Degradation of Chloroacetanilide Herbicides by Anodic Fenton Treatment

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Anodic Fenton treatment (AFT) is an electrochemical treatment employing the Fenton reaction for the generation of hydroxyl radicals, strong oxidants that can degrade organic compounds via hydrogen abstraction. AFT has potential use for the remediation of aqueous pesticide waste. The degradation rates of chloroacetanilides by AFT were investigated in this work, which demonstrates that AFT can be used to rapidly and completely remove chloroacetanilide herbicides from aqueous solutions. Acetochlor, alachlor, butachlor, metolachlor, and propachlor were treated by AFT, and parent compound concentrations were analyzed over the course of the treatment time. Degradation curves were plotted and fitted by the AFT kinetic model for each herbicide, and AFT model kinetic parameters were used to calculate degradation rate constants. The reactivity order of these five active ingredients toward hydroxyl radical was acetochlor ≈ metolachlor > butachlor ≈ alachlor > propachlor. Treatment of the chloroacetanilides by AFT removed the parent compounds but did not completely mineralize them. However, AFT did result in an increase in the biodegradability of chloroacetanilide aqueous solutions, as evidenced by an increase in the 5-day biochemical oxygen demand to chemical oxygen demand ratio (BOD_5/COD) to >0.3, indicating completely biodegradable solutions. Several degradation products were formed and subsequently degraded, although not always completely. Some of these were identified by mass spectral analyses. Among the products, isomers of phenolic and carbonyl derivatives of parent compounds were common to each of the herbicides analyzed. More extensively oxidized products were not detected. Degradation pathways are proposed for each of the parent compounds and identified products.

INTRODUCTION

Pesticide contamination of water resources has become a concern in the United States, especially in regions dominated by farmland. Monitoring of groundwater and surface waters such as lakes and rivers for pesticide parent compounds and metabolites has repeatedly resulted in the detection of chloro-acetanilide herbicides and their ethanesulfonic and oxanilic acid metabolites (*1*, *2*). Chloroacetanilide herbicides are some of the most widely used herbicides in the United States. The U.S. EPA reports that in 2001 acetochlor, metolachlor, and alachlor were the 4th, 10th, and 16th most widely used pesticide active ingredients in the United States, with 30−35 million, 15−22 million, and 6−9 million lb applied, respectively (*3*). Several chloroacetanilide herbicides have been identified as possible or probable human carcinogens (*4*), and there is concern about the effects of parent compounds and metabolites on aquatic ecosystems (*5*). These reports have led to an effort to reduce

the use of at least one of the chloroacetanilides and to remediate already contaminated water resources.

The development of anodic Fenton treatment (AFT), an advanced oxidation treatment process that generates highly reactive hydroxyl radicals via the Fenton reaction

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \qquad (1)$$
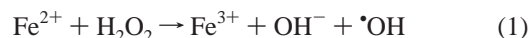
provides an opportunity to control several sources of chloro-acetanilide contamination. AFT was developed with the goal of creating a cost-effective and user-friendly treatment method for the remediation of low-volume, high-concentration pesticide wastes, such as applicator rinse water or unused stocked commercial mixes (*6*). AFT is an improvement on other Fenton processes, such as classic Fenton treatment (CFT) and electro-chemical Fenton treatment (EFT), in that the system is divided into anodic and cathodic half-cells separated by an ion-exchange membrane, allowing for treatment and the Fenton reaction to occur in an optimal pH environment (pH ∼2−3) in the anodic half-cell (see ref *7* for diagram). AFT also has greater potential to be used on-site, eliminating the need for transportation of

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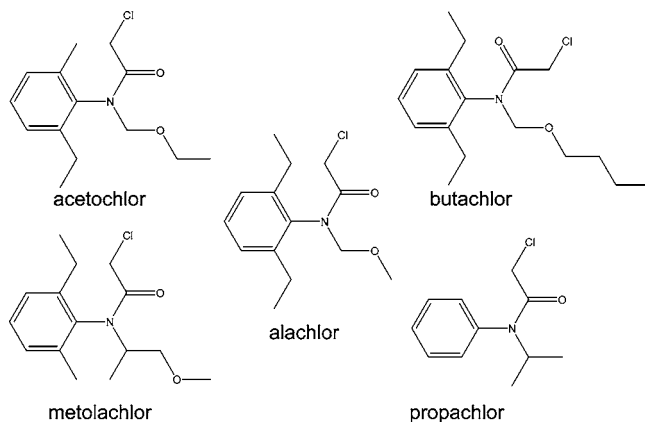
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Figure 1. Chloroacetanilide herbicides.

waste and reducing potential sources of pollution by making remediation easier and more timely. To better understand AFT reaction mechanisms, a kinetic model based on the degradation of 2,4-D was developed in this laboratory (*8*). The AFT model has been shown to accurately describe the degradation kinetics of carbamate and phosphorothiate insecticides (*9*, *10*).

This work describes the evaluation of AFT as an effective method for the degradation of chloroacetanilide herbicides in aqueous solutions. Five chloroacetanilides were chosen as representative compounds: acetochlor [2-chloro-*N*-(ethoxymethyl)-*N*-(2-ethyl-6-methylphenyl)acetamide], alachlor [2-chloro-*N*-(2,6-diethylphenyl)-*N*-(methoxymethyl)acetamide], butachlor [*N*-(butoxymethyl)-2-chloro-*N*-(2,6-diethylphenyl)acetamide], metolachlor [2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl)acetamide], and propachlor [2-chloro-*N*-(1-methylethyl)-*N*-phenylacetamide] (**Figure 1**). Specifically, our objectives were to (i) determine the appropriateness of the AFT model in describing the degradation of chloroacetanilides, (ii) determine rate constants for the reaction of hydroxyl radical with each of the five chosen chloroacetanilides, (iii) assess the effect of AFT on the biodegradability of chloroacetanilide aqueous solutions, and (iv) identify the structures of products generated by the AFT of chloroacetanilides and propose degradation pathways.

MATERIALS AND METHODS

Chemicals. Acetochlor (98%), alachlor (99.5%), butachlor (98%), metolachlor (97.2%), propachlor (99.5%), and catechol (97.5%) were purchased from Chem Service (West Chester, PA). Acetochlor, alachlor, and propachlor degradation product standards [2-chloro-*N*-ethyl-*N*-phenyl-acetamide, 2-chloro-*N*-(2,6-diethylphenyl)-acetamide, and 2-chloro-*N*-(2-ethyl-6-methylphenyl)-acetamide] were purchased from Sigma-Aldrich (St. Louis, MO). Potassium permanganate, potassium dichromate, dibasic sodium phosphate, magnesium sulfate, dichloromethane, acetic anhydride, and potassium carbonate were purchased from Mallinckrodt (Paris, KY). Sodium chloride, methanol, ferrous ammonium sulfate, ferrous sulfate, monobasic potassium phosphate, ferric chloride, and HPLC grade water were purchased from Fisher Scientific (Fair Lawn, NJ). Silver sulfate, dibasic potassium phosphate, ammonium chloride, and calcium chloride were purchased from GFS Chemicals (Columbus, OH). Catalase, glucose, glutamic acid, and sodium sulfite were purchased from Sigma (St. Louis, MO). Mercuric sulfate and 1,10-phenanthroline monohydrate were purchased from Aldrich (Milwaukee, WI). Sulfuric and hydrochloric acids were purchased from EM Science (Gibbstown, NJ). Hydrogen peroxide (30%) was purchased from Fluka (St. Gallen, Switzerland). Polyseed bacterial seed was purchased from Interlab Supply (The Woodlands, TX).

AFT and CFT Apparatus and Operating Conditions. AFT was performed in a glass reactor (Cornell Glass Shop) consisting of two half-cells connected by an anion membrane (ESC-7001) with an

electrical resistance of 8 Ω cm^{-2} purchased from Electrosynthesis Co. (Lancaster, NY). Solutions in each half-cell contained stir bars and were stirred by two stir plates purchased from Corning (Corning, NY) placed directly under each cell. The anode consisted of a 12.5 cm × 2.5 cm × 0.25 cm pure iron bar, whereas the cathode consisted of an 8 cm × 1.25 cm cylindrical graphite rod. A BK Precision DC Power Supply 1610 was used to apply a current to the electrodes. Hydrogen peroxide was pumped into the anodic half-cell with a StepDos 08 S pump purchased from Chemglass (Vineland, NJ). For all kinetics experiments, the delivery ratio of H$_2$O$_2$/Fe^{2+} was kept at 10:1. A 0.311 M solution of H$_2$O$_2$ was delivered at a rate of 0.5 mL/min, or 0.156 mmol/min. The electrolysis current was kept at 0.050 A, equivalent to an Fe^{2+} delivery rate of 0.0156 mmol/min. The concentration of H$_2$O$_2$ was determined by titration with a standard solution of potassium permanganate.

For experiments designed for the analysis of degradation products, the following CFT and AFT procedures were followed. For CFT, a volume of 200 μL of 0.311 M FeSO$_4$·7H$_2$O was added to 200 mL of 200 μM of each herbicide with stirring, followed 30 s later by 2.00 mL of 0.311 M H$_2$O$_2$. This resulted in a 10:1 ratio of H$_2$O$_2$/Fe^{2+} and the delivery of Fenton reagents in an amount equivalent to 4 min of AFT. For AFT, 200 mL of 200 μM metolachlor was treated under the same conditions as with kinetics analysis. All glassware was cleaned thoroughly with HPLC-grade dichloromethane prior to experiments.

Degradation of Chloroacetanilides by AFT. For each treatment, 200 mL of 50 μM propachlor, 50 μM of either acetochlor, alachlor, butachlor, or metolachlor, and 0.02 M NaCl were added to the anodic half-cell. A 200 mL solution of 0.08 M NaCl was added to the cathodic half-cell. At various time intervals, 1 mL samples were taken from the anodic half-cell and were placed in GC vials containing 100 μL of HPLC-grade methanol to quench residual hydroxyl radicals. Concentrations of chloroacetanilides were then analyzed by HPLC. Each treatment trial was replicated in triplicate.

Concentration Analysis of Chloroacetanilides. The concentration of each herbicide in effluent samples was measured with an Agilent 1100 series HPLC equipped with a diode array detector (DAD). The mobile phase for the analysis of metolachlor, acetochlor, or alachlor in solution with propachlor was 67:33 acetonitrile/water with the pH adjusted to 3 using phosphoric acid. Under these conditions, the retention times for acetochlor, alachlor, metolachlor, and propachlor were 8.00, 7.89, 7.94, and 4.86 min, respectively. The mobile phase for the analysis of butachlor in solution with propachlor was 67:33 acetonitrile/water (pH 3) from 0 to 6.5 min, 80:20 at 7 min, 90:10 from 8 to 12 min, and 80:20 at 14 min. The retention times for butachlor and propachlor were 12.3 and 4.68 min. A C$_{18}$ 5 μm, 250 mm × 2.5 mm (i.d.) PRISM reverse phase column was used. DAD wavelength was set at 230 ± 15 nm.

Determination of COD and BOD$_5$. AFT effluent used in COD and BOD$_5$ procedures was generated under the same conditions as for kinetics experiments, only with different initial concentrations of herbicides: a mixture of acetochlor, alachlor, and metolachlor (each at ~60 μM) was tested, as well as a 180 μM solution of metolachlor. Treatment was stopped at several different time points, and samples were taken from the anodic half-cell for COD and BOD$_5$ analysis. The effluent was buffered to pH ~7 with phosphate buffer (4 mL of 1 M NaH$_2$PO$_4$ and 1 M Na$_2$HPO$_4$ per 200 mL of effluent), and catalase was added (0.4 mL of 50 mg/mL in 0.5 M phosphate buffer per 200 mL of effluent) to degrade residual hydrogen peroxide. Concentration analysis for the effluent containing acetochlor, alachlor, and metolachlor used in BOD$_5$/COD experiments was done using GC-MS after extraction with dichloromethane to achieve quantifiable separation of peaks, not possible by HPLC. Extraction efficiencies for these three herbicides were 117.4 ± 2.0, 115.8 ± 3.8, and 108.6 ± 2.1% for acetochlor, alachlor, and metolachlor, respectively. Extractions and GC-MS conditions were the same as those described below for degradation product analyses. Concentration of the metolachlor solution was analyzed using HPLC, as described above. COD and BOD$_5$ determination procedures followed that found in *Standard Methods for the Examination of Water and Wastewater* (*11*) very closely. Potassium dichromate (K$_2$Cr$_2$O$_7$) was used as an oxidizer in COD experiments.
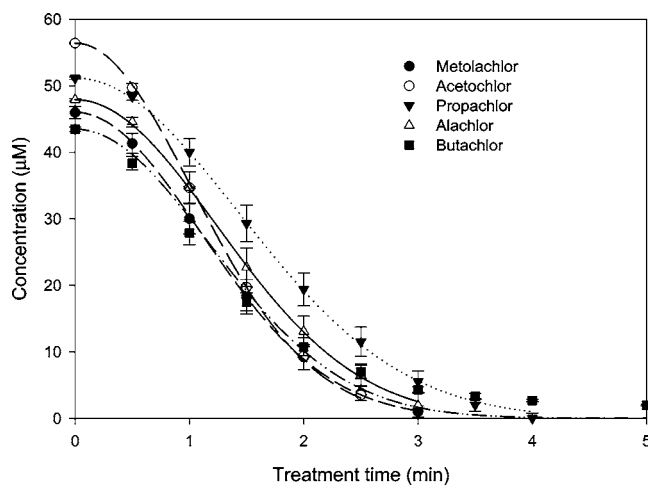
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Figure 2. Degradation of chloroacetanilides by AFT. Error bars are ±SE. Lines are results of AFT kinetic model fit.

Table 1. Rate Parameters and Correlation Coefficients of Each Chloroacetanilide

herbicide	$K\lambda\pi\omega$ (μM^{-2})	R
acetochlor	$(1.543 \pm 0.024) \times 10^{-4}$	>0.999
alachlor	$(1.080 \pm 0.012) \times 10^{-4}$	>0.999
butachlor	$(1.199 \pm 0.096) \times 10^{-4}$	0.981
metolachlor	$(1.359 \pm 0.013) \times 10^{-4}$	>0.999
propachlor	$(8.106 \pm 0.106) \times 10^{-5}$	>0.999

Table 2. Degradation Rate Constants of Chloroacetanilides by AFT

herbicide	k $(M^{-1} s^{-1})$	herbicide	k $(M^{-1} s^{-1})$
acetochlor	8×10^9	butachlor	7×10^9
metolachlor	8×10^9	propachlor	5×10^9
alachlor	7×10^9		

Dissolved oxygen was measured using a calibrated YSI oxygen meter with a BOD stirring probe.

Identification of Degradation Products. Treatments were stopped at different times. For both CFT and AFT 10 mL of solution was withdrawn and extracted with 3 mL of HPLC-grade dichloromethane. After separation, the organic layer was dried with anhydrous sodium sulfate and immediately analyzed by an Agilent 6890N Network GC equipped with an Agilent 5973 Network mass selective detector and an Agilent 7683 series injector. The GC-MS conditions were as follows: 30 m × 0.25 mm (i.d.) fused silica capillary column with 0.25 μm film thickness (Supelco); carrier gas of helium (13.0 psi); initial temperature, 100 °C, increasing to 280 °C at a rate of 10 °C/min and held at 280 °C until 20.5 min; injector port temperature, 220 °C; detector temperature, 310 °C. Identification of products was based on mass spectra interpretation, comparison with relevant literature, and, when available, comparison to standards.

Derivatization of Products. After 10 mL of effluent was taken for degradation product analysis, the pH of the effluent was brought up to ~10 using K_2CO_3. A volume of 100 μL of acetic anhydride was added to the effluent, and the solution was left to incubate, benchtop, for 20−30 min. The pH was then brought back down to ~4 using one drop of HCl. Dichloromethane (3 mL) was added, and the solution was extracted immediately. Catechol was used as a control to determine the efficacy of the derivatization process.

AFT Kinetic Model. A full account of the development of the AFT kinetic model and all of its assumptions has been published elsewhere (*8*). The kinetic model consists of the equation

$$\ln \frac{[D]_t}{[D]_0} = -\frac{1}{2} K\lambda\pi\omega\nu_0^2 t^2 \qquad (2)$$

where $[D]_t$ and $[D]_0$ (μM) are the concentrations of the target compound D at time t and 0 min, respectively; $K = k_F k_{tc}$ (μM^{-2} min^{-2}), where k_F (μM^{-1} min^{-1}) is the second-order rate constant of the Fenton reaction and k_{tc} (μM^{-1} min^{-1}) is the second-order rate constant of the reaction between hydroxyl radical and the target compound; λ (min) is the average life of the hydroxyl radical; π (min) is the average life of the ferrous ion; ω is a constant related to the delivery ratio of the Fenton reagents and to the consumption ratio of hydrogen peroxide; ν_0 (μM min^{-1}) is the delivery rate of ferrous iron into the reaction system; and t (min) is time.

RESULTS AND DISCUSSION

Degradation Kinetics. The results of the degradation of chloroacetanilides by AFT are shown in **Figure 2**. The results indicate that AFT can completely remove the parent compound from 200 mL of ~50 μM chloroacetanilide in 4 min under the

given conditions. The kinetic model rate parameters ($K\lambda\pi\omega$) provided a good fit for the experimentally derived data as evidenced by the high correlation coefficients listed in **Table 1**. The correlation coefficient of the AFT model fit to butachlor degradation is somewhat lower than that for the other chloroacetanilides. This is likely due to its very low aqueous solubility.

In the kinetic studies, all aqueous solutions treated contained 50 μM propachlor and 50 μM of one of the other four herbicides. Thus, all treatments were of two-component systems and resulted in competition for hydroxyl radical. As shown in previous work, when two herbicides are treated in the same solution at the same time, the parameters λ, π, ω, and ν_0 can be assumed to be the same for both target compounds (*9*). The second-order rate constant for the Fenton reaction, k_F, is also the same for both target compounds. Thus, the value of the parameter $K\lambda\pi\omega$ for a given target compound is dictated by k_{tc}, the rate constant between hydroxyl radical and the target compound. Therefore, it follows that

$$\frac{k_{tc1}}{k_{tc2}} = \frac{(K\lambda\pi\omega)_1}{(K\lambda\pi\omega)_2} \qquad (3)$$

where k_{tc1} and k_{tc2} are the second-order rate constants between hydroxyl radical and target compounds 1 and 2, respectively. Using the literature value of 7×10^9 M^{-1} s^{-1} (*12*) as the rate constant for aqueous alachlor and hydroxyl radical, the rate constant for propachlor was calculated. Using the propachlor value, the other three chloroacetanilide rate constants for reaction with hydroxyl radical were calculated and are listed in **Table 2** (k_{tc} of each herbicide is referred to simply as k in the table and from here onward). It should be noted that an unknown quantity of additional error is introduced into the calculation of k for acetochlor, alachlor, and metolachlor by using the method of comparison to propachlor. It should also be noted that error for k values is not listed in **Table 2** because the literature value for k of alachlor was not reported with error. However, error estimates are available for the $K\lambda\pi\omega$ values (**Table 1**) upon which k is based. Also, t tests were performed, pairwise, to assess significant differences in $K\lambda\pi\omega$ values (**Table 3**). The results give the following reactivity order for the chloroacetanilides with hydroxyl radical: acetochlor ≈ metolachlor > alachlor ≈ butachlor > propachlor. It is interesting to note that the reactivity order of these five herbicides coincides with the way in which the herbicides can be grouped on the basis of their phenyl ring substituents. Acetochlor and metolachlor have similar k values and are most reactive toward the hydroxyl radical. They both have 2-ethyl and 6-methyl phenyl substituent

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Table 3. Results of t Tests of $K\lambda\pi\omega$ Values between Pairs of Chloroacetanilides

comparison		p
acetochlor vs	alachlor	0.005
	propachlor	0.000
	butachlor	0.006
	metolachlor	0.119
alachlor vs	propachlor	0.041
	butachlor	0.191
	metolachlor	0.092
propachlor vs	butachlor	0.009
	metolachlor	0.012
butachlor vs	metolachlor	0.203

groups. Butachlor and alachlor have similar k values and are less reactive toward hydroxyl radical than acetochlor and metolachlor. They both have ethyl groups at the 2- and 6-positions. Propachlor is the slowest to degrade and does not have any phenyl substituents. The only two t tests that do not agree with this grouping are those of alachlor versus metolachlor and butachlor versus metolachlor. This is likely due to a relatively greater amount of variation in metolachlor's $K\lambda\pi\omega$ values. Variation in this parameter depends largely on experimental dexterity. This grouping observation is discussed further in relation to degradation products.

Determination of BOD$_5$/COD and Effect of AFT on Biodegradability. The BOD$_5$/COD ratio was used as a measure of AFT's ability to increase the biodegradability of a given aqueous solution. The ability of a treatment process to increase the biodegradability of pesticide waste is an important consideration given that chemical treatments coupled with biological treatments are becoming some of the more cost-effective methods for disposing of pesticide waste. COD can be defined as the amount of organic material present in a solution that is susceptible to oxidation by a strong oxidant, measured in oxygen equivalents. In this study, the strong oxidant used was potassium dichromate. BOD$_5$ is a measure of the dissolved oxygen consumed by bacteria incubated with a waste solution for 5 days and can be interpreted as a measure of the bioavailability of the organic material in the waste solution. It has become standard practice to accept a BOD$_5$/COD value of ≥ 0.3 to signify a biodegradable solution (*13*). AFT is able to decrease the COD, increase the BOD$_5$, and therefore increase the BOD$_5$/COD ratio of aqueous chloroacetanilide solutions, as shown in **Figure 3**.

The BOD$_5$/COD ratio was determined for an ~ 160 μM solution of metolachlor throughout treatment by AFT under the conditions described in Materials and Methods. The degradation of metolachlor and increase in BOD$_5$/COD to a value >0.3 at ~ 10 min of AFT is shown (**Figure 3a**). It is interesting to note, however, that complete removal of the parent compound has already occurred by 5 min of treatment. It can therefore be assumed that the initial degradation products of metolachlor are nearly as recalcitrant toward biodegradation as the parent compound and that further degradation of the initial products must occur before the effluent can be considered biodegradable. Similar results were observed when the BOD$_5$/COD ratio was determined for a mixture of acetochlor, alachlor, and metolachlor, each at ~ 60 μM, throughout treatment by AFT. **Figure 3b** demonstrates that AFT can increase the biodegradability potential for a mixture of chloroacetanilide herbicides to >0.3, an important finding given that wastewater generally contains many components, including both active ingredients and inert substances.
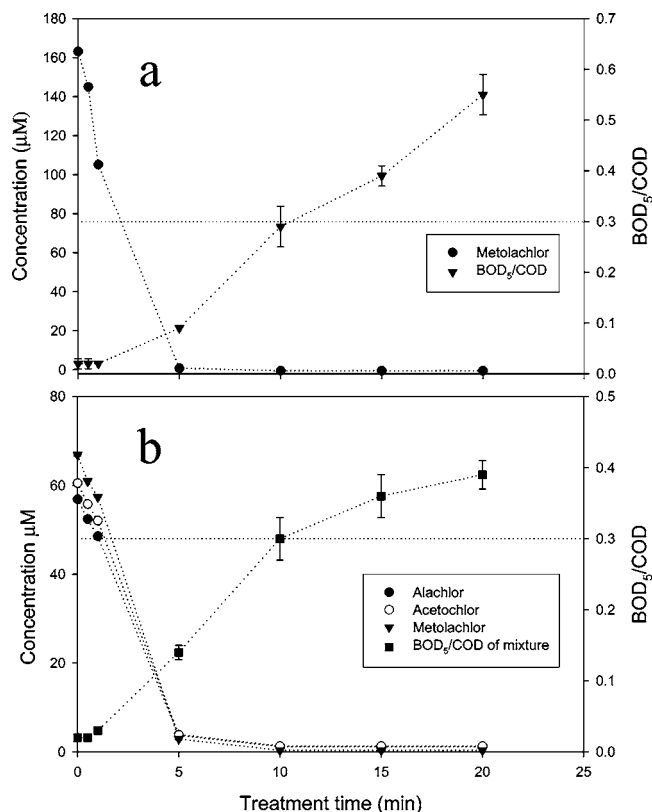
Figure 3. (**a**) Degradation of metolachlor and simultaneous increase in BOD$_5$/COD and (**b**) degradation of mixture of acetochlor, alachlor, and metolachlor and simultaneous increase in BOD$_5$/COD.

As with metolachlor aqueous solutions, the disappearance of the other chloroacetanilide herbicides was observed at 5 min of treatment, whereas the BOD$_5$/COD values did not indicate biodegradability until 10 min of treatment. This again suggests that initial AFT products of these three chloroacetanilides need to be degraded in addition to parent compounds to produce a biodegradable effluent. It is interesting to note that BOD$_5$/COD did not increase with treatment time as rapidly with the mixture as during the treatment of only metolachlor. At 20 min of treatment, metolachlor effluent demonstrated a BOD$_5$/COD of nearly 0.6, whereas the mixture had a BOD$_5$/COD value of only 0.4. Although both solutions can be considered to be biodegradable by 20 min, the mixture exhibits more recalcitrant transformation products. Future work should focus on the BOD$_5$/COD of alachlor and acetochlor treated individually to determine which herbicide in the mixture is limiting the increase in BOD$_5$/COD.

Degradation Products and Pathways. Classic Fenton treatment was used initially in determining degradation products to generate greater concentrations of products for the purposes of extraction and identification. Products of CFT were later compared to products of AFT (metolachlor only). Degradation product analysis proved unsuccessful for butachlor, likely due to butachlor's very low aqueous solubility. The resulting low aqueous concentration of the initial solution did not allow for generation of a significant concentration of products. The parent molecule itself could not be extracted from the untreated solution. **Table 4** summarizes the GC-MS information obtained for parent compounds and degradation products for the other four chloroacetanilides.

Metolachlor was chosen as a representative chloroacetanilide for AFT product analysis. Metolachlor products were analyzed at various time points throughout AFT, and CFT products of

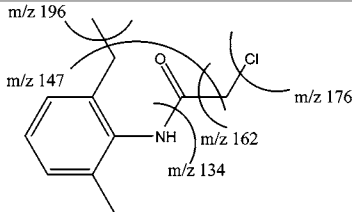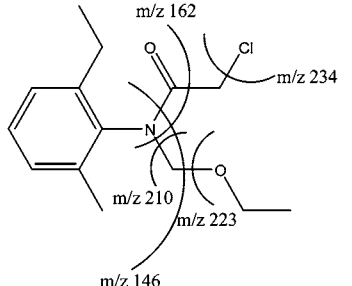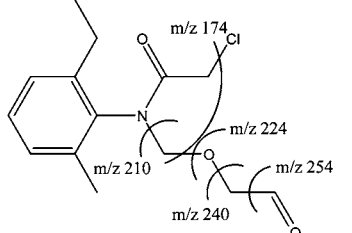**Table 4.** Parent Compound and Degradation Product GC Retention Times (t_r), MS Major Ions, and Proposed Structures
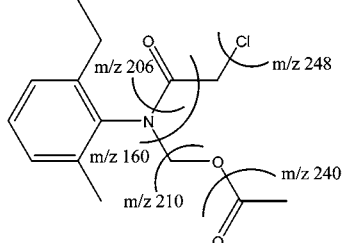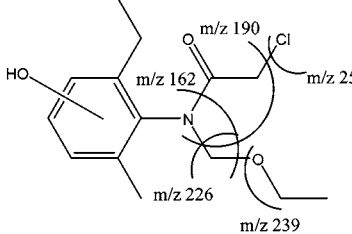
chloroacetanilide	product	t_r (min)	MS major ion, *m/z* (%)	structure
acetochlor	2-chloro-*N*-(2-ethyl-6-methylphenyl)-acetamide (**1a**)	9.71	213 (4.1), 211 (12), 196 (1.4), 162 (100), 147 (8.5), 134 (15), 120 (15), 103 (1.9), 91 (11)	
	parent compound (**1b**)	12.2	271 (3.2), 269 (10), 234 (28), 223 (72), 212 (20), 210 (21), 174 (52), 162 (87), 146 (100), 132 (51), 117 (33), 91 (29)	
	2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-oxo-ethoxymethyl)-acetamide (**1c**)	13.2	285 (1.6), 283 (4), 254 (5.8), 240 (2.2), 224 (22), 174 (100), 162 (70), 146 (62), 132 (41), 117 (20)	
	acetic acid [(2-chloro-acetyl)-(2-ethyl-6-methylphenyl)-amino]-methyl ester	13.6	283 (1), 248 (79), 240 (15), 210 (14), 206 (43), 160 (100)	
	2-chloro-*N*-ethoxymethyl-*N*-(2-ethyl-hydroxy-6-methylphenyl)-acetamide (**1d**)	14.8	287 (3.6), 285 (12), 250 (5.4), 239 (55), 226 (26), 204 (13), 190 (45), 178 (42), 162 (100), 148 (36), 133 (18)	

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Table 4. (Continued)

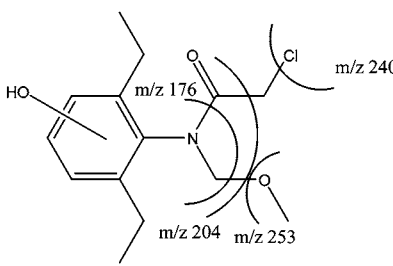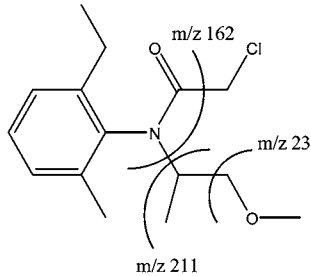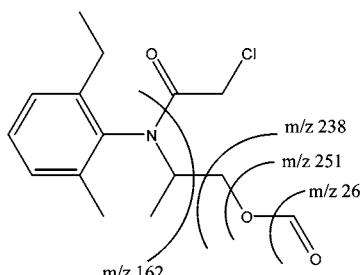| chloroacetanilide	product	t_r (min)	MS major ion, *m/z* (%)	structure
	2-chloro-*N*-ethoxymethyl-*N*-(2-ethyl-hydroxy-6-methylphenyl)-acetamide (**1e**)	15.0	287 (3), 285 (11), 239 (100), 226 (69), 208 (15), 190 (34), 41), 162 (67), 148 (69), 133 (20), 91 (17)	
	2-chloro-*N*-ethoxymethyl-*N*-(2-ethyl-hydroxy-6-methylphenyl)-acetamide (**1f**)	15.3	287 (15), 285 (39), 250 (25), 239 (45), 228 (14), 210 (14), 190 (20), 178 (96), 162 (100), 148 (33), 132 (31)	
alachlor	2-chloro-*N*-(2,6-diethylphenyl)-acetamide (**2a**)	10.4	227 (5), 225 (13), 210 (1.4), 196 (2.9), 176 (100), 161 (2.8), 147 (15), 132 (8), 117 (9.3)	
	parent compound (**2b**)	12.4	271 (0.4) 269 (10), 237 (27), 224 (23), 202 (16), 188 (90), 172 (8.7), 160 (100), 146 (32)	
	N-(2-acetyl-6-ethylphenyl)-2-chloro-*N*-methoxymethyl-acetamide (**2c**)	13.8	283 (0.45), 248 (47), 240 (13), 206 (32), 188 (16), 174 (100), 160 (21), 146 (8.7), 132 (16)	

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Table 4. (Continued)
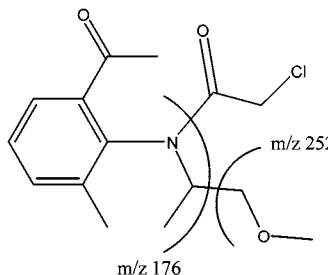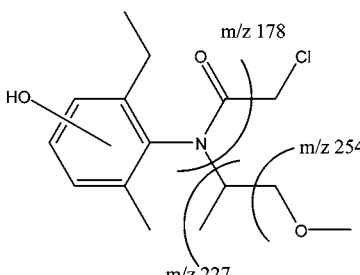
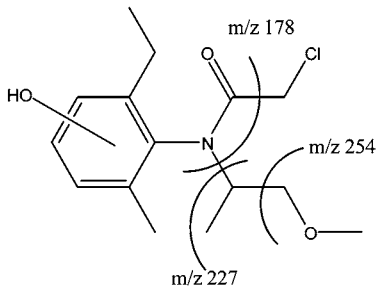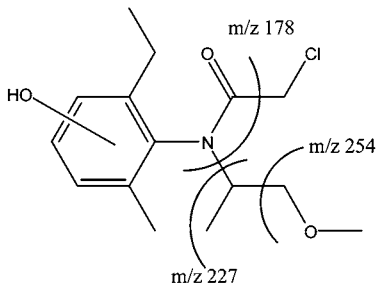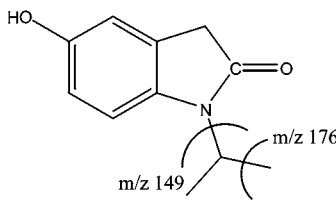| chloroacetanilide	product	t_r (min)	MS major ion, m/z (%)	structure
	2-chloro-N-(2,6-diethyl-hydroxyphenyl)-N-methoxymethyl-acetamide (**2d**)	15.0	287 (3.7), 285 (11), 253 (55), 240 (48), 222 (19), 204 (79), 176 (100), 162 (49), 148 (22)	
metolachlor	parent compound (**3a**)	13.2	285 (0.06), 283 (0.2), 268 (0.09), 238 (63), 211 (10), 162 (100), 146 (13), 131 (5.9), 117 (4.2)	
	Formic acid 2-[(2-chloroacetyl)-(2-ethyl-6-methylphenyl)-amino]-propyl ester (**3b**)	14.3	299 (1.5), 297 (4), 268 (0.5), 251 (4.8), 238 (32), 216 (7.2), 202 (16), 162 (100), 87 (36)	
	N-(2-acetyl-6-methylphenyl)-2-chloro-N-(2-methoxy-1-methylethyl)-acetamide (**3c**)	14.8	266 (0.24), 252 (54), 225 (4.9), 210 (2.4), 176 (100), 158 (34), 148 (7.1)	
	2-chloro-N-(6-ethyl-hydroxy-2-methylphenyl)-N-(2-methoxy-1-methylethyl)-acetamide (**3d**)	15.7	299 (0.82), 268 (0.47), 254 (59), 227 (11), 178 (100), 162 (14), 147 (5.5), 134 (3.3)	

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Table 4. (Continued)
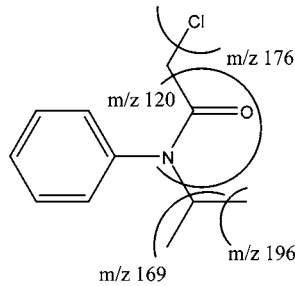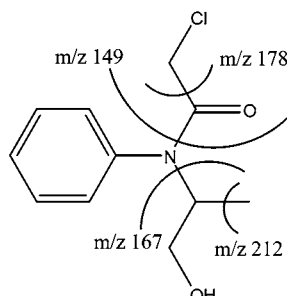
chloroacetanilide	product	t_r (min)	MS major ion, m/z (%)	structure
	2-chloro-N-(6-ethyl-hydroxy-2-methylphenyl)-N-(2-methoxy-1-methylethyl)-acetamide (**3e**)	15.9	301 (0.80), 299 (1.9), 254 (61), 227 (8), 178 (100), 162 (14), 147 (5.9), 133 (2.5), 121 (1.5)	
	2-chloro-N-(6-ethyl-hydroxy-2-methylphenyl)-N-(2-methoxy-1-methylethyl)-acetamide (**3f**)	16.1	299 (1.0), 270 (1.0), 254 (60), 227 (20), 178 (100), 162 (16), 148 (8.8), 133 (4.0)	
propachlor	1-isopropyl-1,3-dihydro-5-hydroxy-2H-indole-2-one (**4a**)	8.48	191 (64), 176 (4), 149 (100), 134 (2.8), 120 (86), 108 (6.4), 93 (7.0)	
	parent compound (**4b**)	9.31	213 (2.9), 211 (9), 196 (11), 176 (41), 169 (18), 134 (5.9), 120 (100), 104 (9.5), 93 (27)	
	2-chloro-N-(2-hydroxy-1-methylethyl)-N-phenyl-acetamide (**4c**)	10.4	229 (5.3), 227 (11), 212 (16), 191 (18), 178 (74), 167 (8), 136 (100), 120 (39), 109 (77)	

Table 4. (Continued)

chloroacetanilide	product	t_r (min)	MS major ion, m/z (%)	structure
	spiro[2,5-cyclohexadien-1-one-4,2 -3 -isopropyloxazolidin-4 -one] (**4d**)	10.5	207 (78), 192 (3.9), 178 (2.0), 165 (100), 150 (7.3), 136 (69), 123 (6.3), 109 (7.6)	
	4-isopropyl-4,4a-dihydro-benzo[1,4]oxazine-3,7-dione (**4e**)	11.9	207 (66), 165 (100), 150 (4.3), 136 (58), 124 (14), 109 (7.4), 95 (9.9)	
	hydroxy-2-chloro-*N*-isopropylacetanilide (**4f**)	12.7	229 (4.8) 227 (15), 212 (8), 192 (33), 185 (14), 150 (9.9), 136 (100), 120 (11), 109 (29)	
	hydroxy-2-chloro-*N*-isopropylacetanilide (**4g**)	13.0	229 (13), 227 (39), 212 (11), 192 (42), 185 (32), 150 (10), 136 (99), 120 (27), 109 (100)	

metolachlor were compared to the AFT products. In general, similar products are formed with both methods. However, with AFT two additional degradation products were detected that were not detected with CFT (see **Figure 4**). One of these products, eluting at 11.6 min, was present at 0 min of treatment time. Its concentration approximately doubled by 30 s of treatment and had degraded completely by 5 min of treatment. This compound could not be identified, although its mass spectrum indicated that it contained one chlorine. This compound is designated **3g**. Product **3g** can be assumed to be either (a) an initial degradation product representing the first attack of hydroxyl radical, (b) an impurity of metolachlor, or (c) a photolysis product. Metolachlor solutions required several hours of stirring to completely dissolve and were exposed to room light during that time. The other product unique to AFT eluted at 12.6 min. It reached its peak concentration at 5 min of

treatment time and tapered off slowly thereafter. This compound was also not conclusively identified. This product is referred to as **3h**.

Five minutes of treatment appeared to be the time at which all products but **3g** reached a concentration maximum. The product demonstrating the greatest total ion current (TIC) response is compound **3c** [*N*-(2-acetyl-6-methylphenyl)-2-chloro-*N*-(2-methoxy-1-methylethyl)acetamide], which exhibits an ethyl substituent oxidation. Products **3d** and **3e**, phenolic derivatives of metolachlor, exhibit lower TIC responses, whereas **3b**, demonstrating aldehyde formation of the ether amine substituent, appears to be a minor product pathway. Product **3f** was not found in AFT analysis, likely due to low concentration because its structural isomers **3d** and **3e** were present. A direct comparison of product concentrations could not be done due to a lack of standards; all concentration comparisons are loosely
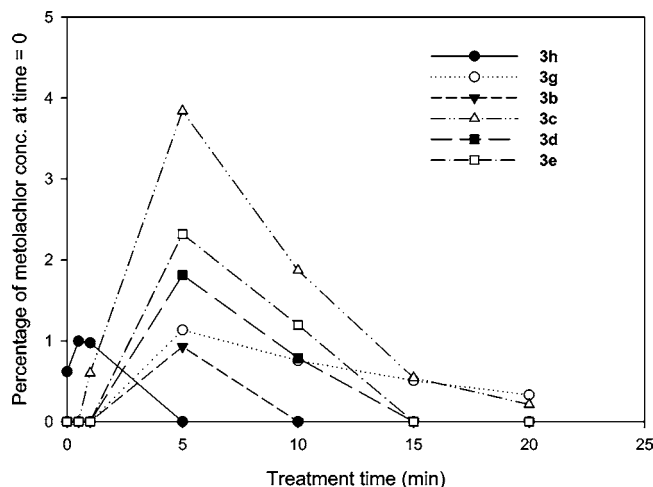
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Figure 4. Generation of metolachlor degradation products from AFT over 20 min of treatment time.

based on TIC responses. Comparison of CFT to AFT demonstrates that products of the two treatments are similar, although the presence of individual products differs throughout treatment time. CFT analysis was done at only one time point (reagent added equivalent to amount added by 4 min of AFT) so it is possible that several products present at earlier and later times were not detected. CFT analysis at all treatment times investigated in AFT analysis would provide more information on the similarity between the two treatments.

The observation that **3g** and most of the other degradation products were maximally abundant at 5 min may explain why the BOD_5/COD of the metolachlor effluent was still very low (<0.1) at 5 min of treatment despite complete disappearance of the parent compound. It appears that these degradation products were either resistant to biodegradation and/or toxic. This is in agreement with the known toxicity of phenols and aldehydes, which represent the most abundant degradation products detected via GC-MS. Phenol toxicity includes respiratory uncoupling and polar narcosis (*14*), whereas aldehydes exhibit electrophilic toxicity via the covalent binding of nucleophilic biological macromolecules (*15*). Interestingly, at 15 and 20 min only small amounts of **3c** and **3g** were present and the BOD_5/COD ratio for 160 μM metolachlor had increased to >0.3, signifying a biodegradable effluent.

On the basis of CFT products identified for each chloroacetanilide and the comparison of AFT products to CFT products for metolachlor, degradation pathways were proposed for all of the chloroacetanilides analyzed. Several general pathways appear to be common to acetochlor, alachlor, and metolachlor, whereas several of the propachlor degradation products were unique. **Figure 5** shows the proposed general pathway for acetochlor, alachlor, and metolachlor. Hydroxylation at all available phenyl sites occurs for each of these herbicides via hydroxyl radical addition, forming a radical which then likely undergoes oxidation by Fe^{3+} to form the phenolic compound. The intermediate radical could also react with molecular oxygen to form a phenolic compound via the Dorfman mechanism (*16*). The location of the hydroxyl groups was confirmed by performing GC-MS analyses of effluent extracts that had been derivatized with aqueous acetic anhydride. This derivatization technique is specific for phenolic hydroxyl substituents and does not result in the acetylation of alkyl hydroxyl substituents (*17*). The mass spectrum for a hydroxylated degradation product of acetochlor and the spectrum for its acetylated derivatized complement are shown in **Figure 6** as an example. Note the
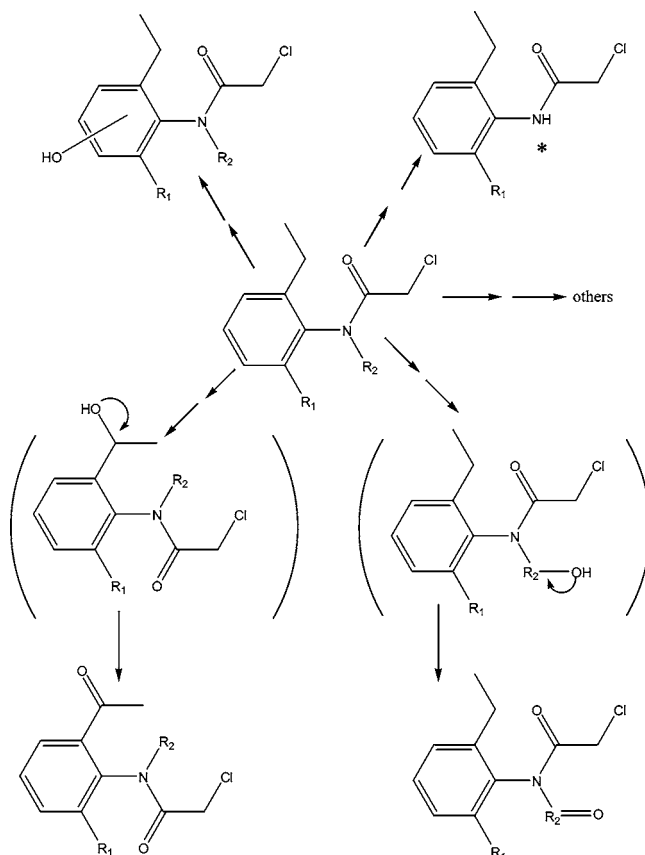

Figure 5. Degradation pathways common to acetochlor, alachlor, and metolachlor: acetochlor, $R_1 = CH_3$, $R_2 = CH_2OCH_2CH_3$; alachlor, $R_1 = CH_2CH_3$, $R_2 = CH_2OCH_3$; metolachlor, $R_1 = CH_3$, $R_2 = CH(CH_3)CH_2OCH_3$. * Acetochlor and alachlor only.
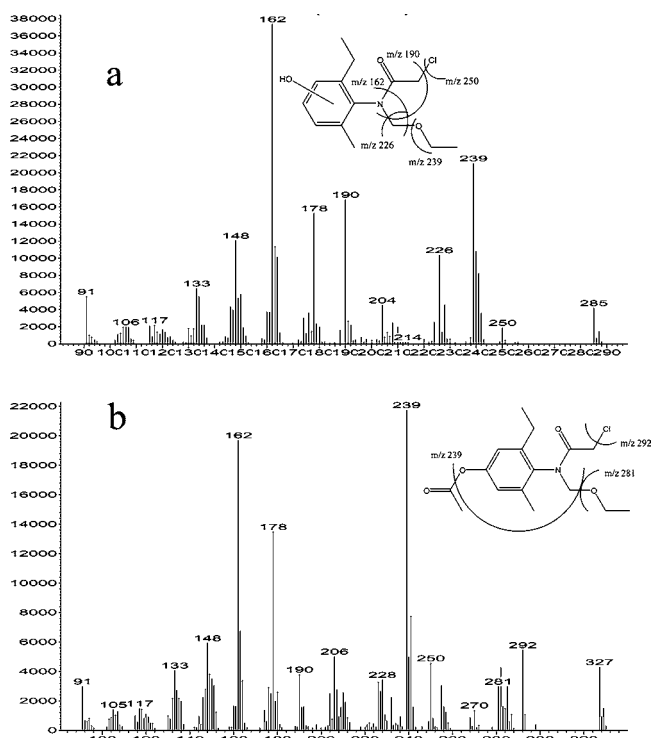

Figure 6. (**a**) MS of hydroxylated acetochlor degradation product and (**b**) MS of same product after acetylation derivatization (abundance vs *m/z*).

addition of 42 *m/z* to the parent ion after derivatization (**Figure 6b**) and the ready loss of this fragment upon electron impact.
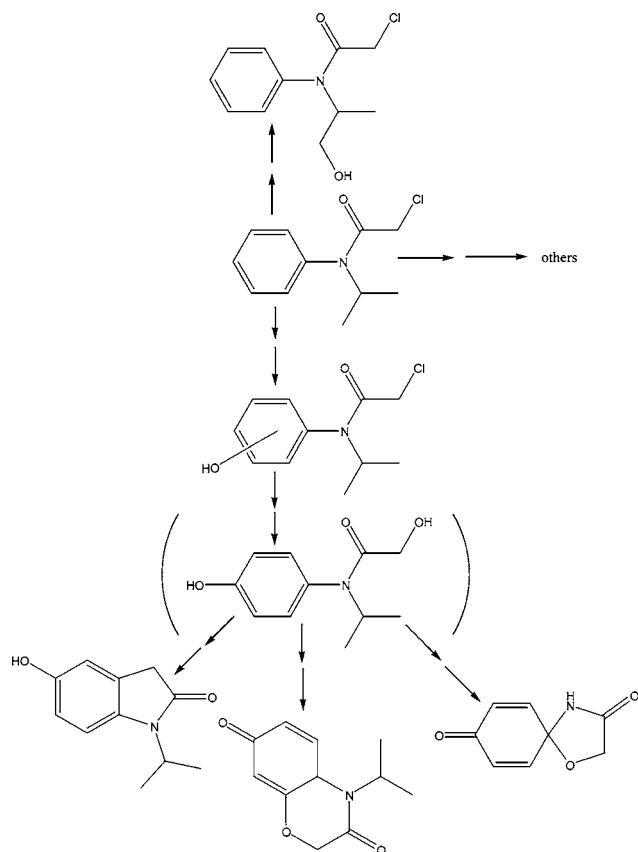
Figure 7. Degradation pathways of propachlor.

These traits are characteristic of aromatic acetyl derivatives. Another degradation pathway is the cleavage of the R_2 group via hydrogen abstraction followed by α/β scission of the $N-R_2$ bond. This is the only pathway proposed that does not involve the addition of a hydroxide group. This pathway is proposed for acetochlor and alachlor only. It is hypothesized that this product is found only for acetochlor and alachlor because the amine substituents of these two herbicides are more reactive than the others due to substitution with a primary carbon (*18*). Also, propachlor and metolachlor exhibit branching of their amine substituents, making them less preferable leaving groups. A third pathway is the formation of a ketone at the ethyl substituent. This pathway requires a hydroxylated intermediate (shown). This intermediate compound was not identified in product studies, presumably because it is very reactive, with its transformation to a carbonyl potentially catalyzed by aqueous Fe(III) (*18*, *19*). Formation of a carbonyl is also proposed to occur for the amine substituent (R_2). A hydroxylated intermediate and the subsequent Fe(III)-catalyzed formation of a carbonyl is also proposed for this pathway. Intermediates are formed via hydrogen abstraction to create a radical, followed by the addition of hydroxyl radical. Although the products of each pathway were not necessarily determined for acetochlor, alachlor, and metolachlor individually (possibly due to low concentration/low extraction efficiency), it is proposed that these pathways occur for all three of those herbicides (except for cleavage of the R_2 group) due to the similarity in their structures.

Proposed degradation pathways for propachlor are shown in **Figure 7**. Propachlor exhibits two pathways shared by the other chloroacetanilides. Hydroxylation of all available phenyl sites was found to occur via hydroxyl radical attack. Several products were discovered for propachlor that were not observed with the others. Hydroxylation of the propyl amine substituent was found to occur, but oxidation to a carbonyl was not observed as it

was for the other herbicides. This is likely due to the fact that the hydroxylated carbon of the propyl group has no neighboring substituents that are electron-donating. Electron-donating groups have been shown to increase the oxidation of an alcohol to a carbonyl by Fe^{3+} (*18*). This pathway occurs via hydrogen abstraction followed by addition of hydroxyl radical. Ring formation within products was found to take place with propachlor but not with the others. The three propachlor products demonstrating ring formation, **4a**, **4d**, and **4e**, share two intermediates. The first is a para-hydroxylated intermediate formed by hydroxyl radical attack. The second is the substitution of OH for Cl in the first intermediate. Although the second intermediate was not detected in AFT effluent, environmental degrades and UV and ozone treatment products demonstrating this substitution reaction have been found for other chloro-acetanilides (*20*−*22*). It is likely that the electron-donating character of the para hydroxide group, combined with the lack of phenyl alkyl substituents, makes ortho sites good targets for ring formation during propachlor degradation. The second intermediate then undergoes hydrogen abstraction, forming a radical at the site of ring formation, and a bond between the amended acetyl group and the radical site is formed. Two of these pathways result in five-membered rings (**4a** and **4d**), one of them an ether (**4d**), and the third pathway results in a six-membered ether ring (**4e**).

In general, for each of the herbicides analyzed, a large percentage of the products determined were hydroxylated derivatives of the parent compound. This finding is in agreement with results showing that the oxidation of benzene to phenol by Fenton's reagent is very rapid (*23*). Other significant products exhibit ketone formation. This is also in agreement with findings by others that alcohols (formed first by hydrogen abstraction and hydroxyl radical addition) are susceptible to α hydrogen abstraction followed by oxidation by Fe^{3+} (*18*). More extensively oxidized products were not detected in appreciable concentrations; it is likely that once a compound has undergone initial hydroxyl radical attack, further oxidation and degradation occurs rapidly and smaller organic products are either not stable in solution or were not extracted/detected with the methods employed here. This is supported by our observation that direct aqueous analysis of AFT effluent with infusion MS/MS demonstrated several unidentified ions that were not present in dichloromethane extracts (data not shown).

Comparison of degradation rate constants within this group of herbicides suggests a possible correlation between number and length of phenyl alkyl substituents and reactivity toward hydroxyl radical. Acetochlor and metolachlor, the two chloro-acetanilides with 2-methyl, 6-ethyl substituents, degraded most rapidly; alachlor and butachlor, the two chloroacetanilides with 2,6-diethyl phenyl substituents, were slower to degrade; pro-pachlor, the only chloroacetanilide without any alkyl substitu-ents, was the least susceptible to degradation. However, direct oxidation of the methyl and ethyl substituents does not occur in appreciable amounts, so the oxidation of these substituents is not a strong determinant of reaction rate constants. Rather, it is possible that the electronic effect of the alkyl substituents may partially determine degradation rates by altering the susceptibility of the ring to hydroxylation. Acetochlor and metolachlor degrade most quickly, presumably because of the electron-donating effect of the methyl and ethyl substituents to the ring, making phenyl sites more susceptible to attack by hydroxyl radical, which is a very electrophilic species (*18*). However, alachlor and butachlor experience a greater electron-donating effect from their two ethyl substituents, which would

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lead one to expect them to degrade most quickly. It is hypothesized that the increase in length of one of the substituents creates enough steric hindrance to decrease the susceptibility of remaining ring sites to hydroxylation. In contrast, propachlor does not have any electron-donating substituents on the ring and also has the slowest degradation rate despite having more ring sites available for hydroxylation. Another explanation for the slow rate of propachlor degradation may lie in the nature of propachlor's R_2 substituent, which is an alkyl group which differs from the ether found in the other chloroacetanilides. Walling et al. (*18*) have shown that ether oxygen has a weak activating effect on α C−H bonds, providing greater electron density and making these bonds more susceptible to hydrogen abstraction. Thus, propachlor's alkyl substituent may also have reduced the rate of hydroxyl radical attack when compared to the other chloroacetanilides.

Conclusion. AFT can quickly and effectively remove chloroacetanilide herbicides from aqueous solutions. The AFT kinetic model accurately describes the degradation of chloroacetanilide herbicides. The reaction rate constants of chloroacetanilides with hydroxyl radical were determined. The chloroacetanilides tested demonstrated the following reactivity order: acetochlor ≈ metolachlor > alachlor ≈ butachlor > propachlor. AFT can effectively increase the biodegradability of single-component and mixed chloroacetanilide in aqueous solutions. Major proposed degradation pathways for the chloroacetanilides include hydroxyl radical attack of nonsubstituted phenyl sites and terminal ether sites. In the case of propachlor, ring formation between phenyl and acetyl substituents appeared to be common to several major pathways.

ACKNOWLEDGMENT

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