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Occurrence of Alachlor Environmental Degradation Products in Groundwater

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Groundwater samples collected beneath a Massachusetts corn field were analyzed by gas chromatography/mass spectrometry. In addition to alachlor, 20 compounds were detected whose EI and CIMS data indicated that they were derived from alachlor, presumably via environmental degradation. Structural assignments were confirmed for six of these compounds by analysis of standards. They were among 10 alachlor-related compounds that were synthesized by use of either the parent compound or 2,6-diethylaniline as starting material. To our knowledge, none of the confirmed compounds have previously been reported in groundwater samples. The concentration range of the degradation products ranged from 4 to 570 ng L^{-1}. In all samples, the total concentration of the degradation products exceeded the parent compound concentration by at least 2-fold.

Introduction

The herbicide, alachlor, 2-chloro-(2′,6′-diethyl-*N*-(methoxymethyl)acetanilide, is widely used for weed control in corn and soybean production. Concern has arisen regarding health risks associated with its continued use. This is primarily due to its potential to induce cancer in laboratory animals (*1*, *2*). The EPA has classified alachlor as a group *B2* carcinogen (*2*).

Public health concern is also related to its detection in groundwater samples collected in agricultural areas (*3*–*10*). This presents the possibility of human exposure via consumption of untreated groundwater in these regions. EPA has set the maximum contaminant level (MCL) in drinking water at 2 $\mu g\ L^{-1}$ (*2*).

Another feature of alachlor is that there appears to be substantial potential for the formation of stable environmental degradation products which may be leached into groundwater. Laboratory experiments have shown that its degradation by soil microorganisms yields numerous compounds (*11*–*16*). Those detected generally had lower molecular weight than the parent or they were oxidized forms. This confers higher water solubility and enhanced potential for leaching. Alhajjar et al. (*17*) reported detection of 8–12 metabolites of alachlor in leachate collected from large-scale soil column studies. However, structures were not identified.

That alachlor degradation products exist in groundwater has been reported in studies conducted by the U.S. Geological Survey. Pereira et al. (*5*) reported detection of 2-hydroxy-2,6-diethylacetanilide and Koplin et al. (*6*) 2′,6′-diethylaniline (DEA) and 2-[[(2,6-diethylphenyl)methoxy]-methyl)amino]-2-oxoethanesulfonate (ES). In the later study, DEA was detected in 16% of 99 near-surface aquifer samples tested and ES in 45% of 66 samples.

Macomber et al. (*18*) also reported detection of ES in groundwater and Baker et al. (*19*) concluded that the occurrence of ES in groundwater samples was responsible for many of the "false positives" observed when assays were performed with an ELISA test kit (ImmunoSystems). To our knowledge, these studies represent the only evidence that alachlor degradation products occur in groundwater. This is in spite of the fact that the potential exists for formation of a range of compounds that are sufficiently stable to be leached into groundwater.

In this paper, we report on the results of gas chromatography/mass spectrometry (GC/MS) analyses of groundwater samples collected beneath a Massachusetts corn field where alachlor had been used. Numerous substances were detected which had not been previously reported.

Experimental Section

Groundwater Samples. Samples were collected from four monitoring wells installed in a corn field in the Connecticut River valley region of Massachusetts in September 1990. The site has a long history of agricultural use. Alachlor had last been applied in the Spring of 1987. Well construction details, site hydrogeology, and sample collection techniques were described by Jenkins et al. (*4*). Site soils are classified in the *Agawam* series. These soils are rapidly permeable fine sandy loams with 1–5% organic matter in the plow layer. Wells were installed using a hollow stem auger and

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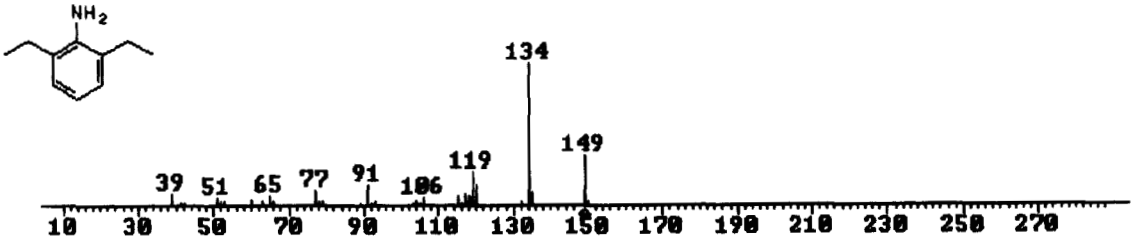
I.

II.



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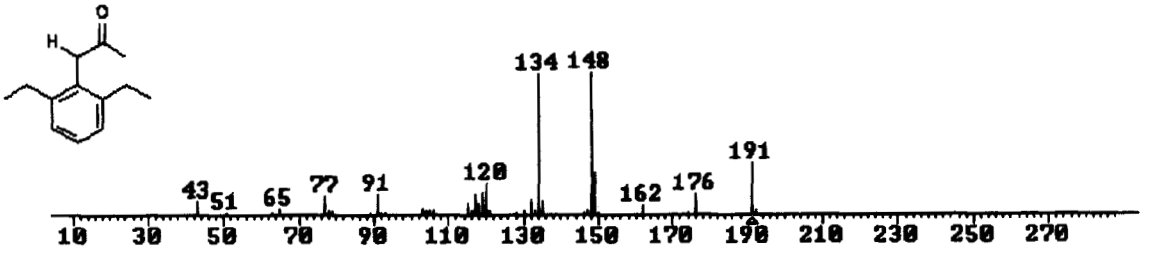

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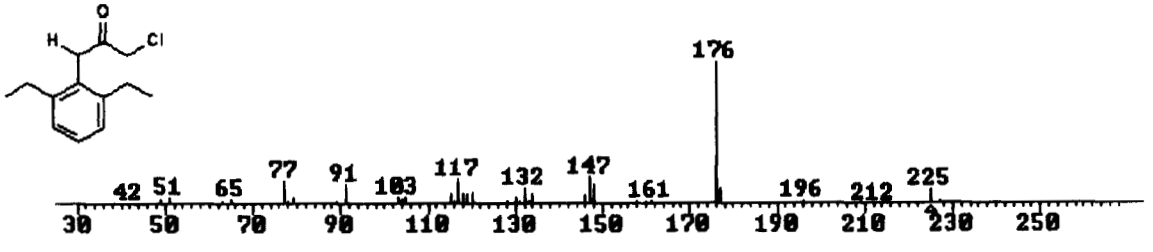

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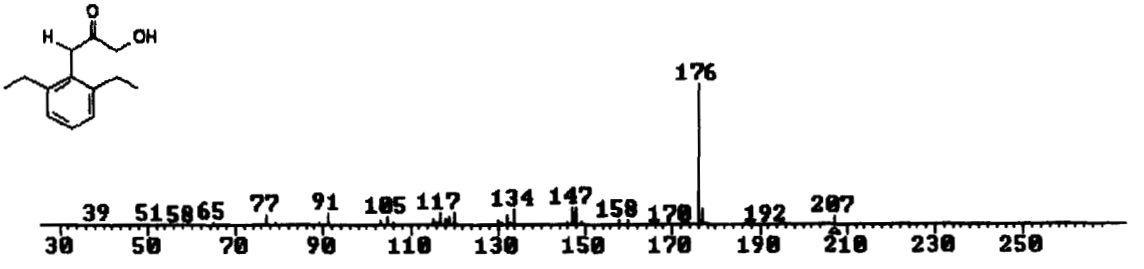

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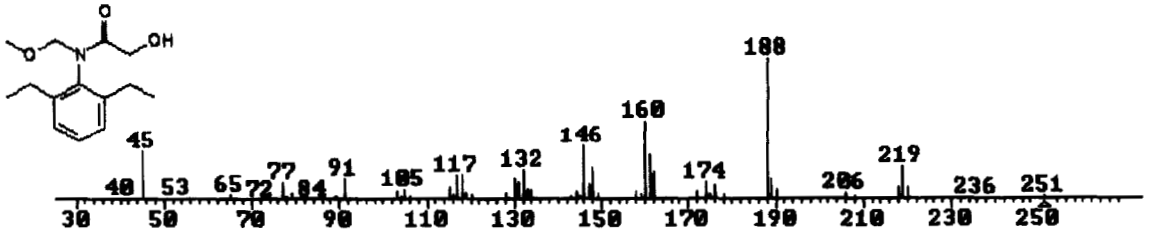

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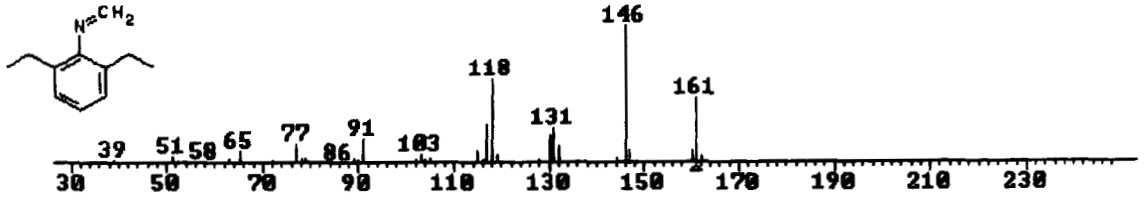

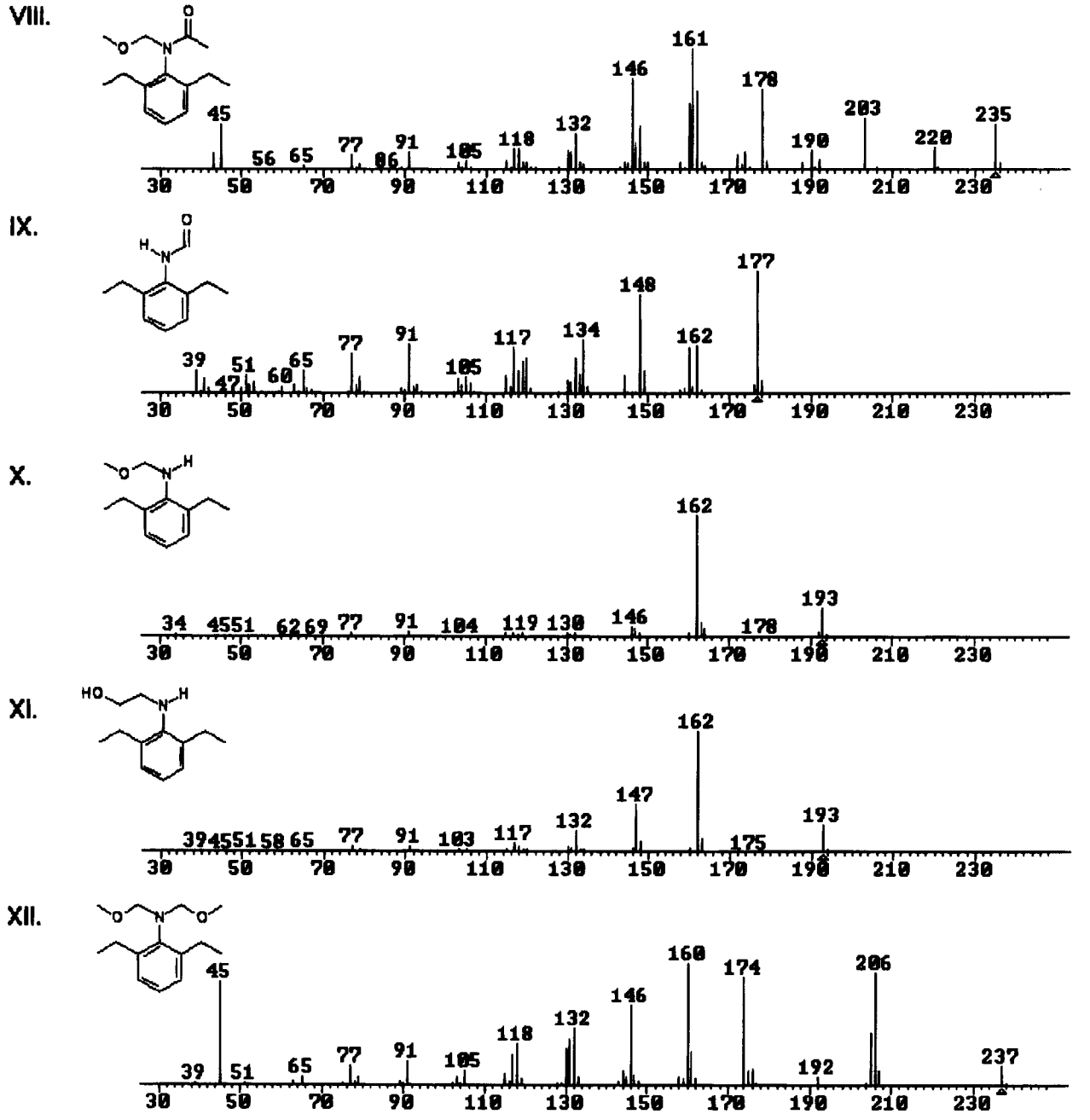

FIGURE 1. Structures and EIMS of synthetic products.

constructed with 2.5-in. PVC. Each had a 5-ft screened interval which spanned the range of seasonal water table fluctuations. Water table elevations averaged 30 ft below grade. Prior to sampling, wells were completely evacuated with a bladder pump constructed with stainless steel and Teflon and allowed to recharge. Samples were then obtained in duplicate 1-L amber glass bottles. They were immediately chilled after collection and stored at 2 °C in the dark until analysis. An initial set of analyses were completed within 14 days of sample collection. Sample duplicates were stored for an additional 30 months, at which time they were analyzed.

Sample Preparation. Samples (1 L) were fortified with anthracene-d_{10} at the rate of 0.5 μg L^{-1} and liquid/liquid extracted with 3 × 50 mL aliquots of dichloromethane (DCM). Extracts were concentrated to less than 5 μL total volume and the entire sample extract was utilized for a single gas chromatography/electron impact mass spectrometry (GC/EIMS) analysis. Duplicate samples, extracted 30 months after collection, were prepared similarly except that the final concentrate volume was 10 μL and 2-μL injections were made. The DCM used was Optima grade obtained from Fisher Scientific (Medford, MA). Three lots were tested before acceptable blanks were obtained. Percent recoveries of alachlor, DEA, and anthracene-d_{10} fortified in distilled/deionized water at 0.5 μg L^{-1} averaged, 20.4, 12.2, and 17.8%, respectively (*20*).

GC/MS of Initial Sample Extracts. Sample extracts were analyzed using a Hewlett-Packard Model 5985B GC/MS system. The GC oven was fitted with a 60-m × 0.32-mm (i.d.) DB-5 (J. W. Scientific, Folsom, CA) fused silica capillary column (0.25 μ film). A head pressure of 101 kPa helium was maintained at the column inlet with the oven temperature profile: 80 °C (hold 1 min), increase at 8 °C min^{-1} to 260 °C, and hold 21.5 min. Injection was in the splitless mode at 250 °C. The column was interfaced to the mass spectrometer through an SGE (Scientific Glass and Engineering, Austin, TX) "open-split" interface. The mass

spectrometer was operated in the electron impact ionization mode at 70eV and immediately prior to use tuned to meet the manufacturer's abundance criteria for PFTBA.

GC/MS of Duplicate Samples. Analyses were performed using a Hewlett-Packard 5989A GC/MS system equipped with a 30-m × 0.25-mm (i.d.) HP5 (Hewlett-Packard) fused silica capillary column (0.25 μm film). The column was directly coupled to the ion source through a heated interface maintained at 280 °C. The GC oven temperature profile was as follows: 60 °C (hold 1 min), increase at 4 °C min^{-1} to 280 °C, and hold 4 min. The helium carrier gas head pressure was fixed at 70 kPa. Injection was at 280 °C in the splitless mode. Electron impact (EI) spectra were obtained at 70 eV following instrument tuning with PFTBA. Chemical ionization (CI) spectra were obtained using methane and ammonia as reagent gases. The source temperature in the CI experiments was set at 150 °C. Source pressures were methane, 1 Torr, and ammonia, 0.87 Torr.

Reference Compounds. Alachlor (**I**)-related products were prepared using alachlor (donated by Monsanto) or DEA (**II**) as primary starting materials. DEA and all other reagents were obtained from Aldrich Chemical Co. (Milwaukee, WI). The alachlor was further purified before use by recrystalization from DCM at −20 °C. Purity was >99% when assayed by GC/MS. The structures of synthetic compounds, alachlor, and DEA and their EIMS are shown in Figure 1. Purity data given for synthetic products (see below) were based on GC/MS analyses.

*2',6',-Diethylacetanilide (**III**).* DEA was reacted with acetic anhydride in 50:50 acetone/2 N HCl. The resulting white solid was recovered by filtration and purified by successive recrystallizations from 3:1 water/ethanol. Purity >99%.

*2-Chloro-2',6'-diethylacetanilide (**IV**).* Alachlor was refluxed in 1:1 acetone/0.5 N HCl for 4 h. The solution was cooled to room temperature and saturated with NaCl, and the bulk of the acetone removed by rotary evaporation under vacuum. The product was recovered from the remaining aqueous phase by serial extraction with DCM. Evaporation of the DCM under nitrogen yielded a white solid which was successively recrystallized at −20 °C from DCM. Purity >99%.

*2-Hydroxy-2',6'-diethylacetanilide (**V**).* **IV** was dissolved in 35:65 acetone/0.7 M NaOH and refluxed for 8 h. After cooling and saturation with NaCl, the bulk of the acetone was removed by rotary evaporation under vacuum. The product was recovered from the remaining aqueous phase by serial extraction with DCM. Evaporation of DCM under nitrogen yielded a white solid which was successively recrystallized at −20 °C from DCM. Purity >99%.

*2-Hydroxy-2',6'-diethyl-N-(methoxymethyl)acetanilide (**VI**).* Alachlor (**I**) was dissolved in 50:50 acetone/0.7 M NaOH and refluxed for 8 h. The solution was cooled to room temperature and saturated with NaCl, and the bulk of the acetone removed by rotary evaporation under vacuum. An oily solid was recovered after serial extraction of the aqueous phase with DCM and evaporation of the DCM under nitrogen. Purity >90%.

*N-(2,6-Diethylphenyl)methyleneamine (**VII**).* Isooctane was dried by reflux under a Dean−Stark trap for 1 h. To this solvent, DEA (**II**) and paraformaldehyde (1:8 mole ratio) were added, and the mixture was refluxed for 1 h and then filtered. Purity >88%.

*N-(2,6-Diethylphenyl)-N-(methoxymethyl)acetamide (**VIII**).* To the reaction mixture of **VII**, acetyl chloride was added, followed by addition of cold triethylamine and methanol. The solvent was removed under vacuum and the residue taken up in DCM. Purity >89%.

*2,6-Diethylformanilide (**IX**).* To the reaction mixture of **VII**, formic acid (88%) was added with further refluxing for 3 h. The organic layer was separated and evaporated under N_2. Purity >92%.

*N-(Methoxymethyl)-2,6-diethylaniline (NMM; **X**).* Attempts made at the synthesis of this compound yielded many related compounds and possibly the target compound. Reactions details are summarized elsewhere (*20*). Among the reaction schemes utilized, a product whose EIMS data were consistent with the target compound was obtained in milligram amounts. The MS data included M^+ = 193 and a prominent neutral 31 loss, yielding m/z = 162 (base peak). If the compound were NMM, the ion m/z = 162 presumably represents the "retro"-Schiff base which would be produced by cleavage of a methoxy group from the *N*-methoxymethyl of NMM. Such a cleavage is plausible. A principal ion, and on occasion, the base peak of the EIMS of alachlor is m/z = 160. Using alachlor labeled at varying positions with deuterium, Jacobsen et al. (*21*) showed that m/z = 160 is in essence, a "retro"-Schiff base of DEA. It retains the α-methylene carbon of the methoxymethyl group with cleavage of OCH_3 and the chloroacetyl group. They noted that the difference in two mass units is a likely result of unsaturation of one of the electron-rich ethyl side chains. Another consideration is the EIMS of bis-*N*-(methoxymethyl)aniline (**XII**). The spectrum had a base peak at m/z = 206^+. This represents a neutral loss from the parent molecule of 31 and indicates that loss of OCH_3 from *N*-methoxymethyl groups is favored. Complete cleavage of the group would give a neutral loss of 45.

*2-[(2,6-Diethylphenyl)amino]ethanol (**XI**).* The reaction scheme for this compound was based on syntheses of related compounds (*22*). DEA was dissolved in toluene to which 2-chloroethyl chloroformate was added dropwise with vigorous stirring. After addition of this reagent, the reaction mixture was stirred for an additional 15 min with the temperature maintained at 25 °C. Adjustment to *p*H 11 with KOH followed. After the aqueous layer was discarded, the toluene was removed under N_2. The residue was refluxed with solid KOH and methanol for 2 h. The reaction mixture was filtered, diluted with distilled water, and extracted with DCM. DCM was removed under vacuum. Purity >50%.

*Bis(N-methoxymethyl)-2,6-diethylaniline (**XII**).* Methanolic K_2CO_3 was added to the reaction mixture of **VII**. The solution was allowed to stand overnight and then partitioned into water and liquid/liquid extracted with dichloromethane (DCM). The target compound was detected in the DCM extract. Purity >26%.

Results and Discussion

In addition to alachlor, 20 compounds were detected whose mass spectral data indicated that they were derived from alachlor via environmental degradation (see Table 1). The 20 were among 41 compounds that were detected in groundwater sample extracts. Atrazine, metolachlor, carbofuran, and selected degradation products of these compounds were among the others detected.

The EI and CIMS data of alachlor and compounds assigned as degradation products summarized in Table 1 were derived from analyses of samples and their duplicates. Qualitatively the data obtained from the two sets of analyses

TABLE 1

Alachlor Degradation Products Detected in Monitoring Well Samples

mass spectral data[a]								
peak	MW	BP	secondary ions				compound	ID[b]
1	161	146	118	161	123	77	*N*-(2,6-diethylphenyl)methyleneamine	s
2	149	134	149	119	118	91	2,6-diethylaniline	s
3	147	132	117	118	130	146	7-ETHYLINDOLINE	int
4	177	177	148	134	133	162	2′,6′-diethylformanilide	s
5	191	134	71	43	148	149	alachlor related	int
6	191	148	134	181	120	43	2′,6′-diethylacetanilide	s
7	193	45	148	120	193	134	α-*N*-[(2′,6′-diethylphenyl)amino]ethanol	int
8	205	148	162	43	163	205	2′-acetyl-6′-ethylacetanilide	int
9	235	45	161	146	178	203	*N*-(2,6-diethylphenyl)-*N*-(methoxymethyl)acetamide	s
10	221	162	204	177	77	163	2-hydroxy-2′,6′-diethyl-*N*-methylacetanilide	ref 24
11	249	45	43	174	189	206	2′-acetyl-6′-ethyl-*N*-(methoxymethyl)acetanilide	int
12	251	45	188	160	146	175	2-hydroxy-2′,6′-diethyl-*N*-(methoxymethyl)acetanilide	s
13	255	148	146	175	160	255	structure 20, ref 15	int
14	269	45	160	188	146	117	*alachlor*	s
15	231	45	43	188	189	220	alachlor related	int
16	283	45	188	160	146	204	alachlor related	int
17	283	45	174	43	248	206	2-chloro-2′-acetyl,6′-ethyl-*N*-(methoxymethyl)acetanilide	ref 21
18	269	176	172	148	269	190	structure 18, ref 15	int
19	313	45	202	160	146	79	alachlor related	int
20	331	45	176	158	286		alachlor related	int
21	315	45	160	91	186	144	alachlor related	int

[a] Molecular weight (MW) based on methane and ammonia chemical ionization data. BP, base peak. Secondary ions listed in descending order of relative abundance. [b] ID (identification): s, standard; int, interpretation.

TABLE 2

Approximate Concentration of Alachlor and Alachlor Degradation Products in Four Monitoring Well Samples

	concentration (ng L^{-1})			
compound[a]	MW-4	MW-2	MW-5	MW-3
N-(2,6-diethylphenyl)methylene amine	4	6	<2	10
2′,6′-diethylaniline	5	10	<2	16
7-ethylindoline	13	37	<2	35
2′,6′-diethylformanilide	62	87	<2	74
alachlor related	69	78	28	97
2′,6′-diethylacetanilide	47	<2	<2	130
α-N-[(2′,6′-diethylphenyl)amino]ethanol	410	480	66	<2
2′-acetyl-6′-ethylacetanilide	56	110	28	120
N-(2,6-diethylphenyl)-N-(methoxymethyl)acetamide	120	100	130	550
2-hydroxy-2′,6′-diethyl-N-methylacetanilide	58	130	29	<2
2′-acetyl-6′-ethyl-N-(methoxymethyl)-acetanilide	110	170	68	240
2-hydroxy-2′,6′-diethyl-N-(methoxymethyl)acetanilide	100	<2	<2	<2
structure 20 ref 15	68	<2	<2	<2
alachlor	500	<2	370	1100
alachlor related	120	<2	<2	<2
alachlor related	120	<2	<2	<2
2-chloro-2′-acetyl,6′-ethyl-N-(methoxymethyl)acetanilide	140	<2	110	310
structure 18 ref 15	120	340	110	530
alachlor related	180	400	170	570
alachlor related	84	280	<2	<2
alachlor related	<2	180	<2	10

[a] Mass spectral data and the basis for structural assignments are provided in Table 1.

were remarkably consistent. Only one of the 20 degradation products detected in the initial analyses was not detected when duplicates were analyzed 30 months later. The compound was 7-ethylindoline.

The quantitative data provided in Table 2 were obtained from the initial sample analyses only. Duplicate sample data were not included, considering the possibility that degradation or transformation may have taken place in storage. Concentration values were determined by calculating the relative total ion current (TIC) response of each compound to the internal standard (IS) and then multiplying this value times the nominal IS concentration. This may impose uncertainty on the order of 2× to the results. The principal contributing factor to this uncertainty was the anticipated variation in the relative response factors of the internal standard and the analytes detected. Another factor to consider is the possibility of coeluting interferences; however, examination of the mass spectral data indicated coelution was a minor contributor.

Among the structural assignments, six were confirmed by analysis of standards of which five were synthesized. All other structures were assigned through comparisons with published MS data and by use of standard interpretative techniques. Compounds that were not assigned structures but were concluded to have been derived from alachlor were classified as such on the basis of similarity of their

TABLE 3

EIMS Data: Alachlor-Related Compounds with $M^+ = 193$

	relative abundance		
m/z	groundwater extracts[a]	ref 11[b]	NMM[c]
193	38.5	48	24.7
178	2.2	19	2.5
162	1.1	nr	100.0
148	74.7	77	4.8
146	2.2	nr	9.5
134	29.7	nr	3.6
132	19.8	100	4.7
120	42.9	nr	2.5
117	3.8	20	4.1
45	100.0	nr	1.3

[a] Peak detected in monitoring well sample extracts, tentative structural assignment, α-*N*-[(2′,6′-diethylphenyl)amino]ethanol. The initial structural assignment was *N*-(methylmethyl)-2,6-diethylaniline (NMM). [b] Compound assigned as NMM by Tiedje and Hagerdorn (*11*). [c] Data obtained for synthesis product assigned to NMM.

EIMS to that of the parent compound. In particular, the presence of a prominent $m/z^- = 45$ was noted. These compounds are referred to as, "alachlor related".

In all samples, the total concentration of degradation products exceeded that of alachlor by at least 2×. Moreover, alachlor was not detected in sample MW-2, yet its degradation product concentration was >2.0 μg L^{-1}, exceeding alachlor's MCL (*2*).

In two samples, MW-4 and MW-2, peak 7 (Table 1), was quantitatively prominent. It had the highest concentration among the degradation products and in MW-2, its concentration exceeded alachlor's. It should be noted that the structural assignment shown for this compound is tentative. It was arrived at in a process of elimination.

Initially, the compound was identified as N-methoxymethyl 2,6-diethylaniline (**X**). This provided a "good fit" to the mass spectral data and agreed with an assignment made by Tiedje and Hagerdorn (*11*). Their compound had been isolated from experiments in which alachlor was incubated with *Chaetomonium globosum*. EIMS data obtained for peak 7 and Tiedje and Hagerdorn's compound are summarized in Table 3. The two data sets give a reasonable match.

Uncertainty in this structural assignment arose from the fact the Tiedje and Hagerdorn did not provide data for a synthetic standard and a report that *N*-alkoxyarylamines are relatively unstable compounds. Barleunega et al. (*23*) observed that *N*-(methoxymethyl)-2-toluidines decomposed unless solutions were stored at −20 °C and kept strongly alkaline.

A concerted effort was made to synthesize the target compound (*20*). More than 10 synthetic approaches were taken, yielding only milligram quantities of a substance classified as NMM (*20*). Its EIMS data are included in Table 3. The data for the substance detected in groundwater samples and Tiedje and Hagerdorn's compound and synthetic NMM exhibited substantial qualitative differences, leading to the conclusion that NMM was not detected in the environmental samples.

The alternate structural assignment α-*N*-[(2′,6′-diethylphenyl)amino]ethanol was made in consideration of the EIMS of 2,6-diethylacetanilde (**III**) and 2-[(2,6-diethylphenyl)amino]ethanol (XII). The M^+ of the unknown was two mass units greater than that of synthetic 2′,6′-diethylacetanilde. Taking this "shift" into account, the mass spectra of the two compounds were similar. Their structural similarity is also notable. It is conceivable that the alcohol could be formed by chemical reduction of the acetanilide. The occurrence of OH on the α-carbon is also expected to promote α-cleavage, yielding the prominent neutral 45 loss observed. In EIMS of the β-alcohol **XII** the loss was 31, which was expected given the stability of the "retro-Schiff base" of DEA.

Two compounds that were notable because they were not detected were **V** and ES. Pereira et al. (*5*) reported detection of **V** in selected groundwater samples, whereras various reports have indicated that ES occurs widely in groundwater in regions where alachlor has been used (*6, 18, 19*). We note in our study that the presense or absense of ES in samples tested remains uncertain. The solvent extraction and GC/MS procedures used do not appear to have the potential to detect the compound at trace levels in water samples.

Overall, the data showed that dechlorination and cleavage of the *N*-methoxymethyl (MOM) group are significant features of the environmental degradation of alachlor. Only a single degradation product containing chlorine was detected, 2-chloro-2′-acetyl-6′-ethyl-*N*-(methoxymethyl)-acetanilide (oxo-alachlor). It presumably was derived from oxidation of an arylethyl group. Jacobsen et al. (*21*) identified this compound as the principal product of permanganate oxidation of alachlor. Somich et al. (*24*) and Hapeman-Somich (*25*) have also reported it as a product of alachlor UV photolysis and ozonation.

That dechlorination and cleavage of the MOM group are primary elements of alachlor degradation is not surprising. The MOM group and the Cl of alachlor were found to be quite labile in synthesis experiments. MOM groups were readily hydrolyzed under acid conditions, and the Cl was subject to nucleophilic substitution. In mammalian systems, Sharp (*15*) reported that the MOM group is the principal site of metabolic attack of alachlor. It is also notable that products of MOM cleavage do not cross-react with immunoassay test kits (*26–28*).

Taking the hypothesis of Jacobsen et al. (*21*) into account, it appears that MOM cleavage from alachlor may constitute detoxification. In their studies, they showed that formaldehyde is liberated from alachlor's MOM in mouse MFO liver systems. They also suggested that *in vivo* formaldehyde liberation may account for the observation that carbon derived from the MOM group contributed more in percentage terms than aromatic ring carbon to labeling mouse DNA and proteins. This leads to the conclusion that cleavage of the MOM group from alachlor reduces sites available for metabolic formation of formaldehyde. Mutagenic potential is thus reduced.

Companion data that support this hypothesis was provided by Tessier (*28*). He found that 2-chloro-2′,6′-diethylacetanilde and 2-hydroxy-2′,6′-diethylacetanilde were only weakly mutagenic to *Salmonella* strain TA100. These compounds were derived from alachlor by cleavage of the MOM group (see **IV** and **V**, Figure 1).

A final point is that the data obtained through analysis of the groundwater samples and their duplicates 30 months apart have implied stability under groundwater conditions. In a qualitative sense the two data sets were nearly identical. This is consistent with published results. Cavalier et al. (*29*) reported that the $t_{1/2}$ of alachlor in groundwater samples fortified at 1 and 5 μg L^{-1} and incubated at 15 and 22 °C

ranged from 808 to 1518 days. Pothuluri et al. (*30*) observed $t_{1/2}$ values in other aquifer samples ranging from 320 to 324 days. These results are possibly explained by Rodosevich et al. (*31*), who noted that alachlor degradation, i.e., disappearance of the parent compound, was detected in only 4 of 83 aquifer sediment enrichment cultures.

In short, alachlor degradation potential of subsurface microorganisms appears to be limited. Given this, alachlor and its degradation products if leached into groundwater may remain unaltered for extended periods.

Conclusions

Degradation of alachlor results in the formation of numerous products which can be leached into groundwater. Several products that had not previously reported were identified in the shallow groundwater samples analyzed for this study. Moreover, the concentration of the degradation products generally exceeded the parent compound by at least a factor of 2×.

Some published data (*21*) have indicated that degradation, in particular, cleavage of alachlor's MOM group, contributes to detoxification; thus some of the products detected in groundwater may not present serious health hazards if introduced into water supplies. Other studies have indicated that at least one of the residues, DEA, is a promutagen and may be transformed by rat liver enzyme preparations, to 2,6-diethylnitrosobenzene (*1*). The latter compound is strongly mutagenic in Ames assay type tests (*1*, *28*). Given this uncertainty, inclusion of degradation products in environmental monitoring programs where alachlor has been or is in use appears warranted. The relatively high concentrations of peak 7 (Table 1) in several samples also indicates that additional effort should be placed on its specific identification. Structural assignments presented were tentative.

Acknowledgments

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