Identification of UV Photoproducts and Hydrolysis Products of Butachlor by Mass Spectrometry

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The photoproducts and hydrolysis products of butachlor in water were identified by gas chromatography/mass spectrometry. When exposed to UV light, butachlor in aqueous solution was rapidly degraded, giving at least 11 photoproducts as a result of dechlorination with subsequent hydroxylation or cyclization processes. The chemical structures of nine degradation compounds were identified on the basis of mass spectrum interpretation and literature data. Major photoproducts are identified as 8-ethyl-1-butoxymethyl-4-methyl-2-oxo-1,2,3,4-tetrahydro-quinoline, 2-hydroxy-2',6'-diethyl-*N*-(butoxymethyl) acetanilide, and a compound related to butachlor. Minor photoproducts are identified as 2,6-diethylaniline; 1-acetyl-7-ethylindole; *N*-(2,6-diethylphenyl)-*N*-(butoxymethyl)acetamide; 2-oxo-*N*-(2,6-diethyl-phenyl)-*N*-(butoxymethyl)acetamide; 1-hydroxyacetyl-2-butoxyl-3-methyl-7-ethylindole; 1-acetyl-2-butoxyl-3-methyl-7-ethylindole; and two compounds with the chemical structure unknown. The half-lives of butachlor UV photolysis were 7.54, 10.56, and 12.22 min in deionized water, river water, and paddy water, respectively. The half-lives of butachlor hydrolysis at pH 4, 7, and 10 were 630, 1155, and 1155 days at 25 ± 1 °C, respectively. A hydrolysis product at pH 4 was identified by GC/MS to be 2-hydroxy-2',6'-diethyl-*N*-(butoxymethyl) acetanilide.

Introduction

Butachlor [2-chloro-*N*-(2,6-diethylphenyl)-*N*-(butoxymethyl)acetamide] (Figure 1), a chloracetamide herbicide, is a germination inhibitor used widely for weed control of grasses in rice. More than 5.0 × 10⁶ kg of butachlor (active ingredient) is applied annually in China (1–2). It is the most heavily used agricultural herbicide in rice fields in China.

There is little information in the open literature on the occurrence of butachlor. More information is required on its occurrence in water, its toxicity to aquatic organisms, its persistence, and its environmental fate in order to assess the hazards of butachlor use to aquatic ecosystems. Chen et al. (3–4) reported the photodegradation of butachlor. When exposed to UV light, thin films of butachlor were rapidly degraded, giving at least seven products on thin-layer and gas chromatograms. One was identified as 2-chloro-2',6'-diethylacetanilide and three others were assumed to be 2-hydroxyl-2',6'-diethyl-*N*-(butoxymethyl)-acetanilide, 1-chloroacetyl-2,3-dihydro-7-ethylindole, and *N*-2,6-diethyl-phenyl-2,5-dihydroxazol-4-one. Under UV or sunlight irradiation in aqueous solution, butachlor underwent more

FIGURE 1. Chemical structure of butachlor (2-chloro-*N*-(2,6-diethylphenyl)-*N*-(butoxymethyl) acetamide).

FIGURE 2. Emission spectra of medium-pressure quartz mercury vapor lamp.

FIGURE 3. Butachlor adsorption spectrogram. Peaks: 1, in the methanol solution; 2, in the water solution.

complex decomposition than it did as a thin film, and gave at least 24 products. Four of them were identified as 2-chloro-2',6'-diethylacetanilide, 2,6-diethylaniline, *m*-xylene, and toluene. Chen et al. (5) also reported degradation of butachlor by soil microbes. Six metabolites were identified: 2',6'-diethylacetanilide, 2-hydroxy, 2-chloro, and *N*-methyl-2-chloro derivatives of 2',6'-diethylacetanilide, 2,6-diethylaniline, *N*-chloroacetyl-7-ethyl-2,3-dihydroindole.

Butachlor is structurally similar to several other widely used chloracetamide herbicides (alachlor, metalochlor, and acetochlor). Alachlor, metalochlor, and acetochlor have been classified as B-2 carcinogens by the U. S. Environmental Protection Agency (6–7). The Commission of the European Community has classified alachlor among their “high priority pesticides” (8). The USEPA (6) has set the maximum contaminant level of alachlor in drinking water at 2 µg L⁻¹. Chloracetamide herbicide degradation products are generally of lower molecular weight and more oxidized than the parent compound, therefore, they may be more water soluble, more mobile, and have a greater potential to leach (9–11). Somich et al. (12) reported that alachlor was dechlorinated upon UV irradiation and formed a number of intermediates that retained the aromatic ring and carbonyl carbons. Photoproducts included hydroxyalachlor, norchloralachlor, 2',6'-diethyl- acetanilide, 2-hydroxyl-2',6'-diethyl-*N*-methylacet-

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TABLE 1. Photoproducts of Butachlor

peak	mass spectral data						retention time (min)	compound
	MW ^a	BP ^b	secondary ions					
1	149	134	77	91	119	149	4.46	2, 6-diethylaniline
2	189	174	128	146	160	189	6.90	1-acetyl-7-ethylindole
3	263	146	132	164	174	189	7.66	butachlor related
4	277	178	57	161	162	220	7.99	<i>N</i> -(2,6-diethylphenyl)- <i>N</i> -(butoxymethyl)acetamide
5	291	57	41	81	188	217	8.25	2-oxo- <i>N</i> -(2,6-diethylphenyl)- <i>N</i> -(butoxymethyl)acetamide
6	291	160	146	174	176	218	8.40	1-hydroxyacetyl-2-butoxyl-3-methyl-7-ethylindole
7	275	174	57	146	186	201	8.52	8-ethyl-1-butoxymethyl-4-methyl-2-oxo-1,2,3,4-tetrahydroquinoline
8	275	218	57	134	144	201	8.62	butachlor related
9	293	57	148	160	176	188	8.95	2-hydroxy-2',6'-diethyl- <i>N</i> -(butoxymethyl)acetanilide
10	275	57	174	189	201	202	9.03	1-acetyl-2-butoxyl-3-methyl-7-ethylindole
11	275	174	57	188	218	260	9.14	butachlor related
12	311	57	160	176	188	237	9.25	butachlor

^a MW, molecular weight. ^b BP, base peak.

FIGURE 4. Typical GC/MS chromatogram of the photolysis experiments.

anilide, and a lactam. Penuela and Barcelo (13) reported that alachlor gave five photoproducts after UV irradiation. Three photoproducts were unequivocally identified corresponding to 2-hydroxyl-2',6'-diethyl-*N*-methylethanilide, 8-ethyl-1-methoxymethyl-4-methyl-2-oxo-1,2,3,4-tetrahydroquinoline, and hydroxylalachlor. Two photoproducts were identified by GC-MS, but their chemical structures are unknown. Mathew and Khan (14) found that hydroxylation, dehalogenation, oxoquinoline formation, and demethylation were the main processes during the photodegradation of metolachlor. Kochany and Maguire (15) found that photoproducts of metolachlor in water resulted from dechlorination, hydroxylation, dehydrochlorination with subsequent morpholine ring formation, and *N*-dealkylation. Chiron et al. (16) reported that 14 photoproducts resulted from alachlor dechlorination with subsequent hydroxylation and cyclization processes. The two major photoproducts were identified as hydroxylalachlor and 8-ethyl-1-methoxymethyl-4-methyl-2-oxo-1,2,3,4-tetrahydroquinoline. Wilson and Mabury (17) found that monochloroacetic acid was a major photoproduct of alachlor, metolachlor, and butachlor in synthetic field water. Sunlight photodegradation of metolachlor was found slow in aqueous solution, 6–8% in a month (18–19). Alachlor and metolachlor each possess a long hydrolysis half-life (16). According to Potter and Carpenter (20), groundwater samples collected beneath a Massachusetts corn field were analyzed by gas chromatography/mass spectrometry (GC/MS). Twenty compounds were detected whose MS data indicated that they were derived from alachlor, presumably via environmental degradation. Some published data (21) have indicated that degradation, in particular, cleavage of alachlor's *N*-methoxymethyl group, contributes to detoxification. But other studies have indicated that at least one of the residues, 2,6-diethylaniline, is a promutagen (22).

In this paper, photolysis and hydrolysis of butachlor in water were studied. We report the results of GC/MS analyses of UV photoproducts and of hydrolysis products of the herbicide in water. Eleven compounds were identified; for nine compounds chemical structures were presumed.

Materials and Methods

Materials. Butachlor of 99.5% (analytical reference standard) was obtained from the Monsanto Company (St. Louis, MO). Methanol was analytical-reagent grade and purified by redistillation. Supplies of paddy water from a Beijing Haidian rice field and river water from the Jingmi canal which irrigated the Beijing Haidian rice field were filtered with a microporous funnel (4G) prior to use. Other chemicals were of reagent grade and were obtained from various commercial suppliers.

Photolysis. Irradiations were carried out using a 100-W medium-pressure quartz mercury vapor lamp (produced by Beijing Electric Light Source Institute) as the UV irradiation source. The lamp was immersed inside a quartz glass immersion well through which cold tap water flowed to keep the lamp cool. A butachlor aqueous solution in a quartz test tube was irradiated for 40 min. The emission spectrum of the light source is shown in Figure 2. The light intensity is 658 $\mu\text{W}/\text{cm}^2$ (ZDZ-1 UV irradiation photometer, 254 nm). The whole water samples were extracted into petroleum ether and concentrated, then analyzed by GC/MS to determine the products of photodegradation.

Hydrolysis. Buffer solutions were prepared with 0.9 g of $\text{Na}_2\text{HPO}_4 \cdot 12 \text{H}_2\text{O}$ dissolved into 1000 mL of distilled water. The pHs of buffer solutions were adjusted to 4, 7, or 10 by adding appropriate concentrations of NaOH or H_3PO_4 solution. The buffer solutions were sterilized at 121 °C for 30 min. Butachlor aqueous solutions (20 mg L^{-1}) were prepared

at pH 4, 7, and 10 using the buffer solutions, respectively. Butachlor aqueous solutions were placed in an incubator at 25 ± 1 °C without light. Samples were taken at intervals of time for butachlor analysis by HPLC. After 265 days, the sample of butachlor aqueous solution at pH 4 was analyzed by GC/MS to determine the products of hydrolysis.

HPLC–UV. An LC-6A high-performance liquid chromatograph was equipped with a Shimadzu spectrophotometric detector for HPLC–UV analyses. A stainless steel column (25 cm $\times$ 4.6 mm i.d.) was packed with DuPont ODS chemically bonded phase, particle size 10 μ m, and was pretested by the manufacturer. The detection wavelength of 215 nm was selected for all measurements for butachlor. The mobile phase was methanol/water (80:20, v/v) at a flow rate of 1.0 mL min⁻¹. The retention time of butachlor was 11.0 min.

Gas Chromatography. Analyses were performed using a Finnigan Trace gas chromatograph (2000 series) coupled with a Finnigan Voyager mass spectrometer detector (MSD), and Xcalibur Chemstation. A 15 m $\times$ 0.25 mm i.d. RTX-5 column (0.25- μ m film thickness) was used under the following temperature conditions: initial temperature at 50 °C, 20 °C min⁻¹ at 200 °C, 10 °C min⁻¹ at 280 °C, 3 min final hold. The inlet temperature was 250 °C. The helium carrier gas flow rate was 1 mL min⁻¹. The MSD was operated in electron impact mode with detection voltage of 350 V and a source temperature of 200 °C, in full scan mode from m/z 30 to 500.

Results and Discussion

Photodegradation. A solution of butachlor was scanned using a Shimadzu DU-650 spectrophotometer. Butachlor's main absorbance wavelength is less than 280 nm (Figure 3). It was indicated that photodegradation of butachlor was mainly caused by absorbance of ultraviolet light less than 280 nm wavelength. Considering that only little solar radiation below 300 nm reaches the earth's surface because of the protective shield of ozone in the stratosphere, sunlight photodegradation of butachlor must be slow. To study the photolysis mechanism and identify as many photoproducts as possible in a short time, a 100-W medium-pressure quartz mercury vapor lamp was used in our laboratory studies even though the conditions are different from actual environmental sunlight.

The natural logarithm values of the ratio of the initial concentration to the concentration at a given time (t) vs time were plotted and the (pseudo-first-order) rate constants (k) were determined by calculating the slope of the line; half-life $t_{1/2}$ was calculated by $\ln 2/k$. The half-lives of butachlor at an initial concentration of 20 mg/L were 7.54, 10.56, and 12.22 min in deionized water, river water, and paddy water, respectively.

When exposed to UV light, butachlor in aqueous solution was rapidly degraded, giving at least 11 photoproducts (Table 1). After irradiation for 40 min, the major photoproducts were compounds **9**, **7**, and **11**, and minor photoproducts were compounds **1**, **5**, **10**, **4**, **3**, **2**, and **6**. A typical GC/MS chromatogram of the photolysis experiments is shown in Figure 4. The mass spectra of compounds **1**–**12** are shown in Figure 5. Compound **12** is the parent butachlor, the structures of compounds **3** and **8** are unknown. It should be noted that structural assignments shown for those compounds are tentative: their full identification is still under investigation and may require other analytical methods such as NMR after an isolation step. Photoproducts correspond mainly to dechlorination of butachlor. Spectra of the presumed photoproducts were compared with literature data, when available.

Compound **1**, with molecular weight (MW) 149, may correspond to 2,6-diethylaniline. Retention time is 4.46 min. Observing the spectrum, molecular M^+ (149) could lose CH_3 to give the base ion peak at m/z 134, and two CH_3 to give

the ion at m/z 119. Compound **1** matches with previous spectra of photoproduct of alachlor from Potter and Carpenter (20) and Mangiapam et al. (23).

Compound **2**, MW 189, may correspond to 1-acetyl-7-ethylindole. Retention time is 6.90 min. Observing the spectrum, molecular ion M^+ (189) could lose CH_3 to give the base ion peak at m/z 174, CH_3CH_2 to give the ion at m/z 160, and CH_3CO to give the ion at m/z 146. The compound was not reported before.

Compound **4**, with MW 277, may correspond to *N*-(2,6-diethylphenyl)-*N*-(butoxymethyl)acetamide. Retention time is 7.99 min. The ions at m/z 220 and 203 probably result from loss of C_4H_9 and C_4H_9OH , respectively. The molecular ion could lose C_4H_9 and CH_2CO (one γ H rearrange) to give the base peak ion at m/z 178. The base peak ion could lose OH to give the ion at m/z 161. The ion at m/z 57 is $C_4H_9^+$ peak. The mass spectrum of **4** is similar to that of *N*-(2,6-diethylphenyl)-*N*-(methoxymethyl)acetamide, which is one of the metabolites of alachlor (20, 23).

Compound **5**, MW 291, may correspond to 2-oxo-*N*-(2,6-diethylphenyl)-*N*-(butoxymethyl)acetamide. Retention time is 8.25 min. The base ion peak at m/z 57 is $C_4H_9^+$ peak. The molecular ion could lose C_4H_9OH to give the ion at m/z 217, and CHO to give the ion at m/z 188. The mass spectrum of **5** is similar to that of 2-oxo-*N*-(2,6-diethylphenyl)-*N*-(methoxymethyl)acetamide which is one of the metabolites of alachlor (23).

Compound **6**, with MW of 291, may correspond to 1-hydroxyacetyl-2-butoxyl-3-methyl-7-ethylindole. Retention time is 8.40 min. The molecular ion could lose C_4H_9O to give the ion at m/z 218, and C_4H_9OH to give the ion at m/z 217. The molecular ion could lose C_4H_9O and $COCHOH$ (one γ H rearrange) to give the base peak ion at m/z 160, and C_4H_9 and $COCHOH$ to give the ion at m/z 176. The molecular ion could lose C_4H_9OCH and $COCH_2OH$ to give the ion at m/z 146. The compound has not been reported in previous literature.

Compound **7**, with a molecular weight of 275, may correspond to 8-ethyl-1-butoxymethyl-4-methyl-2-oxo-1,2,3,4-tetrahydroquinoline. Retention time is 8.52 min. The molecular ion could lose C_4H_9OH to give the ion at m/z 201, and lose $C_4H_9OCH_2$ to give the ion at m/z 188. The ion at m/z 188 could lose two H to give the ion at m/z 186, and lose CH_2 to give the ion at m/z 174, and lose $COCH_2$ to give the ion at m/z 146. The mass spectrum of compound **6** is similar to that of 8-ethyl-1-methoxymethyl-4-methyl-2-oxo-1,2,3,4-tetrahydroquinoline, which is one of the photoproducts of alachlor (13).

Compound **9**, with MW 293, may correspond to 2-hydroxy-2',6'-diethyl-*N*-(butoxymethyl)acetanilide. Retention time is 8.95 min. The base ion peak at m/z 57 is the $C_4H_9^+$ peak. The ions at m/z 236, 219, 188, and 160 may correspond to loss of C_4H_9 ; C_4H_9OH ; C_4H_9OH and CH_2OH ; and C_4H_9OH and $COCH_2OH$ from the molecular ion, respectively. The mass spectrum of **9** is similar to that of 2-hydroxy-2',6'-diethyl-*N*-(methoxymethyl)acetanilide, which is one of the photoproducts of alachlor (13).

Compound **10**, with a molecular weight of 275, may correspond to 1-acetyl-2-butoxyl-3-methyl-7-ethylindole. Retention time is 9.03 min. The base ion peak at m/z 57 is $C_4H_9^+$. The ion at m/z 201, 189, 174, and 146 may correspond to loss of C_4H_9OH ; C_4H_9OCH ; C_4H_9OCH and CH_3 ; and C_4H_9OCH and $COCH_3$ from the molecular ion, respectively. The compound has not been reported in previous literature.

The mass spectrum of compound **11** showed a molecular ion peak at m/z 275, and ion peaks at m/z 260, 218, 188, and 174, which correspond to loss of CH_3 , C_4H_9 , $C_4H_9OCH_2$, and $C_4H_9OCH_2$ and CH_2 , respectively. Retention time is 9.14 min. The compound was not reported before. We found that compound **11** was transformed to compound **9** when the extracted sample was placed for a few days. Compound **11**

FIGURE 5. GC/MS spectra and presumed chemical structures of metabolites.

FIGURE 6. Presumed mechanism of butachlor photodegradation.

may be not stable enough and reacted with H_2O cleaving the cycle to form **9**.

Comparing with the standard mass spectrum of butachlor, the probability of compound **12** corresponding to butachlor is 97.4%. Its retention time is 9.25 min. The ion at m/z 276, 237, 188, 176, and 160 may correspond to loss of Cl, $\text{C}_4\text{H}_9\text{OH}$; $\text{C}_4\text{H}_9\text{OH}$ and CH_2Cl ; C_4H_9 and H and COCH_2Cl ; and $\text{C}_4\text{H}_9\text{OH}$ and COCH_2Cl from the molecular ion. The base ion peak at m/z 57 is C_4H_9^+ .

We presumed that the molecular weight of compound **3** is 263 and the molecular weight of compound **8** is 275. No structure could be attributed with certainty to either compound **3** or compound **8**.

In our studies, dechlorination is presumably the first step of photodegradation of butachlor in water when irradiated with UV light. Absorption of a photon by the carbonyl of butachlor is followed by loss of chlorine at the α -carbon, affording intermediate compound **13**. Intermediate compound **13** proceeds to a hydroxylation process or a cyclization process to give various photoproducts. Compound **1** may be formed by other photoproducts proceeding to degrade. Figure 6 shows a mechanism of butachlor photodegradation.

However, according to Wilson and Mabury's (17) investigation, monochloroacetic acid was a major photoproduct of chloroacetanilide herbicides in synthetic field water. But monochloroacetic acid has not been detected in our studies. Maybe monochloroacetic acid was neglected because of our analytical method limitation, as monochloroacetic acid is a strong polar product. Monochloroacetic acid may be formed on another pathway of photodegradation (17). It should be noted that photolysis rates and photoproduct formation are actually dependent on the intensity and the wavelength distribution of the light used. The photodegradation mechanism and products of butachlor in our study are not all the same as sunlight photodegradation under natural environmental conditions.

Hydrolysis. The kinetics process of butachlor can also be described by the first-order reaction equation. The experimental results indicated that H^+ can accelerate butachlor hydrolysis. The rate constant k values of butachlor hydrolysis were 1.1×10^{-3} , 6×10^{-4} , and $6 \times 10^{-4} \text{ d}^{-1}$ in pH 4, 7, and 10 aqueous solutions, respectively. The half-life of butachlor hydrolysis at pH 4, 7, and 10 was 630, 1155, and 1155 days at 25°C respectively. Butachlor possesses a long hydrolysis half-life. A hydrolysis product at pH 4 was identified to be compound **9** [2-hydroxy-2',6'-diethyl-*N*-(butoxymethyl) acetanilide]. Retention time of hydrolysis product is 8.95 min. Dechlorination is regarded as a route of hydrolysis. The hydrolysis pathway is still not well elucidated because of the likely formation of the highly polar product monochloroacetic acid, and their extraction from water remains a difficult topic.

Conclusions

Eleven degradation products of butachlor were identified by GC/MS after photolysis and hydrolysis in water. Compound **9** [2-hydroxy-2',6'-diethyl-*N*-(butoxymethyl) acetanilide] was found to be a common product in photolysis and hydrolysis. Major photoproducts are compounds **9**, **7**, and **11**. Dechlorination is presumably the first step of photodegradation of butachlor and is followed by either hydroxylation or cyclization. Hydrolysis of butachlor is a slow process and dechlorination is a route of hydrolysis. The half-life of butachlor hydrolysis at pH 4, 7, and 10 was 630, 1155, and 1155 days at 25°C respectively. However, when exposed to UV light, butachlor in aqueous solution was rapidly degraded, the half-lives at initial concentration of 20 mg L^{-1} butachlor were only 7.54, 10.56, and 12.22 min in deionized water, river water, and paddy water, respectively.

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