

This Errata Sheet describes the deviations from the original report documentation that was originally funded in 1995. Upon converting the original final report file, equations and figures were lost and unable to be recovered. The missing parts are listed as follows:

p. 5: equation

p. 15: Figure 1, Figure 2, and Figure 3

p. 17: Figure 4 and Figure 5,

p. 18: Figure 6, and Figure 7

p. 20: equation

p. 21: Table 3

**IRON-BASED ABIOTIC DESTRUCTION OF  
CHLORINATED SOLVENTS AND PESTICIDES**

**Gerald R. Eykholt**

1996

# **Iron-Based Abiotic Destruction of Chlorinated Solvents and Pesticides**

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## **Final Report**

### **Iron-based abiotic destruction of chlorinated solvents and pesticides**

Pesticide Research Contract #95-05  
UW Research Project 133-Z977

for

Wisconsin Department of Agriculture,  
Trade, and Consumer Protection

over the period  
July 1, 1995 - June 30, 1996

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## A. Introduction and Project Description

From July 1, 1995, to June 30, 1996, Prof. Eykholt and his graduate students, Doug Davenport, Greg Lowry, and Chris Sosnowski, evaluated the reactions of chlorinated herbicides with granular cast-iron metal. The central purpose was to screen one grade of iron with waters containing chlorinated solvents, pesticides, and herbicides to find evidence of reductive dechlorination reactions. If loss could be attributed to dechlorination, the effective reaction rates and rate kinetics would be determined. The original project goal was to perform batch and column tests with spiked site groundwater.

Reactive barrier technology has been applied to remove and contain chlorinated solvents, such as TCE, but there is evidence that other compounds, such as nitroaromatic compounds and the pesticide dichlorobromopentane (DCBP) can also be reduced upon contact with granular iron metal. Most of the reactions inferred are first-order with respect to the contaminant. In the simple analysis, the effectiveness of the iron reactive barrier can be described by plug-flow, first-order conversion:

where  $C$  and  $C_0$  are the effluent and influent concentration,  $k$  is the operative first-order rate constant, and  $\tau$  is the average retention time for fluid within the reactive barrier. The conversion will be higher for higher values of  $k\tau$ .

This project has determined that two of the six compounds screened, the analides Alachlor (Lasso™) and Metolachlor (Dual™), both undergo relatively fast reductive dechlorination when exposed to granular iron. In batches with 113mL solution and 40g granular iron, the degradation reaction rate constants were 0.19 hr<sup>-1</sup> for Alachlor and 0.09 hr<sup>-1</sup> for Metolachlor. Values were corrected for sorption and good chloride mass balances were obtained. With use of fairly straight-forward scaling relationships, we estimate that a 100-fold conversion of Alachlor could be obtained in an iron reactive barrier with a retention time less than 50 hr. For a groundwater velocity of 1.0 ft/day, the barrier length would need to be approx. 2.0 ft. in length (and only 2.7 ft. for 1000-fold conversion).

These preliminary assessments mean that Alachlor and Metolachlor could be treated effectively by in situ reactive barriers or other engineered systems. Further study on these systems and contaminated sites should be performed to investigate potential cost savings over conventional treatment strategies. These results may have important implications for Alachlor and Metolachlor fate in iron-rich natural environments, as well.

The other compounds studied were the s-Triazines, Atrazine and Cyanazine, and the carboxylic acids, Dicamba and 2,4-dichlorophenoxyacetic acid. No evidence of dechlorination was observed for these compounds. Sorption of the s-Triazines was moderate, but minor for the carboxylic acid herbicides. Dechlorination for these compounds under iron-reducing conditions is not likely, since the chlorine is positioned on the benzene ring.

The goal of this report is to summarize the key findings of this Pesticide Research Project. Full detail of the literature review, experimental and analytical work has been reported within the M.S. Thesis of Mr. Doug Davenport (1996). This thesis has been submitted with this report, and electronic copies can also be obtained from Prof. Eykholt.

The six tasks of the proposed study and completed work were:

Task 1. Perform informal survey of key compounds of interest and suitable sampling sites. Screen a variety of chlorinated solvents and pesticides. From informal phone interviews of DNR and DATCP personnel, narrow lists down to the chlorinated solvents and pesticides which pose the greatest problems to remedial actions. At least three chlorinated solvents will be screened from the list of chlorinated ethenes (PCE, TCE, DCE), chlorinated ethanes, chlorinated methanes (CT, DCM), and others. At least four pesticides will be screened from the list of 2,4-dichlorophenol (2,4-D), 1,2-dichloropropane, Alachlor (Lasso™), Metolachlor (Dual™), Atrazine, and others.

Action:After early discussions with Mr. Jeffrey Postle of DATCP, the study was narrowed to the common, chlorinated herbicides Alachlor, Metolachlor, Atrazine, Cyanazine, 2,4-D, and Dicamba. These compounds were quite different in nature than the chlorinated pesticides and solvents that were in the proposed study, so the analytical and literature review strategies were modified. Groundwater matrix and column testing tasks (Tasks 3, 4, and 5) were not completed due to analytical difficulties associated with earlier tasks. However, additional work was provided to investigate the fate of Metolachlor and Alachlor more thoroughly.

Task 2. Perform batch screening tests of iron reduction chemistry for targeted compounds. Batch kinetic tests on lab-spiked water and iron mixtures will be performed to investigate the rates of depletion of the target compounds. At first, a simple assessment of compound loss will be used to infer a rate of dechlorination – and only the compound of interest will be monitored. This information will be used to scale more precise batches and to gain information while methods are developed and standardization is achieved. For these more precise batches, mass balances with respect to chloride and total organics will be assessed. At least three chlorinated solvents and more than four pesticide compounds will be tested.

Action:Thorough screening of the six herbicides were made. However, the detection limits of the GC/FID-based methods were high (generally MDL > 0.5 mg/L). Methods using solid phase extraction cartridges were generally unsuccessful. UV spectrophotometry was used to evaluate 2,4-D and Dicamba (after a derivatization procedure was found to be difficult). UV spectra of aqueous solutions of 2,4-D and Dicamba showed no changes, while significant differences were found for the other four compounds. Atrazine and Cyanazine were shown to adsorb onto the iron, without significant evidence of dechlorination.

Several batches were performed for Alachlor and Metolachlor, showing changes in the UV spectra, GC/FID chromatographs, and chloride levels. Some of the key results are shown in this report, but full detail was provided by Davenport (1996).

Task 3. Obtain groundwater samples. At least two sites from which both contaminated and "clean" groundwater samples can be obtained will be identified from initial interviews.

Task 4. Perform batch reactions in groundwater matrix. This task will be performed to investigate the role of groundwater chemistry on the effectiveness of the reactions. Possible impacts include carbonate levels, pH, dissolved oxygen, and ions or compounds which will precipitate or co-precipitate with iron. Another purpose of this testing is to evaluate the reaction chemistry in specific groundwaters.

Action: No action was taken on Tasks 3 and 4, due to the significant changes in the list of compounds to be studied. For instance, the proposal relied, to a certain extent, on the ability to extend recent work with iron and chlorinated solvents. The difficulties associated with herbicide analyses were more significant than anticipated, so the groundwater screening tests were not performed. The promising results regarding Alachlor and Metolachlor dechlorination were not identified until late in the study.

Task 5. Perform column testing of chlorinated solvent "cocktail", spiked into specific groundwater. A cocktail of the three or more chlorinated solvents will be spiked into "clean" groundwater and pumped through columns packed with coarse iron filings.

Action: No action was taken. After there was good indication of reductive dechlorination of Alachlor and Metolachlor, a decision was made to provide more conclusive batch results. For instance, ion chromatography and GC/MS work were used to demonstrate good chloride balance relative to controls and MS evidence of compound transformation and dechlorination. Another reason for this decision was that several other reactive iron studies by Prof. Eykholt and others have shown good scaling relationships between batch and column conversions. These scaling predictions, based on iron surface area per unit volume, were reasonably consistent with batch and column experimental results with iron and TCE (Lowry 1996).

Task 6. Report findings. The findings of this research will be summarized in a final report, as well as a seminar presentation. Key trends in the reactivity of the chlorinated solvents and pesticides will be discussed. Recommendations for future work, and the implications of the results for in situ installations will be shared.

Action: This task was completed, with the major conclusions and recommendations summarized in this report, described in detail in an M.S. Thesis (Davenport, 1996), and presented in a seminar presented by Doug Davenport at the University of Wisconsin - Madison. Mr. Davenport and/or Prof. Eykholt will provide another oral presentation to DATCP personnel, upon request.

## B. Description of Completed Work

A description of the completed work will be discussed with references to the M.S. thesis of Davenport (1996), with summaries of the work involved for each chapter:



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Chapter	1.	Introduction
study		<ul style="list-style-type: none"> <li>- Review of EPA National Pesticide Survey</li> <li>- Compound descriptions and chemical behavior of herbicides of this study</li> <li>- Review of environmental regulation and risk considerations for compounds of this study</li> </ul>
Chapter	2.	Passive Treatment of Ground Water Using Reaction Walls
		Literature review of remediation concept, system size, desired and hydraulic characteristics, and reactive barrier pilot tests.
Chapter	3.	Discussion of the proposed reaction mechanism
		Review of iron-based reductive dechlorination, with discussion and evaluation of reduction potentials of chlorinated herbicides.
Chapter	4.	Analytical and experimental methods

Detail of analytical method development for gas chromatography, extraction methods, error analysis, and spectrophotometry. GC work was delayed several months due to heavy research use, ordering delays, and student training. Approx. 16 various extraction methods were tested in order to refine the herbicide analysis by GC/FID.

GC analysis of carboxylic acid herbicides Dicamba and 2,4-D was attempted using esterification by BSA, but this method resulted in a severe amount of interference. Instead, a spectrophotometric method was performed to evaluate any losses of these compounds.

Five series of sacrificial batch tests at room temperature were performed to identify whether sorption or conversion were notable. The sequence of tests performed can be described as follows:

Batch conditions A: Solutions contained approx. 10 mg/L each of Alachlor, Metolachlor, Atrazine, and Cyanazine. 100 mL serum vials with 40.0g VWR coarse iron filings. 5-day testing. Compound detection by GC/FID.

Batch conditions B: Solutions contained either 10 mg/L of Dicamba or 2,4-D. 100 mL serum vials with 40.0g VWR coarse iron filings. 5-day testing. Low rpm mixing. Compound detection by spectrophotometry (UV @ 220 nm and UV spectra).

Batch conditions C: Solutions contained varying amounts herbicide mixtures. 100 mL serum vials with 40.0g VWR coarse iron filings. Sacrificial sampling. Acetonitrile extraction of iron. Compound detection by UV spectrophotometry and/or GC/FID.

Expt. 1 Batch conditions A, sacrificial sampling, high rpm mixing, poor mass balances.

Expt. 2 same conditions as Expt. 1, with much lower mixing rpm, better mass balances. Solid phase and aqueous phase concentrations were determined.

Expt. 3 Batch conditions B. Aqueous phase concentrations were determined and were constant over 5 days.

Expt. 4a Batch conditions C. Atrazine/Cyanazine mixtures at 0, 1, 3, 7, and 10 mg/L each to determine sorption isotherms at 42 hours.

Expt. 4b Batch conditions C. Individual batch tests of 10 mg/L solutions of Alachlor or Metolachlor. Sacrificial sampling at 0, 1, 29, 74, and 123 hours. Poor GC sensitivity/ detection of herbicides in aqueous samples. Spectrophotometry on aqueous and extract solutions used to demonstrate conversion.

Expt. 4c Batch conditions C. Dicamba or 2,4-D at 10 mg/L. Aqueous and Acetonitrile extracts of iron were tested at 0, 1, 29, 74, and 123 hours. UV spectra analysis only.

Expt. 5 Batch conditions C. Alachlor or Metolachlor at 100 mg/L. Iron was prewashed with potassium nitrate to remove residual chloride. Sacrificial batches taken at 1 and 124 hours. Aqueous and acetone extracts of iron were tested by GC/FID and later by GC/MS. Chloride was measured by ion chromatography.

#### Chapter 4. Analytical and experimental methods (continued)

Methods of data analyses and modeling of rate-limited sorption and first-order decay were discussed. Analytical models were derived and fitted to determine effective reaction and sorption mass transfer constants for the Alachlor and Metolachlor systems. A full derivation of the analytical model was presented in an appendix.

#### Chapter 5. Discussion of batch test results

Experimental results from experiments 1-5 and analytical modeling were discussed. The key findings will be summarized in section C of this report, but full detail is provided in the thesis. GC/MS results were discussed in an appendix.

## Chapter 6. Engineering implications of the experimental findings

The effective sorption of Atrazine and Cyanazine and the effective sorption and transformation of Alachlor and Metolachlor within in situ iron barriers were estimated in order to reflect the engineering implications of the batch test results. Key findings from this section will also be discussed in section C of this report.

## Chapter 7. Summary, Conclusions and Recommendations

A summary of the predicted and observed behavior of the six herbicides with zero-valent iron was prepared, and the fate of each compound was summarized. Recommendations were made regarding future herbicide study, analytical method improvements, column studies, possible treatment enhancements, and natural system effects.

The research study involved the PI (Prof. Eykholt), the principal graduate research assistant (Doug Davenport), two other graduate research assistants (Lowry and Sosnowski), and a lab manager/chemist (Mr. Paul Fritschel). The time load and tasks were divided as follows:

Individual	Task	# of Hours (est.)
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Jerry Eykholt (PI)		
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Project management, QA/QC, instruction, data analyses, UV spectrophotometry, reporting, budget		
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240		
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Doug Davenport (RA)		
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Lab analysis, literature reviews, data reduction, GC/FID analyses, batch kinetic testing, reporting		
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1200		
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Greg Lowry, Chris Sosnowski (RA's)		
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Ion and gas chromatography training and support.		
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60 each		
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Prof. Bill Hickey		
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GC/MS analysis		
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10		
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Paul Fritschel (lab manager/ chemist)		
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Gas chromatography training, maintenance, and support. Ordering and QA/QC.		
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40		
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The salaries of Davenport, Lowry, and Sosnowski were supported through this project, but those of Eykholt, Hickey, and Fritschel were not.

## C. Major Conclusions of Project

### Summary

1. This project has determined that two of the six compounds screened, the analide herbicides Alachlor (Lasso™) and Metolachlor (Dual™), both undergo relatively fast reductive dechlorination when exposed to granular iron. In batches with 113mL solution and 40g granular iron, the degradation reaction rate constants were 0.19 hr<sup>-1</sup> for Alachlor and 0.09 hr<sup>-1</sup> for Metolachlor. Values were corrected for sorption and good chloride mass balances were obtained. With use of fairly straight-forward scaling relationships, we estimate that a 100-fold conversion of Alachlor could be obtained in an iron reactive barrier with a retention time less than 50 hr. For a groundwater velocity of 1.0 ft/day, the barrier length would need to be approx. 2.0 ft. in length (and only 2.7 ft. for 1000-fold conversion).

2. There was no evidence for iron-promoted dechlorination or transformation of the s-Triazines (Atrazine and Cyanazine) or the carboxylic acid herbicides (Dicamba and 2,4-D) in this study. In addition, very little sorption was observed for the carboxylic acid herbicides.

3. Sorption isotherms for Atrazine and Cyanazine were linear, with  $K_{id}$  of 1.56 g/mL and 1.42 g/mL, respectively. For a typical reactive iron barrier with a porosity of 0.60 and bulk density of 4 g/mL iron, the calculated retardation coefficients ( $R_d$ ) for Atrazine and Cyanazine were 11.4 and 10.5, respectively. Thus, only moderate sorption should be expected in field applications.

The rationale of these results is expressed in terms of predicted and observed behavior, and is summarized in Table 1.

Table 1. Summary of predicted and observed behaviors in experiments

Herbicide Group	Predicted Behavior	Observed Behavior
Analides: Alachlor, Metolachlor	Reduction of C=O group possible, dechlorination possible if Cl distance from benzene ring is sufficient to allow nucleophilic attack.	Mass balance suggests conversion is occurring; individual byproducts detected by GC/FID. Changes in absorbance spectra in reacted aqueous samples are apparent. Chloride analysis shows Cl <sup>-</sup> accumulation proportional (on a molar basis) to compound reduction.
s-Triazines: Atrazine, Cyanazine	Reduction or dechlorination highly unlikely due to location of Cl on benzene ring.	Mass balance shows conversion to be unlikely, sorption appears linear and consistent.
Carboxylic Acids:	Reduction of carboxyl group	Spectrophotometry shows aqueous

Dicamba 2,4-D	possible, dechlorination highly unlikely due to location of Cl on benzene ring.	concentrations to remain constant over time. Absorbance profiles were of similar magnitude and shape for all aqueous samples.
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Specific behavior of herbicide compounds tested in this study are summarized below. The section is organized by herbicide group, and includes results from experiments which produced the most reliable information.

#### Analide Herbicides: Alachlor and Metolachlor

Alachlor and Metolachlor solutions (ca. 10 ppm) exposed to granular iron in sacrificial batch reactors showed significant degradation over a period of 5 days. All experiments conducted with the compounds ended with concentrations near or below the detection limit, including a test with concentrations in excess of 100 ug/mL. Analysis of iron rinsate samples in acetone showed that sorbed phase concentrations increased, then decreased in response to a decrease in aqueous concentration.

Chloride analytical data performed on aqueous samples suggest strongly that the reaction byproducts are dechlorinated forms of their parent compounds. Aqueous samples analyzed via GC/MS showed that the principal ions associated with the byproducts were not chlorinated. The data presented in this study suggest that Alachlor and Metolachlor, and likely all other similar compounds in the Analide family, may be dechlorinated using granular iron.

#### Alachlor and Metolachlor: Evidence of dechlorination.

Spectrophotometric analysis of aqueous and iron rinsate samples suggest that conversion did occur for Alachlor and Metolachlor, characterized by a shift in UV absorbance at about 220 nm. These results are shown in Figure 1 and Figure 2. UV absorbance spectra measured for an initial concentration of over 100 ug/mL Alachlor and Metolachlor in separate batches also showed strong evidence of conversion.

GC/FID analytical data of aqueous and iron rinsate samples showed individual degradation byproducts of Alachlor and Metolachlor appearing at retention times of 34.2 and 36.6 min., respectively. A summary series of chromatograms is shown in Figure 3. These byproducts were not fully identified. However, the retention times were not consistent with other chromatographic peaks found in the iron rinsate controls and could not be attributed to either s-Triazine herbicide. Davenport (1996, Fig 5-22) showed two other sets of chromatograms with similar behavior.

Figure 1. UV absorbance spectra ( $\lambda = 200-300$  nm) of iron rinsate samples from Alachlor sacrificial batch reactors - Experiment 4.

Figure 2. UV absorbance spectra ( $\lambda = 200-300$  nm) of iron rinsate samples from Metolachlor sacrificial batch reactors - Experiment 4.

Figure 3. Comparison of chromatograms of an analytical standard with reacted aqueous samples, aqueous blanks, and an iron rinsate blank. Herbicide cocktail standard retention times increased in the order of Atrazine (35.9 min.), Alachlor (41.7 min.), Metolachlor (44.1 min.), and Cyanazine (44.4 min.). All standard compounds were at 10 mg/L. Reacted water and rinsate blank chromatograms have been amplified 1.5x to accentuate smaller peaks.

If the transformation reactions of Alachlor and Metolachlor were from reductive dechlorination with the zero-valent iron, chloride should be produced from the reaction. In Experiment 5, chlorine was shown to be removed from Alachlor and Metolachlor and appeared as chloride in aqueous solution (in comparison to blank). The mass balances with respect to chlorine for Alachlor and Metolachlor at 124 hours were 84% and 68%, respectively. Both mass balances were determined after corrections for the initial chloride and final blank chloride levels. These mass balances are reported in Table 2. Since chloride has been found to adsorb and complex with iron compounds, the mass balances were considered to be good evidence of reductive dechlorination.

The reaction byproducts identified by GC/FID were also identified via GC/MS. Mass spectra of the byproduct peaks, shown in Appendix B of the thesis, are only partially conclusive. Analysis of the principal ions in the spectra indicate that the ions are not chlorinated. This is known by convention, wherein the abundance at the location two mass units above the principal ion is compared to the abundance at the principal ion location. A ratio of abundance of less than 1:3 indicates that the compound is not chlorinated (Davenport personal conversation with W. H. Hickey, August 8, 1996).

Table 2. Determination of chlorine mass balance: Comparison of aqueous molar concentrations of Alachlor, Metolachlor and Chloride from exposure of aqueous solutions to granular iron for 5 days (from Experiment 5).

Alachlor			
Time	Aqueous Concentration (ug/mL)	Aqueous Molar Concentration (umol/mL)	Chloride Molar Concentration (umol/L)
0	101.7	0.377	0.054
1	84.2	0.312	0.038
124	nd	nd	0.356
Metolachlor			
Time	Aqueous Concentration (ug/mL)	Aqueous Molar Concentration (umol/mL)	Chloride Molar Concentration (umol/L)
0	110.6	0.410	0.008
1	78.4	0.291	.052
124	nd	nd	.360
Reacted Blank (5 day)			.089

The mass of the principal ions (last ion on spectra) can be compared to an assumed reduction byproduct of each compound. Dechlorinated, deoxygenated and dechlorinated/ deoxygenated forms of Alachlor and Metolachlor would be seen at molecular masses as listed in Table 3. Comparison of the table to principal ion (Davenport, Fig. B-5, p. 95) suggests that the byproduct is dechlorinated Alachlor. However, the principal ion in Figure B-6 is lower in molecular weight than dechlorinated Metolachlor, but higher than dechlorinated/deoxygenated Metolachlor. Although the ion is dechlorinated, it is apparent that the byproduct remaining after 5 days of exposure to iron has undergone some further reduction in an unknown path. More work should be done to identify the specific organic products of the reaction.

Alachlor and Metolachlor: Estimation of the rate and order of dechlorination.

The batch kinetic data of Alachlor and Metolachlor were fit to a model depicting instantaneous and rate limited sorption with first-order degradation in both the solid and aqueous phases. The resulting model fits to batch data for Alachlor and Metolachlor are shown in Figures 4 and 5. There was excellent agreement with the model, showing first-order reaction kinetics at rate constants at or above 0.1 hr<sup>-1</sup> for each compound. Alachlor was sorbed more strongly, but both exhibited moderate levels of rate-limited sorption.



Figure 4. Two region sorption and first-order degradation model, Alachlor in zero-valent iron batches. Data are from experiment 2.

Figure 5. Two region sorption and first-order degradation model, Metolachlor in zero-valent iron batches. Data are from experiment 2.

Alachlor and Metolachlor: Preliminary scaling of reactive barriers.

With use of fairly straight-forward scaling relationships, we estimate that a 100-fold conversion of Alachlor could be obtained in an iron reactive barrier with a retention time less than 50 hr. For a groundwater velocity of 1.0 ft/day, the barrier length would need to be approx. 2.0 ft. in length (and only 2.7 ft. for 1000-fold conversion). These calculations have been described by Davenport (1996, p. 74ff). Further work should be done to assess the sensitivity of these rates to groundwater chemistry, temperature, and other long-term site conditions.

#### s-Triazine Herbicides

Atrazine and Cyanazine solutions (ca. 10 ppm) were exposed to granular iron in sacrificial batch reactors in several experiments. Both compounds' aqueous concentrations were reduced by exposure to iron. Analysis of iron rinsate, obtained by immersing the iron from each batch reactor in 25 mL of acetone or acetonitrile, showed that the compounds were accumulating on the iron. Comparison of cumulative mass (aqueous and iron) of each compound in batch reactors suggests that neither are being degraded by the iron. Atrazine mass balance was poor, but there is no evidence that degradation took place. Qualitative analysis of aqueous samples from batch reactors by spectrophotometry showed no evidence of changes in UV absorption spectra, other than in magnitude, over 5 days of exposure to iron.

Sorption studies yielded linear sorption isotherms for both compounds, shown in Figures 6 and 7. Linear sorption coefficients of 1.56 mL/g for Atrazine and 1.31-1.42 mL/g for Cyanazine were obtained. For a typical reactive iron barrier with a porosity of 0.60 and bulk density of 4 g/mL iron, the calculated retardation coefficients (Rd) for Atrazine and Cyanazine were 11.4 and 10.5, respectively. Thus, only moderate sorption should be expected in field applications.

Figure 6. Sorption isotherm for Atrazine onto VWR iron (40 g iron, 100 mL solution).

Figure 7. Sorption isotherm for Cyanazine onto VWR iron (40 g iron, 100 mL solution).

#### Carboxylic Acid Herbicides: Dicamba and 2,4-D

Dicamba and 2,4-D solutions (ca. 10 ppm) were exposed to granular iron in sacrificial batch reactors for up to 5 days. Analysis of water samples via spectrophotometer at 220 nm showed no reduction in apparent concentration over time. UV absorbance spectra from 200 to 300 nm show no evidence of conversion or reduction in concentration. Comparison of iron rinsate (acetonitrile) samples to an aqueous blank exposed to iron for 5 days suggest no significant accumulation of the compounds on the iron. The data suggest no significant effect by the iron on the compounds. However, the method of analysis was qualitative, and may overlook minute changes in concentration or accumulation of degradation byproducts. The data are sufficient to suggest, however, that the effect by the iron was not significant in terms of treatment in the environment.

#### D. Recommendations for Future Work

Prof. Eykholt and Mr. Davenport plan to submit a research paper or technical note on this work to a peer-reviewed journal before January, 1997. In addition, a new research proposal addressing iron-herbicide interactions will be submitted to the University Groundwater Coordinating Council by Dec. 8, 1996.

The following recommendations regarding this study were made by Davenport (1996):

**Survey of Pesticide Compounds** - The research was intended to screen classes of herbicides for their viability to be degraded with granular iron. A means by which cyclic herbicides may be evaluated for their potential to be degraded was provided, and was verified in experiments. The observations by Behar and Neta (1981, 1981a), Neta and Behar (1981) and Andrieux, et al. (1986) discussed in Chapter 3 could be applied to other families of cyclic pesticides to determine which may be most feasible for future study (see thesis for references).

**Improvement of Analytical Method** - The analytical methods of this study were sufficient to observe general degradation and sorption behavior in the batch tests. However, the detection limits are likely to be too high for precise analysis at sub-ppm concentrations. Liquid chromatography may be a more straightforward and precise analytical method for detection of herbicides. The direct extraction method applied in the experiments showed very good recovery (generally greater than 95%) based on spike additions. However, the recovery was variable, and thus was a significant source of error in the data. If higher analytical precision is desired, a solid phase extraction method with a high concentration factor (25:1 or greater) and highly reproducible recovery may need to be developed.

**GC/MS analysis of reacted aqueous samples of Alachlor and Metolachlor** provided insight as to the nature and potential chemical makeup of the reaction byproducts identified. Detailed analysis of the reaction byproducts, and identification of intermediaries, would aid researchers in understanding the overall reaction pathway taken by these compounds. Detailed research into mass spectra for all reaction byproducts would be necessary.

**Focused Column Studies** - Column tests with Alachlor and Metolachlor would provide an approximation of steady state behavior in a reactive gate system. The two region sorption and first-order degradation model used in this study may be insufficient to model the overall reaction if multiple intermediary products are identified. A thorough experimental design would include end-point sampling of reacted water, monitoring of pH and chloride (or conductivity), and sacrificial sampling of the media to verify compound concentration on the solid surface. Tests of iron preconditioning or additives would aid understanding the role of the iron surface (as opposed to iron oxides) in the fate of the compounds.

One important aspect of future studies is the consideration of groundwater conditions and matrix effects on the conversion rates and effective "lifetime" of the iron. Prof. Eykholt has directed one recent study on the flow performance of granular iron column exposed for several weeks to hard and alkaline groundwater. There was clear evidence of inorganic precipitation that would affect both reactivity with respect to chlorinated organics and the uniformity and velocity of fluid flow. Two M.S. Theses were generated from this study, and are available on request (Sosnowski 1996, Hoffman 1996).

#### Nitrate fate in iron barriers

Another aspect for future studies important to DATCP is the fate of nitrate through reactive barriers. Several column tests were performed by Hoffman (1996) and Sosnowski (1996) with groundwater of high alkalinity and hardness to evaluate the fate of nitrate in granular iron columns. The dominant reduction half-reaction is likely:

At pH 7.5-9, the  $p$  controlled by the iron system in water is approximately -8 ( $E = -0.5V$ ). The reduction reactions of nitrate to nitrite to ammonium will occur in that pH range if the  $p$  less than approximately +2 ( $E = 0.1 V$ ). Nitrate reduction to ammonium by iron mixtures in water is favored thermodynamically. Denitrification to  $N_2$  gas is not favored under these conditions, but may be enhanced by microbiological activity (Stumm and Morgan, 1996, p. 461).

In addition to four column tests performed with Milwaukee groundwater at 13 °C, one room temperature column test was performed to investigate nitrate fate. This test was fed with nitrate-spiked Madison tap water and was described by Sosnowski (1996, pp. 50ff, 83ff). Sosnowski showed that nearly 10% of the nitrate was converted to ammonium. An approximate first-order rate constant for these tests would be  $2.3 \times 10^{-3} \text{ min.}^{-1}$ , or  $0.14 \text{ hr}^{-1}$ . One should note that these rates are reported for a different grade of iron (Peerless +8-50 mesh) and for column conditions. Using this rate constant, a retention time of 33 hours would be needed to obtain a 100-fold reduction in nitrate levels.

If coupled with microbiological denitrification, reactive iron systems may be an effective means of treating high nitrate-contaminated groundwaters.

#### E. Budget and schedule

The project was funded by DATCP from July 1, 1995, to June 30, 1996. However, most of the research activity occurred during the academic year, from Sept. 1, 1995, to Aug. 30, 1996. The project expenses were within budget (\$24950), but a rebudgeting request was made on 5/28/96 and subsequently approved by Jeff Postle of Wisconsin DATCP. A summary and breakdown of project expenses is shown in Table 3.

One important impact on the budget was the change of work plan, especially regarding the compounds to be studied. The lack of experience with herbicide analyses caused a significant delay and increased analytical expenditures. Because the effort was shifted towards analytical determinations and demonstration of Alachlor and Metolachlor dechlorination reactions, travel to obtain groundwater samples became unnecessary.

Table 3. Summary and breakdown of project expenses.

Other budget deviations related to salary. Hourly staff were not used since two other RA's Lowry and Sosnowski were trained and ready to perform critical analytical tasks for the study. In addition, salary was not used for Mr. Fritschel, due to the increased need for analytical expenditures.

A copy of the final control sheet from the project is attached as an Appendix to this report.

#### F. Conclusion

A twelve-month screening study was performed to evaluate the fate of six chlorinated herbicides (Alachlor, Metolachlor, Atrazine, Cyanazine, Dicamba, and 2,4-Dichlorophenoxyacetic acid) when exposed to granular zero-valent iron. Although reaction byproducts have not been fully assessed, there was convincing evidence for relatively rapid, reductive dechlorination of Alachlor and Metolachlor by iron metal. This evidence included UV spectrophotometry, chloride analysis, GC/FID, and GC/MS analyses. The chloride and GC/MS evidence was the most significant evidence of dechlorination.

The reaction kinetics for Alachlor and Metolachlor were apparently first-order, although there was indication of rate-limited and instantaneous sorption. A two-site batch kinetic model was derived and fitted to the batch test results.

There was no evidence of significant reaction of the other four herbicides with iron. Dechlorination was ruled unlikely due to the difficulty of displacing chlorine from aromatic positions. A moderate level of sorption was found with Atrazine and Cyanazine with iron, such that a retardation coefficient of approx. 10 might be found in reactive barriers. There was no apparent sorption for Dicamba or 2,4-D.

Future work should focus on providing a more thorough assessment of the reaction chemistry of Metolachlor and Alachlor with iron metal. This work should be based on GC/MS methods. Other extensions include providing long-term column studies with actual site groundwaters and finding novel treatment schemes for sites contaminated with large quantities of Alachlor and Metolachlor. Assessments of other chlorinated herbicides, with aliphatic chlorine groups, may also prove to be successful.

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