-unsaturated solution, the effect of O<sub>2</sub> was not significant. It suggested that oxidation might not be the main route of photodegradation. The half-life of 20 mg/L acetochlor in 10 mg/L of hydrogen peroxide solution was 5.54 min. Hydrogen peroxide could promote photodegradation (Figure 6). Hydrogen peroxide irradiated by UV light absorbed light energy to produce hydroxyl radicals, then hydroxyl radicals proceeded to react with acetochlor. It indicated hydroxylation should be one of steps of photodegradation. The half-lives of 20 mg/L acetochlor in 10 mg/L of Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, MgSO<sub>4</sub>, and NaNO<sub>2</sub> solution were 9.07, 9.35 and 9.34 min, respectively. Ten mg/L of Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, MgSO<sub>4</sub>, and NaNO<sub>2</sub> showed a significant quenching effect on acetochlor photodegradation. Probably they and acetochlor completed to adsorb less than 280

nm ultraviolet wave-length. The photodegradation of acetochlor was restrained though hydroxyl radicals can be produced in water by photolysis of nitrite and ferric ions. It also showed that hydroxylation may not be a control step of photodegradation rate of chloroacetanilide herbicides in water.

In conclusion, the photodegradation of acetochlor and butachlor was mainly caused by adsorption less than 280 nm wave-length ultraviolet. The photodegradation rates of acetochlor and butachlor have an order of in de-ionized water greater than in river water and greater in paddy water. River water and paddy water might have a higher concentration of DOM and inorganic ions, which can adsorb light energy and impede light transmitting. Alkaline solution could remove  $H^+$  formed by photodegradation and increase the rate. The effect of  $O_2$  in air-saturated solution was not significant. It suggested that oxidation might not be the main routes of photodegradation. Five-20 mg/L of HA, and 10mg/L of  $Fe_2(SO_4)_3$ ,  $MgSO_4$ , and  $NaNO_2$  had a significant quenching effect on photodegradation of acetochlor. Hydrogen peroxide could promote photodegradation of acetochlor. Although hydroxylation was one of routes of photodegradation, hydroxylation may not be a control step of photodegradation rate of chloroacetanilide herbicides in water.

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