Environ. Sci. Technol. **1998**, *32,* 1482−1487

Dechlorination of the Chloroacetanilide Herbicides Alachlor and Metolachlor by Iron Metal

GERALD R. EYKHOLT* AND
DOUGLAS T. DAVENPORT†
Department of Civil and Environmental Engineering, University of Wisconsin—Madison, Madison, Wisconsin 53706

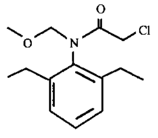
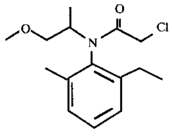
Granular iron metal has been found to cause the reductive dechlorination of two important chloroacetanilide herbicides, alachlor and metolachlor. Aqueous solutions (113 mL) of the herbicides were contacted with 40 g of granular cast iron (CCI coarse, 40 mesh) with mild agitation at room temperature. First-order degradation rate constants were 0.12 and 0.10 h^{-1} for 10 mg/L solutions of alachlor and metolachlor, respectively. A two-site, rate-limited sorption and first-order degradation model was applied to both batch data sets, with excellent agreement for alachlor and fair agreement for metolachlor. The products of the reaction were chloride (84% mass balance for alachlor and 68% for metolachlor) and dechlorinated acetanilides. Supported by GC/EIMS analysis, two sequential reactions may have occurred for alachlor, hydrogenolysis of the chloroacetyl group followed by an N-dealkylation reaction. However, only one product was confirmed by GC/FID, and the mechanism for the N-dealkylation reaction is unknown. Metolachlor was found to produce one dechlorinated product consistent with hydrogenolysis. These results are encouraging, as granular iron may be used at spill sites contaminated with these herbicides and related compounds.

Introduction

Alachlor and metolachlor are structurally related chloroacetanilide herbicides used for broadleaf weeds and annual grasses in domestic soybean and corn crops. They are used most heavily in the North Central United States. The main structural differences are in the nonchlorinated alkyl group attached to the anilide moiety and in the choice of methyl vs ethyl substituents on the benzene ring. These factors regulate selectivity and water solubility (*1*). Pertinent physical and chemical properties are presented in Table 1. Alachlor is listed as a probable (U.S. EPA group B2) human carcinogen, and metolachlor is listed as a possible (group C) carcinogen (*2*).

Chesters et al. (*1*) presented an extensive review of alachlor and metolachlor degradation mechanisms relevant to fate and toxicology in soil. Other reviews have been presented for alachlor (*3*) and metolachlor (*4*). Most of the discussion is focused on biochemical reaction mechanisms, and little discussion is devoted to abiotic mechanisms. However, dechlorinated byproducts of hydrogenolysis reactions were found among the more than 30 byproducts identified for each parent compound, predominantly when these herbicides were contacted with both sterile (autoclaved) and nonsterile sediments or flooded soils. Potter and Carpenter (*5*) also identified several dechlorinated byproducts of alachlor by GC/MS in a Massachusetts corn field groundwater monitoring study. Three main alachlor related products found were *N*-(2,6-diethylphenyl)-*N*-(methoxymethyl)acetamide, *N*-(methoxylmethyl)-2,6-diethylaniline, and 2′-acetyl-6′-ethyl-*N*-(methoxymethyl) acetanilide. These products are consistent with a combination of processes including reductive dechlorination (via hydrogenolysis), dealkylation, and oxidation reactions. Chesters et al. (*1*) note that the above products may be produced abiotically, although few details regarding reaction mechanism are presented.

TABLE 1. Chemical Structure and Properties of Alachlor and Metolachlor (1)

	Alachlor	Metolachlor
Herbicide Product	Lasso™ (Monsanto, 1969)	Dual™ (Novartis, 1976)
Structure	 2-chloro-(2’,6’-diethyl)-*N*-(methoxymethyl)-acetanilide	 2-chloro-(2’-ethyl,6’-methyl)-*N*-(methoxyprop-2-yl)-acetanilide
molecular weight	269.8	283.8
solubility (20°C)	240 mg/L	530 mg/L
octanol-water partition coefficient, K_{ow}	430	2800

Zero-valent iron has been employed in reactive barriers to treat groundwaters contaminated with chlorinated solvents such as trichloroethylene (*6*−*8*), with chromate solutions (*9*), and with technetium (*10*). This research was part of a broader screening study that also included *s*-triazine (atrazine and cyanazine) and carboxylic acid (2,4-dichlorophenoxyacetic acid, dicamba) herbicides (*11*). The focus of the study was to evaluate whether the reduction chemistry provided by zero-valent iron might also be used for the remediation of herbicide product spills at mixing and loading facilities and farm cooperatives. As we found that the other four herbicides were not reactive with granular iron metal under the study conditions, this paper will focus on the degradation of alachlor and metolachlor by granular iron metal.

Since 1984, the Wisconsin Departments of Natural Resources (DNR) and Agriculture, Trade and Consumer Protection (DATCP) have studied cases of soil and groundwater contamination at facilities where pesticides and herbicides are mixed and loaded. Environmental sampling surveys conducted in 1989 and 1991 by DNR and DATCP for soil and groundwater contaminants revealed prevalent contamination at these facilities. Choroacetanilide herbicides were found at concentrations above 5 mg/L in 25% of sites investigated and were above groundwater quality standards in nearly 30% of the sites investigated (*12*). In mixed pesticide contamination settings, a common occurrence at mixing and loading facilities, chloroacetanilide herbicides are a major concern. Compared to the more commonly used herbicide atrazine, alachlor and metolachlor have higher solubilities in water and sorb less to the soil.

---

* Corresponding author phone: (608)263-3137; fax: (608)263-5199; e-mail: eykholt@engr.wisc.edu.

† Current address: MSA Professional Services, Baraboo, WI.

S0013-936X(97)00678-0 CCC: $15.00

Alachlor concentrations measured at some sites are higher than atrazine for this reason. In addition, the extent of the contamination plume may be governed by chloroacetanilide herbicides at some sites.

Experimental Section

Two sets of iron/water batch experiments were performed. One set was used to identify and confirm byproducts of the reaction by evaluating chloride mass balance and GC/EIMS spectra of the initial and 5-day batches. The other set, sampled periodically over 5 days, was used to study reaction kinetics and sorption characteristics. For the kinetics set, measurements focused on parent compound sorption and transformation. Although byproducts were detected and subsequently identified, no effort was made to quantify byproduct accumulation or subsequent degradation. The experimental conditions and analytical methods are summarized below, and a more complete discussion is provided by Davenport (*11*).

Batch Reactor Conditions and Sample Preparation. Tests were conducted at room temperature in dark, 100-mL glass serum vials, each sealed with a Teflon plug and an aluminum crimp cap. Herbicide stock solutions at 10 mg/L were prepared from analytical grade herbicides (AccuStandard, New Haven, CT) and Type I water. Solutions at 100 mg/L were prepared from technical grade herbicides, with purities between 94.5% and 96%. Technical grade alachlor was obtained from Monsanto Corporation (St. Louis, MO), and technical grade metolachlor was obtained from Ciba Corporation (now Novartis Crop Protection, Greensboro, NC).

Each vial was filled with approximately 113 mL of herbicide stock solution and 40 g of 40-mesh cast iron filings with a surface area of roughly 1.4 m^2/g (Columbus Chemical Industries, Columbus, OH). For most tests, the iron was used without any purification measures. However, for the tests involving chloride measurements, batches of 40 g of iron were rinsed with three 100-mL exchanges of 65 mg/L potassium nitrate in order to remove residual chloride prior to herbicide exposure. Quality assurance measures included periodic use of blanks, controls (no iron), and duplicates.

Batch reactors were turned radially at 3 rpm for up to 5 days and were sampled sacrificially. To measure sorbed herbicides and their products, the iron was vacuum filtered (Whatman 9340-AH glass microfiber filter). Aqueous filtrates were retained for analysis by GC/MS, GC/FID, and chloride analysis. The iron and filter were placed in 25 mL of acetone and shaken on a vortex mixer for 2 min. After particles in the iron rinsates were allowed to settle, the supernatant extract was analyzed by GC/FID without further purification.

Gas Chromatography. Aqueous samples (2 mL) were extracted into 2 mL of methylene chloride (Fisher, pesticide grade). A few grains of anhydrous sodium sulfate (Fisher) were added to enhance the extraction. Samples were shaken by a vortex mixer for 2 min and placed into 2-mL amber glass screw thread autosampler vials with open top closures and PTFE-lined silicone septa (Supelco, Bellefonte, PA). Samples of 1 μL were injected at 195 °C onto a Varian 3600-6C gas chromatograph (Palo Alto, CA), equipped with a 60 m × 0.32 mm i.d. Supelco SPB-5 fused silica capillary column (0.25 μm film) and a flame ionization detector held at 325 °C. The column temperature was held at 110 °C for 8.0 min and then increased to 225 °C at a rate of 3 °C/min. The final temperature was held for 8.0 min. Helium carrier gas and nitrogen makeup gas flow rates were 10 and 20 mL/min, respectively. The GC/FID method was calibrated using analytical standards of each herbicide (AccuStandard, New Haven, CT). Method detection limits were 0.5 mg/L for alachlor and metolachlor.

A limited number of aqueous batch samples, stored at 4 °C for less than 5 days and extracted into equal volumes with ethyl acetate (Fisher, optima), were also analyzed by gas chromatography/electron impact mass spectrometry (GC/EIMS). Samples of 1 μL were injected splitless at 250 °C onto a Hewlett-Packard 6890 series gas chromatograph (Palo Alto, CA), equipped with a 30 m × 0.25 mm i.d. HP-5 fused silica capillary column (0.25 μm film) and a HP mass selective detector with an interface temperature held at 280 °C. The column temperature was held at 70 °C for 1.5 min, then increased to 140 °C at a rate of 25 °C/min, and then increased 190 °C at a rate of 2 °C/min. The temperature was then held for 10 min at 190 °C, then increased to 240 °C at 30 °C/min, and held constant for 5 min. Helium carrier gas flow rate was constant at 1.0 mL/min. The GC/MS method was used for identification rather than for compound quantification. No efforts were made to determine calibration factors or detection limits.

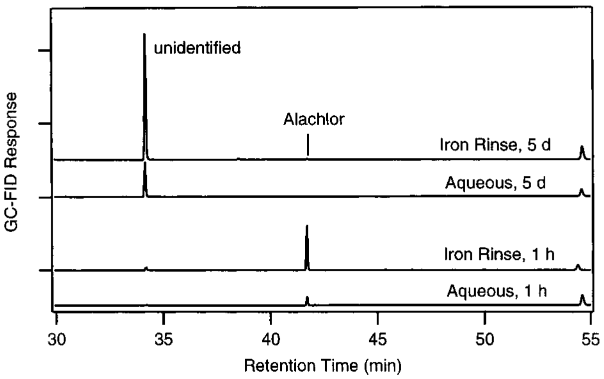


FIGURE 1. GC/FID chromatograms of alachlor and byproduct formed after contact with iron metal. Chromatograms have not been normalized to reflect relative masses on iron and aqueous phases.

EIMS spectra were compared (visually) to alachlor byproduct spectra reported by Potter and Carpenter (*5*) and Mangiapan et al. (*13*). For the metolachlor product, a Novartis spectroscopist was consulted, and comparisons were made to a company archive of common metolachlor byproduct spectra (*14*). Spectra measured from alachlor and metolachlor standards also matched closely with the spectra downloaded from a NIST webpage database (http//webbook.nist.gov/chemistry).

Chloride Analysis. Chloride was determined by ion chromatography, using a dilute sodium hydroxide eluent and suppressed conductivity detection (Dionex DX-500 HPLC, IONPAC AS11 column, Palo Alto, CA). The instrument detection limit less was than 0.1 mg/L. Background levels of chloride were measured from herbicide stock solutions (54 and 8 μM for alachlor and metolachlor, respectively) and from a 5-day iron blank (89 μM). The 5-day mass balances with respect to chloride were determined for batch reactions by subtracting the amount of chloride present in the 5-day iron blank and in the initial stock herbicide solutions.

Evaluation of Reaction Kinetics. A two-site, rate-limited sorption and first-order degradation model discussed by van Genuchten and Wagenet (*15*) was simulated and plotted using the software Igor Pro (WaveMetrics, Lake Oswego, OR) on a Power Macintosh 7100/66 (Apple Computer, Cupertino, CA). The model assumes instantaneous (region I) and rate-limited (region II) sorption and first-order degradation. A fraction f of available sorption sites is occupied in instantaneous sorption, and the remaining fraction $(1 - f)$ is available for rate-limited sorption. Mass action for the system is described below:

$$\left.\frac{\partial C}{\partial t}\right|_{\text{total as aqueous}} = \frac{fm}{V}\frac{\partial C_{\text{sI}}}{\partial t} + \frac{(1-f)m}{V}\frac{\partial C_{\text{sII}}}{\partial t} + \frac{\partial C_{\text{aq}}}{\partial t} \qquad (1)$$

where m is the mass of iron in the system, and V is the volume of water. C_s is the concentration on the solid-phase attributed to region I or II, and C_{aq} is the aqueous concentration. Each component of the above expression has subcomponents of sorption and reaction normalized to an aqueous concentration. For this application of the model, the equilibrium sorption coefficient K_{eq} for each region was set equal. While an initial aqueous concentration $C_{aq,0}$ was considered, the initial solute concentrations at each of the solid regions were assumed to be zero. The expressions for reaction and sorption in each of the components are as follows:

$$R_{sI}\frac{\partial C_{aq}}{\partial t} = -kC_{aq} - k_{sorb}(C_{aq} - C^*) \tag{2}$$

$$\frac{\partial C_{sI}}{\partial t} = K_{eq,I}\left[\frac{\partial C_{aq}}{\partial t}\right] \tag{3}$$

$$\frac{1}{K_{eq,II}}\frac{\partial C_{sII}}{\partial t} = \frac{\partial C^*}{\partial t} = \kappa_{sII}(C_{aq} - C^*) \tag{4}$$

R_{sI} is a retardation coefficient for region I sites:

$$R_{sI} = 1 + \frac{fmK_{eq,I}}{V} \tag{5}$$

k is the first-order degradation rate constant, k_{sorb} is the rate-limited sorption coefficient associated with region II, and C^* is the time-dependent, aqueous concentration in pseudo-equilibrium with the solid-phase concentration C_{sII}. The coefficient κ_{sII} is calculated from k_{sorb} and phase and equilibrium parameters of region II:

$$\kappa_{sII} = \frac{k_{sorb}V}{(1 - f)mK_{eq,II}} \tag{6}$$

Although the model expresses a single apparent rate constant for degradation in the aqueous phase, degradation could occur in any of the aqueous or solid phases.

Later, an analytical solution was derived for the above equations through Laplace transforms. The solutions for the aqueous and region II solid-phase concentrations are

$$C_{aq}(t) = \frac{C_{aq,0}}{m_1 - m_2}[(\kappa_{sII} + m_1)e^{m_1 t} - (\kappa_{sII} + m_2)e^{m_2 t}] \tag{7}$$

$$C_{sII}(t) = \frac{C_{aq,0}\kappa_{sII}K_{eq,II}}{m_1 - m_2}[e^{m_1 t} - e^{m_2 t}] \tag{8}$$

The solution parameters m_1 and m_2 are the roots of the quadratic equation:

$$m_1, m_2 = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \tag{9}$$

where the parameter a is 1 and the other parameters are

$$b = \kappa_{sII} + \frac{k + k_{sorb}}{R_{sI}} \tag{10}$$

and

$$c = \frac{\kappa_{sII}k}{R_{sI}} \tag{11}$$

The solution for the region II solute concentration is equivalent to the aqueous concentration multiplied by K_{eq}. The agreement with the numerical solution was excellent.

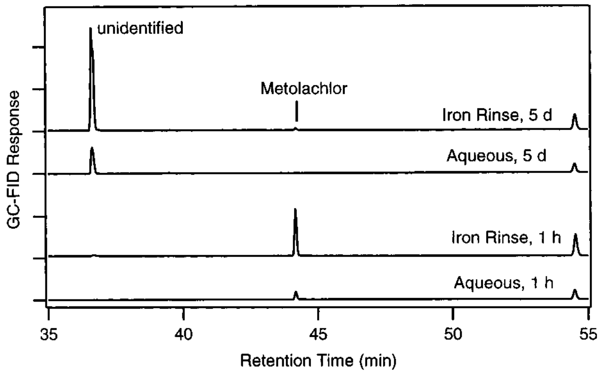


FIGURE 2. GC/FID chromatograms of metolachlor and byproduct formed after contact with iron metal. Chromatograms have not been normalized to reflect relative masses on iron and aqueous phases.

Results and Discussion

Byproduct Formation and Identification. Aqueous batches of 100 mg/L alachlor or metolachlor solutions (technical grade) were contacted with granular iron metal, gently tumbled, and sampled sacrificially after contact periods of 1 h and 5 days. GC/FID chromatograms of aqueous samples and acetone iron rinses for alachlor and metolachlor batches are shown in Figures 1 and 2, respectively. Both herbicides showed significant loss and formation of a different, single byproduct over the 5-day contact period. At this stage, byproducts of alachlor and metolachlor, appearing in both aqueous extractions and iron rinsates, were unidentified. Retention time of alachlor was 41.7 min, and one byproduct was observed at a retention time of 34.2 min. Retention time of metolachlor was 44.1 min, and the byproduct was observed at a retention time of 36.6 min. Aqueous samples from these batches were analyzed for chloride. After correction of chloride levels in untreated herbicide solutions and iron blanks, chloride mass balances of 84% and 68% were determined for alachlor and metolachlor, respectively. No efforts were made to quantify levels of the byproducts or to resolve an organic carbon mass balance.

Aqueous fractions from these experiments were later analyzed by GC/MS for byproduct identification. Normalized GC/EIMS spectra for standards and byproducts identified from 5-day batches for alachlor and metolachlor are shown in Figures 3 and 4, respectively. Parent compounds were not detected by GC/MS for reacted alachlor and metolachlor solution samples from the 5-day batch. Two byproducts were found in the alachlor sample, and one was found in the metolachlor sample. For solutions initially spiked with alachlor, the two principal products eluted at 12.5 and 15.6 min. Approximately 9% of the total chromatograph area was observed at 12.5 min, and 91% of the area was observed at 15.6 min. Whereas aqueous solutions of alachlor contacted with iron for 1 h and a 10 mg/L alachlor standard showed a single peak at 23.7 min, alachlor was not detected in the 5-day aqueous sample. For the 5-day metolachlor extract, the only organic product detected eluted at 18 min. The chromatographic retention time for the metolachlor standard was 26.7 min.

Identification of alachlor reaction byproducts was made by comparison of byproduct mass spectra to those presented by Potter and Carpenter (*5*). Identification was also confirmed upon comparison with mass spectra presented by Mangiapan et al. (*13*). The reaction byproducts were identified as 2′,6′-diethyl-*N*-(methoxymethyl) acetanilide and 2′,6′-diethylacetanilide. These byproducts were named by

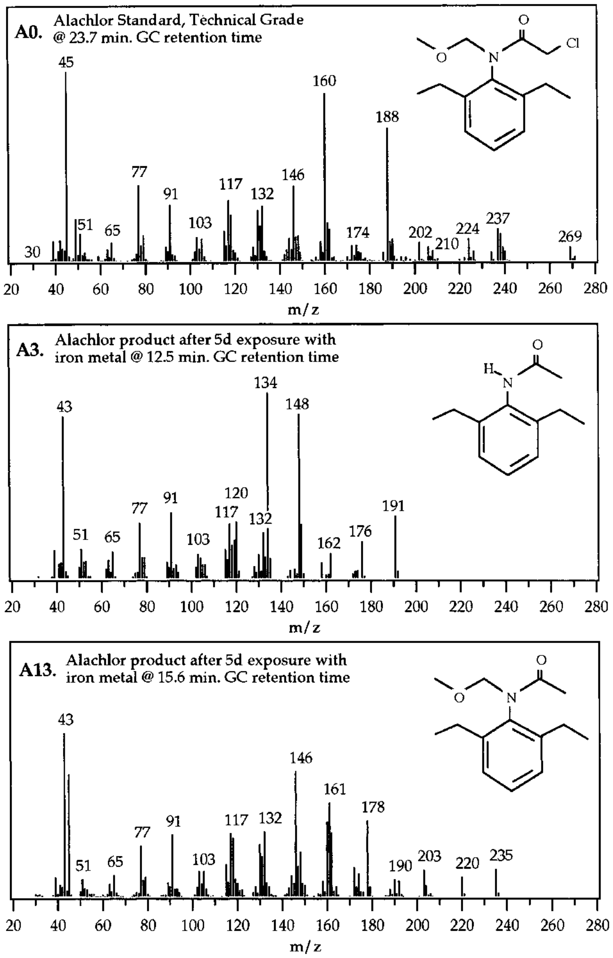


FIGURE 3. GC/EIMS spectra of alachlor and byproduct formed after 5-day batch contact with iron metal. Alachlor was not detected in 5-day batches.

Chesters et al. (*1*) as products A13 and A3, respectively, noted as byproducts of alachlor (A0) from reduction and subsequent N-dealkylation. Chesters et al. concluded that these reduction reactions were likely chemical (abiotic). These compounds were also found and identified (by comparison to MS of synthesized compounds) as major alachlor byproducts by Potter and Carpenter in a Massachusetts groundwater study (*5*). They identified these products as VIII (A13) and III (A3), respectively. For convenience, symbols for the herbicides and their products discussed in this paper will be consistent with those presented by Chesters et al. (*1*).

From interpretation of its EI mass spectra, the organic product identified for metolachlor was 2′-ethyl,6′-methyl-*N*-(methoxyprop-2-yl)acetanilide, a dechlorinated compound designated as M2 by Chesters et al. (*1*). The molecular ion of metolachlor ($m/z = 283$) was not detected under EIMS conditions (see Figure 4, upper panel). Rather, a prominent ion at m/z 238 was detected, probably formed via the loss of the neutral fragment $CH_3OCH_2^\bullet$ (β-cleavage to nitrogen). The related ion $CH_3OCH_2^+$ ($m/z = 45$) was also detected. The EI spectra of the reaction product (see Figure 4, lower panel) revealed a prominent ion at m/z 204, indicating dechlorination with a mass change of 34 from the parent compound. The spectra was otherwise very similar to that of metolachlor. It was hypothesized that the ion at m/z 204 corresponded to the β-cleaved ion for the reductively dechlorinated compound M2 (noting that the molecular ion at $m/z = 249$ was not observed). Dechlorination was also indicated by a low Cl^{37}/Cl^{35} abundance ratio detected for the prominent ions. The identification was then confirmed by comparison with the EI mass spectra of the authentic compound M2 (CGA 41507, courtesy Novartis, ref *14*).

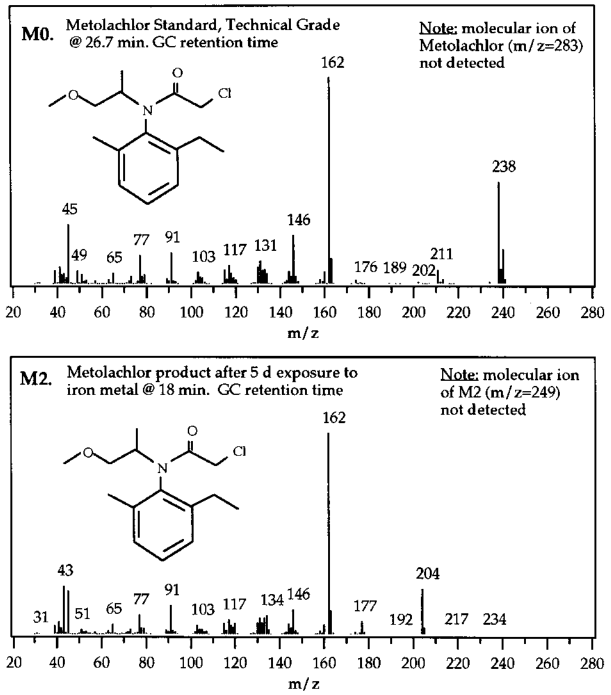


FIGURE 4. GC/EIMS spectra of metolachlor and byproduct formed after 5-day batch contact with iron metal. Metolachlor was not detected in 5-day batches.

The reductive dechlorination of alachlor and metolachlor occurs by hydrogenolysis at the chloroacetyl group:

$$\text{R-COCH}_2\text{Cl} + 2e^- + H^+ \rightarrow \text{R-COCH}_3 + Cl^- \quad (12)$$

This reduction can be provided at the iron surface upon the oxidation of iron metal:

$$Fe^0 \rightarrow Fe^{2+} + 2e^- \quad (13)$$

As reported above, chloride mass balance from the 5-day experiments was 84% and 68% for alachlor and metolachlor, respectively. While not excellent, these balances are good considering that no attempt was made to extract any chloride sorbed or complexed to the iron. These chloride balances do reflect, however, corrections of the amount of leachable chloride from the iron determined from blanks.

The cause for the N-dealkylation reaction evident from the alachlor byproduct A3 is unknown. N-Dealkylation reactions have not been shown to occur by direct electrochemical reduction by iron metal but have been observed in anaerobic soil microcosms and photochemical or biochemical oxidizing conditions. Although A13 and the dealkylated product A3 were found by GC/MS, only one product, presumably A13, was observed by GC/FID (see Figure 1). This discrepancy may be due to transformation of the aqueous samples during preparation or storage after GC/FID analysis and prior to GC/MS analysis. Since the samples were prepared from dry cast iron filings and Type I water and stored at 4 °C with pH 9−10, biochemical degradation is unlikely (but cannot be ruled out). An indirect photolysis pathway, such as discussed by Torrents et al. (*16*) for the N-dealkylation of atrazine, seems more probable. This hypothesis assumes that there was adequate light during the preparation of samples for GC/MS. Hydrogen produced by reduction of water may also be important to the overall reaction mechanism (*8, 17*). A followup study is being

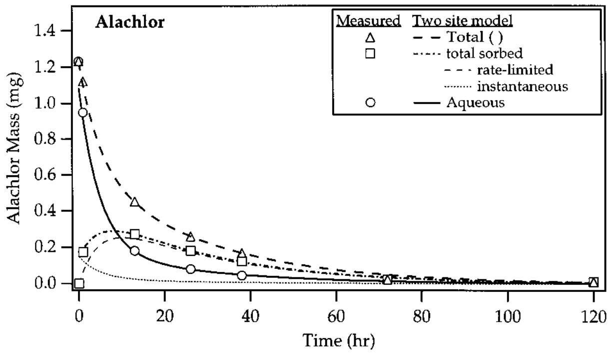


FIGURE 5. Alachlor degradation kinetics by iron metal described by a two-site, rate-limited sorption and degradation model (parameters: $k = 0.12$ h^{-1}, $k_{\mathrm{sorb}} = 0.068$ h^{-1}, $K_{\mathrm{eq}} = 3.2$ mL/g, $f = 0.12$, $C_0 = 10.9$ mg/L, $m = 40$ g, $V = 113$ mL).

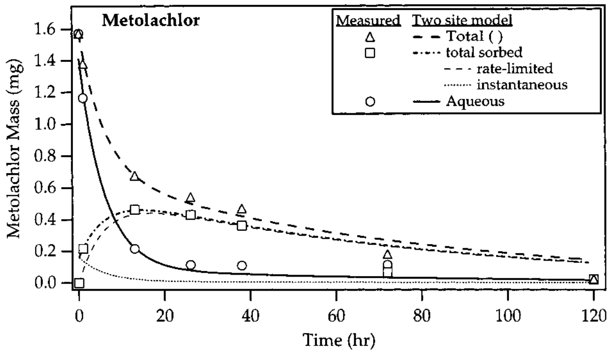


FIGURE 6. Metolachlor degradation kinetics by iron metal described by a two-site, rate-limited sorption and degradation model (parameters: $k = 0.10$ h^{-1}, $k_{\mathrm{sorb}} = 0.06$ h^{-1}, $K_{\mathrm{eq}} = 8$ mL/g, $f = 0.04$, $C_0 = 13.9$ mg/L, $m = 40$ g, $V = 113$ mL).

conducted to better understand the conditions that promote the N-dealkylation reaction.

Assessment of Reaction Kinetics. Experimental and modeled distributions of alachlor and metolachlor mass between the aqueous and solid phases are presented in Figures 5 and 6. For each, the rate of loss of the parent herbicide mass in the system over 5 days was roughly first-order. Examination of mass distribution between the phases suggests instantaneous and rate-limited sorption occurred. The two-site sorption and degradation model was fitted by trial and error to alachlor and metolachlor aqueous and iron rinsate data from the batch experiments. The resulting model fits, with approximations of f, k, k_{sorb}, and K_{eq} are also presented in Figures 5 and 6. The model indicates similar reaction kinetics for alachlor and metolachlor, with half-lives of 5.8 and 6.9 h, respectively. The sorption characteristics for the compounds are also similar. The relative instantaneous partitioning (quantity fK_{eq}) of alachlor was 0.38 mL/g, roughly equivalent to a value of 0.32 mL/g for metolachlor. Apparently, the higher solubility of metolachlor is offset somewhat by its higher octanol−water partition coefficient (see Table 1). Such inferences on sorption, however, should be considered preliminary as these results were obtained with only one general test condition. Results may differ under different levels of herbicide and iron concentration, temperature, and agitation.

The model agreement for alachlor was superior to that obtained for metolachlor, especially for times greater than 40 h. At times greater than 40 h, the modeled aqueous and solid phase concentrations for metolachlor are significantly higher than the measured concentrations. The metolachlor is more reactive and more freely associated with the aqueous phase than the model suggests. In this regard, the reaction rate identified for metolachlor should be seen to be somewhat conservative. Conversely, the amount of sorption for metolachlor suggested by the model should be considered underconservative. It is possible that the products formed from the alachlor reaction do not interfere with subsequent sorption of alachlor, whereas the product formed from metolachlor may compete for nonreactive sorption sites with metolachlor, leaving it more readily available for reaction on active iron sites.

The half-lives presented above for these iron experiments were at least 1 order of magnitude lower (faster) than half-lives reported by Chesters et al. (*1*) for a variety of field soil conditions. The reported half-lives, which also include effects of microbial activity, range from 6.0 to 40 day for alachlor, and from 13 to 203 day for metolachlor. The rates for metolachlor degradation are generally slower than the rates for alachlor degradation in microbial studies (*1, 18*). For this iron study, there was only a slight difference in the reaction rate constants determined for alachlor and metolachlor. The higher rates and lack of selectivity also suggest that the reactions are predominantly abiotic.

The purpose of the batch experiments was to observe changes in aqueous and solid phase concentrations of alachlor and metolachlor and to reach some preliminary conclusions on the viability of granular iron as a remediation tool for spill sites with high concentrations of these herbicides. The data presented in this study suggest that alachlor and metolachlor, and structurally similar compounds, may be dechlorinated rapidly using granular iron. Reactive iron barriers or granular iron treatments might be applied to spill site groundwaters and soils, although reactions with site groundwaters or natural soils have not yet been performed. While one might expect that the dechlorinated products are less toxic, the relative degradability and toxicology of the dechlorinated byproducts of alachlor and metolachlor are not yet known. Future work is needed to confirm dechlorination, to quantify kinetics of product formation, and to resolve carbon mass balances. Further studies initiated in summer 1997 focus on fate of the compounds in iron/water/soil systems, improved analytical methods (*13, 18*), and an investigation of the degradability and toxicity indications of iron reaction byproducts.

Acknowledgments

This research was supported by the Wisconsin Department of Agriculture, Trade and Consumer Protection, as part of groundwater research consortium associated with the University of Wisconsin System. The authors wish to acknowledge the assistance of Paul Fritschel and Greg Lowry for GC/FID analyses, Prof. W. J. Hickey and Dr. H. Read for GC/MS analyses and interpretation, and Prof. Lynn Roberts of Johns Hopkins University for careful review of the manuscript. Drs. J. McFarland and W. Eberle of Novartis Crop Protection assisted the authors by providing GC/EIMS spectra for metolachlor and its product.

Literature Cited

(1) Chesters, G.; Simsiman, G. V.; Levy, J.; Alhajjar, B. J.; Fathulla, R. N.; Harkin, J. M. *Rev. Environ. Contam. Toxicol.* **1989**, *110*, 1−74.
(2) *Open-File Rep.—U.S. Geol. Surv.* **1994**, *No. 94−44.*
(3) Sharp, D. B. Alachlor. In *Herbicides: Chemistry, Degradation, and Mode of Action*; Kearney, P. C., Kaufman, D. D., Eds.; Marcel Dekker: New York, 1988; pp 301−333.
(4) Lebaron, H. M.; McFarland, J. E.; Simoneaux, B. J.; Ebert, E. Metolachlor. In *Herbicides: Chemistry, Degradation, and Mode of Action*; Kearney, P. C., Kaufman, D. D., Eds.; Marcel Dekker: New York, 1988; pp 335−382.
(5) Potter, T. L.; Carpenter, T. L. *Environ. Sci. Technol.* **1995**, *29*, 1557−1563.
(6) Wilson, E. K. *Chem. Eng. News* **1995**, *73* (27), 19−22.

(7) Gillham, R. W.; O'Hannesin, S. F. *Ground Water* **1994**, *32*, 958–967.
(8) Johnson, T. L.; Scherer, M. M.; Tratnyek, P. G. *Environ. Sci. Technol.* **1996**, *30*, 2634–2640.
(9) Powell, R. M.; Puls, R. W.; Hightower, S. K.; Sabatini, D. A. *Environ. Sci. Technol.* **1995**, *29*, 1913–1922.
(10) Del Cul, G. D.; Bostick, W. D.; Trotter, D. R.; Osborne, P. E. *Sep. Sci. Technol.* **1993**, *28* (1–3), 551–564.
(11) Davenport, D. T. Degradation and Sorption of Select Triazine, Analide and Carboxylic Acid Herbicides Using Zero Valent Iron. M.S. Thesis, Department of Civil and Environ. Engineering, University of Wisconsin—Madison, 1996.
(12) Wisconsin Department of Agriculture, Trade and Consumer Protection, *Report on Wisconsin Mixing and Loading Site Study* Wisc. DATCP: Madison, WI, 1991, 8 pp.
(13) Magiapan, S.; Benefenati, E.; Grasso, P.; Terreni, M.; Pregnolato, M.; Pagani, G.; Barcelo, D. *Environ. Sci. Technol.* **1997**, *31*, 3637–3646.
(14) Eberle, W. Personal communication June 19, 1997.
(15) van Genuchten, M. Th.; Wagenet, R. J. *Soil Sci. Soc. Am. J.* **1989**, 53, 1303–1310.
(16) Torrents, A.; Anderson, B. G.; Bilboulian, S.; Johnson, W. E.; Hapeman, C. J. *Environ. Sci. Technol.* **1997**, *31*, 1476–1482.
(17) Orth, W. S.; Gillham, R. W. *Environ. Sci. Technol.* **1996**, *30*, 66–71.
(18) Müller, M. D.; Buser, H. *Environ. Sci. Technol.* **1995**, *29*, 2031–2037.

Received for review August 1, 1997. Revised manuscript received January 26, 1998. Accepted February 17, 1998.

ES970678N