

## Studies on the Chemistry of Alachlor and Disinfectant Agents (HOCl and ClO<sub>2</sub>)

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### ABSTRACT

Alachlor was incubated with hypochlorous acid for 24 hours. The herbicide and its transformation products were extracted by liquid-liquid extractions and analyzed by gas chromatography/ mass spectrometry. Six compounds were detected in the residue of the reaction between Alachlor and HOCl after 24 hr. of incubation at room temperature, whose spectral data indicated that they were derived from Alachlor via chlorination and hydrolysis reactions. Among the structural assignments, two products were confirmed by analysis of standards of which they were synthesized. The Alachlor was not detected in the reaction residue. In quantitative studies, at all of the concentrations of HOCl, the percentage remaining of the parent compound at pH 3.0 was significantly lower compared to the reaction at pH 7.0. The major product of Alachlor and ClO<sub>2</sub> is N-(methoxycarbonyl)-N-(2,6-diethylphenyl) oxamic acid. The data showed that chlorination and cleavage of the N-methoxymethyl (MOM) group are significant features of the environmental degradation of Alachlor during water treatment with Cl<sub>2</sub>.

### 1. Introduction

Institution of disinfection to drinking water treatment has been one of the key successes of public health policy. Since 1908, chlorination has remained the most widely used method for disinfection of public water supplies. In recent years, however, it was clear that treatment of drinking water with chlorine results in the formation of trihalomethanes [1, 2]. Chlorine dioxide is a very attractive alternative to chlorine as a disinfectant. Kály-Kullai et al., 2020 hypothesize on methods to control the spread of viral infections using aqueous ClO<sub>2</sub> solutions [3]. For all intents and purposes, its disinfectant properties are equivalent to or perhaps exceed those of chlorine [4]. The use of chemical disinfectants in water treatment usually results in the formation of chemical by-products, some of which are potentially hazardous. By-products may be formed during water disinfection from either naturally occurring substances in water or from contaminants.

The present study investigates the nature of disinfection by-products formed when drinking water is contaminated with the herbicide Alachlor.

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Alachlor, 2-chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl) Acetamide, is preemergence herbicide of the chloroacetanilide family, widely used on different crops since 1969. Concern about Alachlor degradation is mainly focused on the possibility of detecting its transformation products in surface and ground waters, which they can contaminate by run-off or leaching, or where they can originate from the pesticide. These compounds present the possibility of human exposure via consumption of untreated ground water in these regions. Indeed, in some cases transformation products can be at least as toxic as the parent compound [5, 6]. EPA has set the maximum contaminant level (MCL) in drinking water at 2 µg/ L [7]. Thus, above these levels removal of Alachlor from natural water is necessary. Among treatment methods, ozonation of Alachlor has been carried out to gain information of its removal from the surface water [8-10]. Consistent with our previous published work, the by-products formed from Alachlor on treatment with chlorine were more toxic on glutathione than this formed during ClO<sub>2</sub> treatment [11]. This study investigates the mechanism of disinfection by-product formation utilizing example of common occurring substance in drinking water. The most heavily used herbicide, Alachlor, was evaluated after its reaction with HOCl.

## 2. Materials and methods

Alachlor was purchased from Chem Services (Westchester, PA). Phenanthrene-*d*<sub>10</sub> Aldrich (Milwaukee, WI) was used as an internal standard in the quantitative analysis. DPD powder was obtained from Lamotte Chemical (Chestertown, MD). All other chemicals and reagents utilized were of the highest purity obtained from Sigma Chemical Company (St. Louis, MO). Samples were analyzed using a Hewlett-Packard 5890 gas chromatograph equipped with 5988 mass spectrometer. Operating conditions were as follows: a direct capillary interface at 280 °C, ionization voltage 70 eV, ion source temperature 200 °C, electron multiplier 400 V above autotune, tuned daily with perflourotributylamine. Samples were injected in the splitless mode into the gas chromatograph. Alachlor and its by-products were separated on a 15 m × 0.2 mm ID., DP-5 fused-silica capillary column with a film thickness of 0.33 μm. The helium was used as carrier gas of flow-rate 1 mL/min. The initial column temperature of 60 °C was programmed up to 280 °C at 16 °C/min. hold at 280 for 6.25 min. The peak area for each compound was divided by the peak area of phenanthrene-*d*<sub>10</sub> (internal standard).

Compounds confirmation was based upon the presence of the molecular ion, and several fragments as well as the retention time. Gas chromatographic analysis was conducted on a Varian, Model 3700, GC equipped with a Ni<sup>63</sup> high temperature electron capture detector (ECD). A capillary column 30 m × 0.25 mm (I.D) packed with AT-5 was used. The nitrogen gas flow-rate 30 mL/min. <sup>1</sup>H-NMR spectra were run on Gemini-300 instrument and obtained using dilutes solution in CDCl<sub>3</sub>. Multiple comparisons were performed using ANOVA followed by Tukey-Kramer Honestly Significant Difference (HSD) test to study the reaction of Alachlor with chlorine and chlorine dioxide. All analyses were performed using the statistical software package JMP 3.2.1 (SAS Institute, Inc., Cary, NC). Results are expressed as means ± S. E. M. for all analyses. *P* value <0.05 was used for statistical significance.

*Preparation of chlorine dioxide and hypochlorous acid solutions:*

### 1. ClO<sub>2</sub> solution

Chlorine dioxide solution was prepared daily by the following procedure:

Conc. H<sub>2</sub>SO<sub>4</sub> was added drop-wise to a mixture of (2:1 wt/wt) potassium chlorate and anhydrous oxalic acid. The generated ClO<sub>2</sub> gas was passed through a trap containing sodium chlorite powder to convert any chlorine gas which produced as a by-product. The gas was then collected into a flask containing cold distilled water.

The concentrations of ClO<sub>2</sub> and HOCl in water were determined daily by the diethyl-p-phenyl diamine (DPD) method of Plain, 1967.

An aliquot of ClO<sub>2</sub> stock solution was placed in a flask containing 100 mL distilled water followed by the addition of 1.0 mL of 1% (w/v) malonic acid. The solution was mixed

for 1 min. and 0.5 g DPD powder was added. The mixture was then titrated rapidly with freshly prepared ferrous ammonium sulfate solution (0.0028 N) till the pink color was discharged, record the reading (M). The following equation was used to determine the concentration of ClO<sub>2</sub> solution:

$$\text{ClO}_2 \text{ (mg/L)} = 100 \times M / 0.526 \times m$$

Where

100; for a 100 mL sample, 1 mL FAS solution (0.0028 N) equals 1mg/L available chlorine.

0.526; chlorine in ClO<sub>2</sub> is 52.6 % by weight.

M; Burette reading.

m; volume of ClO<sub>2</sub> stock solution added to 100 mL distilled water.

### 2. HOCl solution

Chlorine gas was generated daily by adding conc. HCl to KMnO<sub>4</sub>. The generated gas was bubbled into trap containing cold distilled water.

An aliquot of HOCl stock solution was placed in a flask containing 100 mL distilled water, after stirring for 1 min., 0.5 g DPD powder was added. The solution was then titrated with freshly prepared ferrous ammonium sulfate solution (0.0028 N) to the first colorless end point, record the burette reading (A).

$$\text{Cl}_2 \text{ (mg/L)} = 100 \times (A-M) / m$$

### *Qualitative analysis of Alachlor and disinfectants reaction*

Standard solutions were prepared daily, for Alachlor (10 mg/ mL) and phenanthrene-*d*<sub>10</sub> (10 mg/ 10 mL), in EtOH: H<sub>2</sub>O and DCM, respectively. Dilute directly from the stock solution of Alachlor to reach the following concentrations 5, 20, 50 and 100 μg/ mL in 1 mL total volume. 100 μg/ mL phenanthrene-*d*<sub>10</sub> was added. The procedures of extraction, evaporation and reconstitution were performed as that will be described for the reaction mixture.

The peak area ratio of the Alachlor/ internal standard was plotted against the concentrations of Alachlor (μg/ mL), then the generated standard curve was used to calculate the concentrations of Alachlor in samples after its reaction with HOCl or ClO<sub>2</sub>. The reaction started by the addition of HOCl (5, 10 and 20 ppm), at pH 3.0 and 7.0, or ClO<sub>2</sub> (5 ppm) to a solution of Alachlor (50 μg/ mL). All vials caps were equipped with Teflon-lined silicon septa to prevent adsorption of materials by the caps. At the end of incubation, aliquots were removed from the reaction mixture and immediately prepared for extraction. The aliquot was spiked with phenanthrene-*d*<sub>10</sub> (50 μg/ mL), which was used as an internal standard. After extraction, the samples were refrigerated at 4 °C and analyzed 24 hr. later. The time course of the reaction of Alachlor (50 μg/ mL) and HOCl (5 ppm) at pH 3.0 and 7.0 was also studied. An aliquot was removed following 15, 30 and 60 min. The same procedure for extraction, evaporation and reconstitution was also performed.

### *Synthesis of 2-chloro-N-(3-chloro-2,6-diethylphenyl)acetamide*

Chloroacetyl chloride (0.09 mL, 1.2 mmol) was added to a solution of 3-chloro-2,6-diethylaniline (0.15 g, 0.092 mmol) and triethylamine (0.4 mL, 2.7 mmol) in  $\text{CH}_2\text{Cl}_2$  (15 mL), maintained at  $-20^\circ\text{C}$ . The reaction mixture was then stirred at  $20^\circ\text{C}$  for 24 hr.. The reaction mixture was then extracted with DCM and crystallized from ethanol. Also it was prepared by refluxing of a crude oily precipitate of 2-chloro-N-(3-chloro-2,6-diethylphenyl)-N-(methoxymethyl)acetamide, which was formed during the reaction of Alachlor and HOCl, with 6 N HCl for 2 hr..

### *Synthesis of 2-chloro-N-(3-chloro-2,6-diethylphenyl)-N-(methoxymethyl)acetamide*

To a solution of the amide, 2-chloro-N-(3-chloro-2,6-diethylphenyl)acetamide (0.10 g, 0.52 mmol), methoxymethyl chloride (75  $\mu\text{L}$ , 1 mmol) and phenyl triethylammonium chloride (2.7 mg) in  $\text{CH}_2\text{Cl}_2$  (150  $\mu\text{L}$ ), 50% NaOH (0.27 mL) solution was added drop wise and the reaction mixture was stirred vigorously for 1 hour at  $0-5^\circ\text{C}$ .

### *Quantitative Analysis of Alachlor and Disinfectants Reaction*

Chlorine gas or chlorine dioxide was generated *in situ* and bubbled through a trap containing cold aqueous solution of Alachlor (200  $\mu\text{g}/\text{mL}$ ). Aliquots were removed following 5, 10, 15, 30 and 60 min., and then extracted using  $\text{C}_{18}$  cartridges. The rest of the reaction mixture was left over night to determine by-product in the residue. The reaction mixture was left over night to determine the products in the residue. At the end of incubation, aliquots were removed from the reaction mixture and immediately prepared for extraction. The sample was extracted by addition of 3 mL of DCM and shaking for 15 min. followed by centrifugation at  $4-10^\circ\text{C}$  at 1000 rpm's for 5 minhr.. The aqueous layer was removed and the organic phase was dried over anhydrous sodium sulfate, and then transferred to a clean test tube. Under a stream of nitrogen gas, 2 mL of the extract was evaporated gently till dryness then reconstituted in 100  $\mu\text{L}$  of DCM.

The concentrations of Alachlor and its by-products were analyzed by injection of 1  $\mu\text{L}$  into GC-MS. Samples were analyzed using a Hewlett-Packard 5890 gas chromatograph equipped with 5988 mass spectroscopy. Operating conditions were as follows: a direct capillary interface at  $280^\circ\text{C}$ , ionization voltage 70 eV, ion source temperature  $200^\circ\text{C}$ , and electron multiplier 400 V above autotune, tuned daily with perfluorotributylamine. Samples were injected in the splitless mode into the gas chromatograph. Alachlor and its by-products were separated on a 15 m  $\times$  0.2 mm I.D., DP-5 fused-silica capillary column with a film thickness of 0.33  $\mu\text{m}$ . the helium carrier gas flow-rate was 1 mL/ min. The initial column temperature of  $60^\circ\text{C}$  was programmed up to  $280^\circ\text{C}$  at  $16^\circ\text{C}/\text{min}$ . hold at  $280^\circ\text{C}$  for 6.25 min.

## 3. Result and Discussion

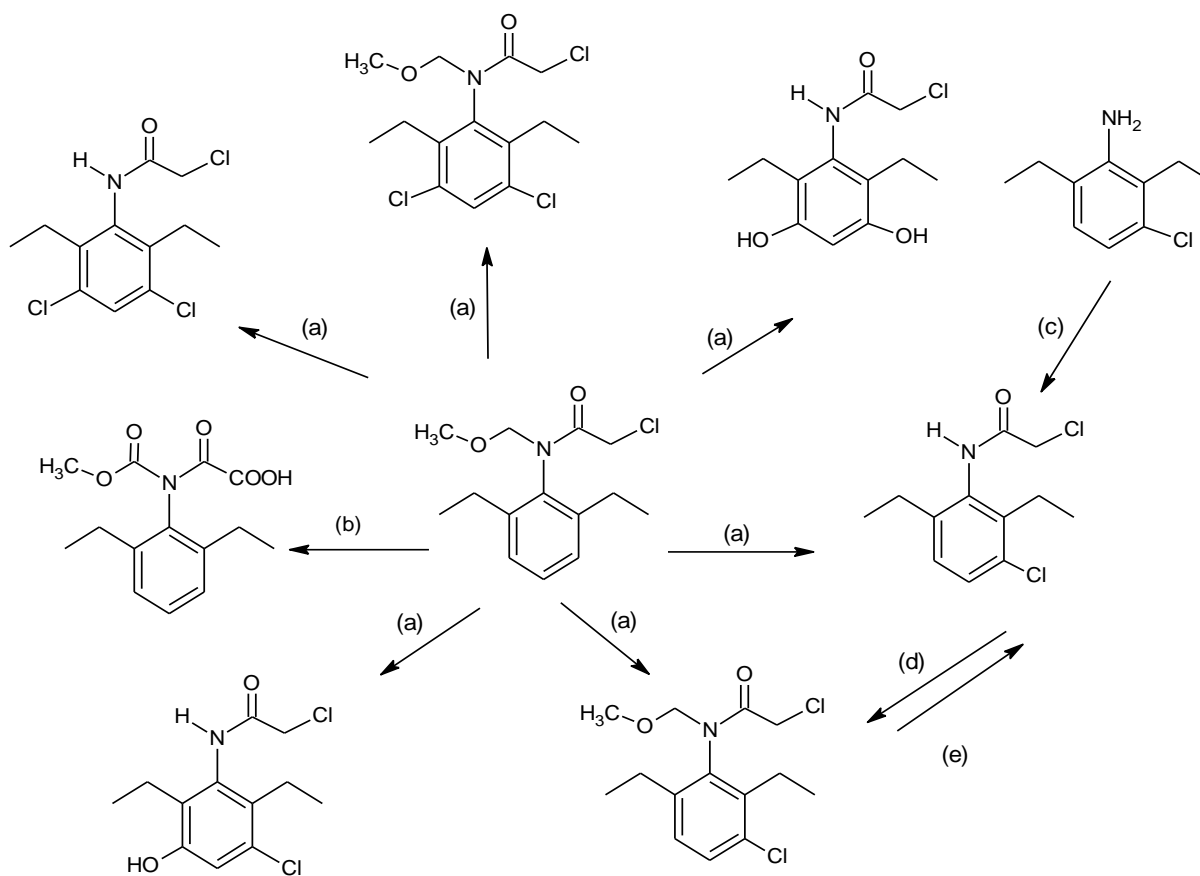
When chlorine gas was bubbled through an aqueous solution of Alachlor, all the Alachlor was depleted within 30 min. The HOCl concentrations of this reaction were followed by Plain methods [12], and after 60 min. the concentration had fallen, indicating the progress of the reaction. The reaction mixture was extracted by Solid Phase Extraction (SPE) as described by Thurman et al., and Aga et al [13, 14]. However, the GC/ECD analysis of the reaction mixture showed that in addition to the parent compound there are two peaks. The peak at about 4.55 min. is corresponding to Alachlor while 6.68 and 9.36 min. retention times are corresponding to new ones 2-chloro-N-(3-chloro-2,6-diethylphenyl)-N-(methoxymethyl)acetamide and 2-chloro-N-(3-chloro-2,6-diethylphenyl)acetamide, respectively. The amount of the major product 2-chloro-N-(3-chloro-2,6-diethylphenyl)-N-(methoxymethyl)acetamide was increased with increasing the time. Although 2-chloro-N-(3-chloro-2,6-diethylphenyl)-N-(methoxymethyl)acetamide was formed as early as 5 min. of the reaction, 2-chloro-N-(3-chloro-2,6-diethylphenyl)acetamide started to appear after 30 min. of the reaction. The structural assignment of this by-product is based on the mass spectral data along with its identity with a synthetic standard sample. There are six compounds, including 2-chloro-N-(3-chloro-2,6-diethylphenyl)acetamide and 2-chloro-N-(3-chloro-2,6-diethylphenyl)acetamide, were detected in the residue of the reaction after 24 hr. of incubation at room temperature, whose spectral data indicated that they are derived from Alachlor via chlorination and hydrolysis reactions (Table 1) and Scheme 1.

The various compounds identified usually exhibited losses of 31, 32, 44, 45, 49 and 77 ions corresponding to  $\text{OCH}_3$ ,  $\text{HOCH}_3$ ,  $\text{CH}_2\text{OCH}_2$ ,  $\text{CH}_2\text{OCH}_3$ ,  $\text{CH}_2\text{Cl}$  and  $\text{COCH}_2\text{Cl}$ , respectively. Overall, the data showed that chlorination and cleavage of the N-methoxymethyl (MOM) group are significant features of the environmental degradation of Alachlor during the water treatment with  $\text{Cl}_2$ . The fast disappearance of the Alachlor is because of the enhance reactivity of the substance towards OH radicals, and these radicals oxidized the side chain on the aromatic ring and hydroxylated the benzene ring. After that, chlorination occurred on the aromatic ring resulting in a substitution of the hydroxyl group with a chlorine atom. However, the products 1, 2, 3 and 4 do not include the methoxymethyl group, which, when present gives a strong ion at  $m/z$  45. The most abundant compound formed during the reaction of Alachlor and HOCl was identified as 2-chloro-N-(3-chloro-2,6-diethylphenyl)-N-(methoxymethyl)acetamide.

By observing the spectrum, the base peak of Alachlor  $m/z$  160, which is corresponding to the aromatic core  $\text{C}_{11}\text{H}_{15}\text{N}$ , was shifted after chlorination to  $m/z$  194, indication that Cl replacement occurred, resulting in a net gain of about 35 amu.

**Table 1:** Mass spectral data of Alachlor and HOCl by-products detected in the residue

Peak	M.Wt	Bp	R.T	Compound
1	257	180	7.87	2-chloro-N-(3,5-dihydroxy-2,6-diethylphenyl) acetamide
2	259	210	8.25	2-chloro-N-(3-chloro-2,6-diethylphenyl) acetamide
3	275	180	8.66	2-chloro-N-(3-chloro-5-hydroxy-2,6-diethylphenyl) acetamide
4	293	244	9.18	2-chloro-N-(3,5-dichloro-2,6-diethylphenyl) acetamide
5	303	194	9.43	2-chloro-N-(3-chloro-2,6-diethylphenyl)-N-(methoxymethyl) acetamide
6	337	45	10.20	2-chloro-N-(3,5-dichloro-2,6-diethylphenyl)-N-(methoxymethyl) acetamide



Reaction Condition: (a) HOCl; (b)  $\text{ClO}_2$ ; (c)  $\text{ClCH}_2\text{COCl}$ ,  $\text{Et}_3\text{N}$ , DCM,  $-20^\circ\text{C}$ , 24 hr.;  
 (d)  $\text{ClCH}_2\text{OCH}_3$ , 50% NaOH; (e) 6 N HCl, Rf, 2 hrs.

**Scheme 1: The Reactions of Alachlor with HOCl and  $\text{ClO}_2$**

The m/z 77 and m/z 45 ions are corresponding to the chlorinated and methoxymethyl acetamide side chains, respectively. These ions were found after chlorination indicates that these side chains are unaltered by chlorination. The spectra suggest that the aromatic ring be modified by the replacement of hydrogen with chlorine. This addition should result in a molecular ion of about 303 amu which is shown in the spectrum. Another conformation was carried out using  $^1\text{H}$  NMR spectra and compared with the parent compound Alachlor. For Alachlor  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.27 (t, Ar-1H-4), 7.24 (d, 2H-3,5), 4.97 (s, 2H- $\text{CH}_2\text{O}$ ), 3.71 (s, 2H- $\text{OCCH}_2\text{Cl}$ ), 3.50 (s, 3H- $\text{CH}_3\text{O}$ ), 2.55 (m, 4H- $\text{CH}_2$ , diethyl), 1.22 (t, 6H- $\text{CH}_3$ , diethyl). However,  $^1\text{H}$  NMR spectra of 2-chloro-N-(3-chloro-2,6-diethylphenyl) acetamide structure was confirmed by comparison with an authentic synthetic standard and its acid hydrolysis to 2-chloro-N-(3-chloro-2,6-diethylphenyl) acetamide.

The structural assignment of this by-product is confirmed by comparison with a synthetic standard. The two data sets give a reasonable match. The second compound, formed during the same reaction and isolated from the reaction mixture, was identified as 2-chloro-N-(3-chloro-2,6-diethylphenyl) acetamide. The structural assignment of this by-product is also confirmed by comparison with an authentic standard. The spectral data of the peak at 8.66 min. retention time shows that the fragment at m/z 77 ions corresponding to the chlorinated acetamide side chain is still intact. However, parent ion  $\text{M}^+$  259 could lose  $-\text{CH}_2\text{Cl}$  to give the ion at 210 (The base peak) which refers to the aromatic  $\text{C}_{11}\text{H}_{14}\text{NOCl}$  core. On the basis of the mass spectrum of the peak at 7.87 min. retention time, the product was identified as 2-chloro-N-(3,5-dihydroxy-2,6-diethylphenyl) acetamide. The m/z 77 ion was found, which is analogous to the chlorinated acetamide side chain, indicating that this side chain unaltered during the incubation period. On the other hand, the m/z 45 ion, the analogous to the methoxymethyl acetamide side chain, was not found indicating a hydrolysis occurrence under the acidic condition. However, the base peak in this spectrum m/z 180 ion referred to 3,5-dihydroxy-2,6-diethylaniline ( $\text{C}_{10}\text{H}_{15}\text{NO}_2$ ) indicating that two hydroxyl groups were added to the aromatic ring. The mass spectrum analysis of the peak at 8 was assigned, on the basis of MS, as 2-chloro-N-(3-chloro-5-hydroxy-2,6-diethylphenyl) acetamide. Also the m/z 45 ion was not found, but the other chlorinated acetamide side chain was present indicating that a cleavage of the methoxymethyl group was occurred but the  $-\text{COCH}_2\text{Cl}$  group still intact. The spectra of that peak suggest that the molecular ion will be 275 amu (not seen in the spectrum), which resulted from the addition of a chlorine atom and a hydroxyl group to the aromatic ring. The base peak at m/z 180 ion was found as a result of loss of m/z 77 and 17 ions from the parent molecular ion m/z 275, these ions refer to the chlorinated acetamide side chain and hydroxyl group, respectively. Studying the spectrum analysis of the peak at 9.18 suggested that the parent ion  $\text{M}^+$  293 could lose m/z 49 ion ( $-\text{CH}_2\text{Cl}$ ) to give the ion at m/z 244 (the base peak) which corresponds to  $\text{C}_{11}\text{H}_{13}\text{NOCl}_2$ . The m/z 77 ion ( $-\text{COCH}_2\text{Cl}$ ) was found indicating that this side chain was unaltered. On the other hand, the m/z 45 ion (MOM) was found indicating that cleavage of this side chain occurred. On the basis of these considerations, a hypothetical structural formula was assigned as 2-chloro-N-(3,5-dichloro-2,6-diethylphenyl) acetamide. From the mass spectrum analysis of the peak at 10.20 min. retention time, the base peak is m/z 45 ion, which corresponds to the methoxymethyl acetamide side chain. This would indicate that this side chain is still intact. Also, the m/z ion is analogous to the chlorinated side chain of the Alachlor molecule. This m/z 77 ion was also found indicating that this side chain was unaltered. The mass spectra suggest that the aromatic ring of the Alachlor was modified by the addition of two chlorine atoms and resulted in a molecular ion of about 337. This molecular ion was not seen, but an ion fragment m/z 292 was seen. The molecular ion  $\sim$  337 of this product with a facile loss of m/z 45 (MOM) would be m/z  $\sim$  292. Hence, this product was identified as 2-chloro-N-(3,5-dichloro-2,6-diethylphenyl)-N-(methoxymethyl) acetamide. It is found that pH plays a major role on the reaction between Alachlor and HOCl. However, at pH 3.0 about 80 % of Alachlor reacts with 5 ppm HOCl for 15 min. and by changing the concentrations of HOCl to 10 and 20 ppm the amount remaining from Alachlor almost the same as that at 5 ppm. While, at pH 7.0 by 10 ppm HOCl the % remaining from the parent compound decreased slightly and by 20 ppm it was significantly different when compared with the reaction at 5 and 10 ppm HOCl. On studying the effect of pH on the time course of Alachlor reaction with HOCl, following a 1 hour reaction period, quantitative analysis revealed that an average of 83 % and 14 % of Alachlor was reacted at pH 3.0 and 7.0, respectively. As early as 15 min. the highest concentration of Alachlor was reacted with chlorine. At pH 3.0 the amount remaining from Alachlor was significantly different than the amount remaining at pH 7.0. Again at pH 3.0, 30 and 60 min reaction time was stronger than pH 7.0 and the percentage remaining from the parent compound were significantly different when compared with the percentage remaining from the parent compound at pH 7.0 (Table 2, 3).

COCH<sub>2</sub>Cl) was found indicating that this side chain was unaltered. On the other hand, the m/z 45 ion (MOM) was found indicating that cleavage of this side chain occurred. On the basis of these considerations, a hypothetical structural formula was assigned as 2-chloro-N-(3,5-dichloro-2,6-diethylphenyl) acetamide. From the mass spectrum analysis of the peak at 10.20 min. retention time, the base peak is m/z 45 ion, which corresponds to the methoxymethyl acetamide side chain. This would indicate that this side chain is still intact. Also, the m/z ion is analogous to the chlorinated side chain of the Alachlor molecule. This m/z 77 ion was also found indicating that this side chain was unaltered. The mass spectra suggest that the aromatic ring of the Alachlor was modified by the addition of two chlorine atoms and resulted in a molecular ion of about 337. This molecular ion was not seen, but an ion fragment m/z 292 was seen. The molecular ion  $\sim$  337 of this product with a facile loss of m/z 45 (MOM) would be m/z  $\sim$  292. Hence, this product was identified as 2-chloro-N-(3,5-dichloro-2,6-diethylphenyl)-N-(methoxymethyl) acetamide. It is found that pH plays a major role on the reaction between Alachlor and HOCl. However, at pH 3.0 about 80 % of Alachlor reacts with 5 ppm HOCl for 15 min. and by changing the concentrations of HOCl to 10 and 20 ppm the amount remaining from Alachlor almost the same as that at 5 ppm. While, at pH 7.0 by 10 ppm HOCl the % remaining from the parent compound decreased slightly and by 20 ppm it was significantly different when compared with the reaction at 5 and 10 ppm HOCl. On studying the effect of pH on the time course of Alachlor reaction with HOCl, following a 1 hour reaction period, quantitative analysis revealed that an average of 83 % and 14 % of Alachlor was reacted at pH 3.0 and 7.0, respectively. As early as 15 min. the highest concentration of Alachlor was reacted with chlorine. At pH 3.0 the amount remaining from Alachlor was significantly different than the amount remaining at pH 7.0. Again at pH 3.0, 30 and 60 min reaction time was stronger than pH 7.0 and the percentage remaining from the parent compound were significantly different when compared with the percentage remaining from the parent compound at pH 7.0 (Table 2, 3).

**Table 2:** Effect of pH on Alachlor and HOCl reaction

pH	HOCl Conc. (ppm)		
	5	10	20
3	18.6 $\pm$ 1.6 <sup>a,b</sup>	17.4 $\pm$ 1.6 <sup>a,b</sup>	16.8 $\pm$ 1.7 <sup>a,b</sup>
7	58.3 $\pm$ 3.0 <sup>a</sup>	53.1 $\pm$ 7.7 <sup>a</sup>	36.0 $\pm$ 5.3 <sup>a,c</sup>

Values represented as the mean ( $\pm$  S. E.) of the percentage of Alachlor remaining after its reaction with different concentrations of HOCl for 15 min. n= 7 (3-4 replicates per reaction).

<sup>a</sup> Significantly different from the reaction at zero HOCl concentration ( $P < 0.05$ ).

<sup>b</sup> Significantly different from the reaction at pH 7.0 ( $P < 0.05$ ).

<sup>c</sup> Significantly different from the reaction at 5 and 10 ppm HOCl ( $P < 0.05$ ).

**Table 3:** Effect of pH on the time course of Alachlor and HOCl reaction

pH	Time (min.)		
	15	30	60
3	18.6±1.5 <sup>a,b</sup>	16.5±1.7 <sup>a,b</sup>	16.8±1.7 <sup>a,b</sup>
7	58.3±3.0 <sup>a</sup>	46.3±5.4 <sup>a,c</sup>	41.1±3.5 <sup>a,c</sup>

Values represented as the mean ( $\pm$  S. E.) of the percentage of Alachlor remaining from the reaction of (50 $\mu$ g/ mL) Alachlor with (5ppm) HOCl.

<sup>a</sup> Significantly different from the reaction at zero time ( $P < 0.05$ ).

<sup>b</sup> Significantly different from the reaction at pH 7.0 ( $P < 0.05$ ).

<sup>c</sup> Significantly different from the reaction after 15 min. ( $P < 0.05$ ).

The GC chromatogram of the reaction mixture of Alachlor and ClO<sub>2</sub> shows the presence of three peaks at retention times 8.43, 9.44 and 11.9 min.. From the mass spectral analysis, it was shown that the first peak is the unreacted Alachlor. The second one at 9.44 min. (negligible amount) was found to be identical with the previously mentioned chlorinated derivative. The major by-product (11.9 min.) was found to N-(methoxycarbonyl)-N-(2,6-diethylphenyl)oxamic acid. The proposed structure is based on the mass spectrum of this compound, which revealed the presence of peak at m/z 149 (base peak), is attributable to the 2,6-diethyl aniline. This indicates that the aromatic nucleus is stable towards oxidation with ClO<sub>2</sub>, which contradicts published data, which showed ring rupture of Alachlor under oxidation with ozone (Somich et al., 1988). The presence of molecular ion peak at 279 adds strong evidence of the proposed structure. It seems that the methylene group of the CH<sub>3</sub>OCH<sub>2</sub>- side chain underwent oxidation to CH<sub>3</sub>OCO- whereas the chloro acetyl group ClCH<sub>2</sub>CO- was oxidized after an alkyl substitution with OH group to give -HOOCO- moiety. However, after the initial attack, ClO<sub>2</sub> in concentrations of > 5 mg/ L failed to oxidize this reaction product to any greater extent. The reaction efficiency was quantitated and appeared to be ~ 10% of the original Alachlor concentration. This data represented as the mean  $\pm$  SE of the % reacted of the parent compound, n= 6 (4 replicates per reaction).

#### 4. Conclusion

Disinfection of water with chlorine afforded more by-product than ClO<sub>2</sub>. The side-chain methoxy methyl group (MOM) was unstable during disinfection process. Treatment with Cl<sub>2</sub> led to cleavage, whereas with ClO<sub>2</sub> it was oxidized. pH of the reaction mixture has considerable effect on the kinetics of the reaction of chlorine with Alachlor. The Isolation and confirmation of these final products in the residue will be the subject of another study.

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