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Vadose Zone Processes and Chemical Transport

Metolachlor Dechlorination by Zerovalent Iron during Unsaturated Transport

H. M. Gaber, S. D. Comfort,* P. J. Shea, and T. A. Machacek

ABSTRACT

Permeable zerovalent iron (Fe^0) barriers have become an established technology for remediating contaminated ground water. This same technology may be applicable for treating pesticides amenable to dehalogenation as they move downward in the vadose zone. By conducting miscible displacement experiments in the laboratory with metolachlor [2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl)acetamide; a chloroacetanilide herbicide] under unsaturated flow, we provide proof-of-concept for such an approach. Transport experiments were conducted in repacked, unsaturated soil columns attached to vacuum chambers and run under constant matrix potential (−30 kPa) and Darcy flux (approximately 2 cm d^{-1}). Treatments included soil columns equipped with and without a permeable reactive barrier (PRB) consisting of a Fe^0–sand (50:50) mixture supplemented with $Al_2(SO_4)_3$. A continuous pulse of ^{14}C-labeled metolachlor (1.45 m*M*) and tritiated water (^3H_2O) was applied to top of the columns for 10 d. Results indicated complete (100%) metolachlor destruction, with the dehalogenated product observed as the primary degradate in the leachate. Similar results were obtained with a 25:75 Fe^0–sand barrier but metolachlor destruction was not as efficient when unannealed iron was used or $Al_2(SO_4)_3$ was omitted from the barrier. A second set of transport experiments used metolachlor-contaminated soil in lieu of a ^{14}C-metolachlor pulse. Under these conditions, the iron barrier decreased metolachlor concentration in the leachate by approximately 50%. These results provide initial evidence that permeable iron barriers can effectively reduce metolachlor leaching under unsaturated flow.

Zerovalent iron (Fe^0) barriers have become an established technology for remediating ground water contaminated with halogenated hydrocarbons (Wilson, 1995). Metallic iron is an avid electron donor and its oxidation ($E_h^0 = -0.409$ V) can drive the reduction of many redox-sensitive contaminants. While oxygen is the normal electron acceptor during iron corrosion in aerobic environments, under anaerobic conditions, such as those encountered in ground water, waterlogged soils, or artificial impoundments (e.g., runoff ponds), electron transfer mediated reactions of many organic contaminants are favored. Permeable reactive barriers (PRB) are particularly attractive for in situ remediation because they provide long-term solutions with low operating costs and are less expensive than conventional cleanup methods (O'Hannesin and Gillham, 1998). Although in situ PRBs have been successfully used to remediate chlorinated solvents in ground water, less emphasis has been placed on PBR use in unsaturated soils. A natural obstacle to this practice is the accelerated aging of iron and loss of reactivity resulting from O_2 in the soil atmosphere. Despite this apparent limitation, situations could arise where soil and site characteristics (i.e., depth to ground water) would allow horizontal placement of a PRB below the source of contamination. One potential application for this approach is the numerous point sources of contamination caused by inadvertent or deliberate pesticide spills. In practice, contaminated soils would be excavated, a permeable iron barrier placed in the pit, and the soil replaced. Theoretically, as the pesticide desorbs from the soil matrix and migrates through the iron barrier it would be transformed and further degraded in the subsoil.

Pesticide spills and inadvertent discharges of agrichemicals are common occurrences on farmstead and agricultural cooperatives. In 1990, it was estimated that there were more than 14 000 agrichemical facilities in the USA that store, sell, mix, or apply pesticides and fertilizers (Norwood and Randolph, 1990, p. 7–15). Although numerous advances have been made in the construction of pesticide containment facilities, recent surveys of pesticide distributors indicate prevalent soil contamination (Minnesota Department of Agriculture, 1997). To combat this problem, researchers have attempted to devise remedial treatments for pesticide-contaminated water and soil. Numerous researchers have proposed the use of advanced oxidation processes for destroying pesticides in rinse water and soil (Tyre et al., 1991; Sun and Pignatello, 1992; Pignatello and Baehr, 1994). Few examples exist, however, where iron has been used as an abiotic reduction treatment for xenobiotic-contaminated soil (Singh et al., 1998a,b).

This study was conducted in conjunction with a larger field-scale demonstration project where contaminated soil from a metolachlor spill site was treated with zerovalent iron in large soil windrows (Comfort et al., 2001). Results from this field trial showed that metolachlor concentrations were decreased by 72 to 99% within 90 d following treatment with various combinations of Fe^0, acetic acid, and $Al_2(SO_4)_3$. Although the metolachlor concentrations were dramatically reduced, the potential for leaching from the treated soil remained, especially if the soil was returned to its original location (runoff pit). To counteract this potential problem, it was proposed that a permeable iron barrier be placed in the bottom of the excavated pit before returning the treated soil. To evaluate whether this approach would be feasi-

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Abbreviations: BTC, breakthrough curve; HPLC, high performance liquid chromatography; PRB, permeable reactive barrier.

ble, our objective was to conduct a series of soil column transport experiments to determine the capacity of Fe^0 to transform metolachlor under unsaturated flow.

MATERIALS AND METHODS

Batch Experiments

Batch experiments were initially conducted to determine the capacity of Fe^0 to transform metolachlor. Aqueous solutions of metolachlor were prepared from the commercial product Dual 8E (Syngenta, Greensboro, NC) and spiked with ^{14}C-ring labeled metolachlor (1.058×10^6 Bq mg^{-1}) to produce a final ^{14}C-metolachlor concentration of 87 Bq mL^{-1}. The initial metolachlor concentration was 0.91 m*M* as determined by comparison with high-purity standards (Syngenta). Experimental units consisted of 250-mL Erlenmeyer flasks that were filled with 100 mL of metolachlor solution, covered with parafilm, and agitated on a reciprocating shaker. The metolachlor solutions were treated with 12.5 g of annealed Fe^0 (indirectly heated under an H_2–N_2 atmosphere), with and without 0.5 g commercial-grade $Al_2(SO_4)_3$. At preselected times, multiple 1.2-mL aliquots were removed and transferred to 1.5-mL polypropylene microcentrifuge tubes, centrifuged at $13\,000 \times g$ for 10 min, and analyzed by high performance liquid chromatography (HPLC) and liquid scintillation counting (LSC). Carbon-14 in the aqueous solution was determined by mixing 1 mL of sample with 6 mL of Ultima Gold cocktail (Packard, Meriden, CT) and analyzing by LSC using a Packard 1900TR liquid scintillation counter (Packard Instrument Co., Downers Grove, IL). Concentrations of metolachlor and dechlorinated metolachlor [2′-ethyl-6′-methyl-*N*-(methoxyprop-2-yl)acetamide] were determined in the same samples using HPLC.

A second batch experiment was conducted to optimize the concentration of $Al_2(SO_4)_3$ required for efficient metolachlor destruction. In this experiment, 20 mL of metolachlor (1.45 m*M*) was treated with 2.5 g annealed or unannealed iron (Peerless Metal Powders, Detroit, MI) and between 0 and 0.5 g of commercial-grade $Al_2(SO_4)_3$. The specific surface areas of the Fe^0 sources were 0.134 m^2 g^{-1} (annealed) and 2.55 m^2 g^{-1} (unannealed) (Micromeritics, Norcross, GA). After 2 h of shaking, 1.2-mL aliquots were removed, centrifuged, and analyzed for metolachlor and dechlorinated metolachlor by HPLC.

Transport Experiments

All transport experiments were conducted in 20-cm (5-cm-diam.) Plexiglass columns (Soil Measurement Systems, Tucson, AZ) using a system similar to that described by van Genuchten and Wierenga (1986, p. 1037). Soil columns were prepared by uniformly packing washed silica sand into columns to yield a bulk density of approximately 1.5 Mg m^{-3}. The columns were equipped with two end caps secured with O-rings that fit closely inside the columns. The bottom end cap supported a porous plastic plate with an air entry pressure of 100 kPa (Soil Measurement Systems, Tucson, AZ); the top end plate secured the eluent delivery tube. Eluent was applied by a MasterFlex multichannel programmable peristaltic pump (Cole-Parmer Instruments, Vernon Hills, IL) set to deliver approximately 1.8 mL h^{-1}. Columns were attached to vacuum chambers (Soil Measurement Systems) that housed fraction collectors (Retriever II; ISCO, Lincoln, NE). The fraction collectors contained multiple glass tubes that advanced beneath the columns after collecting approximately 13 mL of effluent. A vacuum pump connected to the chambers provided a constant matrix potential.

Soil columns were wetted from the bottom and attached to the vacuum chambers set to −30 kPa. Once the initial drainage had been collected, 3 m*M* $CaCl_2$ was supplied to the top of the columns. After steady flow was established (determined by constant volume in collection tubes), the eluent was switched from 3 m*M* $CaCl_2$ to the ^{14}C metolachlor–^3H_2O pulse. Soil water content was determined by detaching and weighing the columns at the beginning and end of each experiment.

Two sets of transport experiments were conducted. The first set (designated Columns A–F, Table 1) used a constant pore water velocity to pass multiple pore volumes of a fixed solution pulse containing ^{14}C-labeled metolachlor in a 3 m*M* $CaCl_2$ matrix and spiked with ^3H_2O (specific activity: 37 MBq g^{-1}; NEN, Boston, MA). The ^3H_2O served as a water tracer for characterizing transport processes. After the metolachlor pulse had passed through the columns, the eluent solution was switched back to 3 m*M* $CaCl_2$ solution. Column effluent fractions were weighed to determine the volume collected as a function of time and pore volumes. A 1-mL subsample of each effluent fraction was mixed with 6 mL of Ultima-Gold scintillation cocktail and ^{14}C and ^3H activity determined on a Packard 1900TR liquid scintillation counter. Effluent was analyzed for metolachlor and dechlorinated metolachlor by HPLC.

Relative concentrations (C/C_o) were calculated by dividing the molar concentration of the metolachlor and dechlorinated metolachlor in the column effluent by the initial molar concentration of the ^{14}C-metolachlor pulse (C_o).

In addition to the above transport experiments, two additional column experiments were conducted (designated Columns G and H, Table 1). Columns were prepared as described above but instead of leaching metolachlor onto the top of the sand column, approximately 16 cm of contaminated soil from a metolachlor spill site (Comfort et al., 2001) was packed at

Table 1. Soil physical properties and experimental parameters of soil column experiments.

	Sand columns						Contaminated soil columns	
Column transport properties	Column A	Column B	Column C	Column D	Column E	Column F	Column G	Column H
Soil water content†, cm^3 cm^{-3}	0.25	0.19	0.22	0.21	0.29	0.28	0.38	0.31
Bulk density†, g cm^{-3}	1.27	1.92	1.49	1.49	1.50	1.49	1.27	1.37
Darcy flux, cm d^{-1}	2.34	2.12	2.34	2.23	2.12	2.28	1.73	1.61
Column length, cm	16	16	12	12	12	12	15.5	15.5
Pore volume, cm^3	77	58	51	50	68	65	145	124
Iron source‡	none	A	A	A	U	U	none	U
Barrier composition, % Fe–sand	NA§	50:50	25:75	25:75	25:75	25:75	NA	25:75
$Al_2(SO_4)_3$ addition¶	no	yes	no	yes	no	yes	no	yes
Metolachlor pulse concentration, m*M*	1.45	1.45	1.34	1.34	1.34	1.34	NA	NA

† Soil water content and bulk density include iron barrier (in Columns B–F and H).
‡ A, annealed; U, unannealed.
§ Not applicable.
¶ $Al_2(SO_4)_3$ was added as a percentage of the iron mass in the barrier (4% w/w).

a bulk density of 1.2 Mg m^{-3} on top of the iron barrier and ^3H_2O in a 3 m*M* $CaCl_2$ matrix was applied at the desired Darcy flux. Effluent was analyzed for metolachlor, dechlorinated metolachlor, and ^3H_2O.

Chemical Analysis

Metolachlor and dechlorinated metolachlor analyses were performed with HPLC by injecting 20 μL of sample into a 4.6- by 250-mm Keystone Betasil NA column (Keystone Scientific, Bellefonte, PA) connected to a Shimadzu (Kyoto, Japan) UV detector or photodiode array detector. The mobile phase was 50:50 CH_3CN–water at 1 mL min^{-1}, with quantification at 220 nm. Under these conditions, typical retention times were 12 min for metolachlor and 8 min for the dechlorinated metolachlor. The dechlorinated metolachlor product in the column leachate was confirmed by comparing UV scans (190–250 nm) and retention times with those of the dechlorinated metolachlor standard (Syngenta).

RESULTS

Batch Studies

Batch experiments using Fe^0–metolachlor suspensions were initially conducted to determine destruction kinetics and degradation products. Temporal changes in metolachlor concentration and ^{14}C activity indicated that two mechanisms were probably operative when the annealed iron was used alone. Initial loss of metolachlor mimicked loss of ^{14}C activity, indicating that adsorption to the iron surface was the primary mechanism. After 24 h, the solution became black due to the formation of magnetite (Fe_3O_4) and temporal changes in metolachlor concentration decreased beyond what could be explained by adsorption alone (^{14}C data). This observation, coupled with the release of Cl^-, indicated that dechlorination was responsible for loss of metolachlor after 24 h (Fig. 1).

When $Al_2(SO_4)_3$ was added with Fe^0, the pH quickly dropped below 6 and a rapid stoichiometric recovery of Cl^- was observed (Fig. 1). Because less ^{14}C was also lost from solution when $Al_2(SO_4)_3$ was included, dechlorination appears to be the main mechanism responsible for metolachlor loss. Reasons for enhanced metolachlor destruction by augmenting Fe^0 with $Al_2(SO_4)_3$ are probably related to the lower pH and its influence on iron oxide formation. As reported in Comfort et al. (2001), we observed that $Al_2(SO_4)_3$ addition during Fe^0 corrosion facilitated Fe(II) release and favored green rust formation. Green rusts are double-layered $Fe(OH)_2$ sheets that contain varying amounts of Fe(III) and interlayers of anions and water molecules (Loyaux-Lawniczak et al., 2000). Green rusts typically form at near-neutral pH and are unlikely to quickly form in highly acidic environments (Taylor, 1980). In a related pH-stat study using Fe^0 and small additions of $Al_2(SO_4)_3$ and $FeSO_4$, we observed more rapid metolachlor loss at pH 5 than at pH 4 or 3 (data not shown). Consequently,

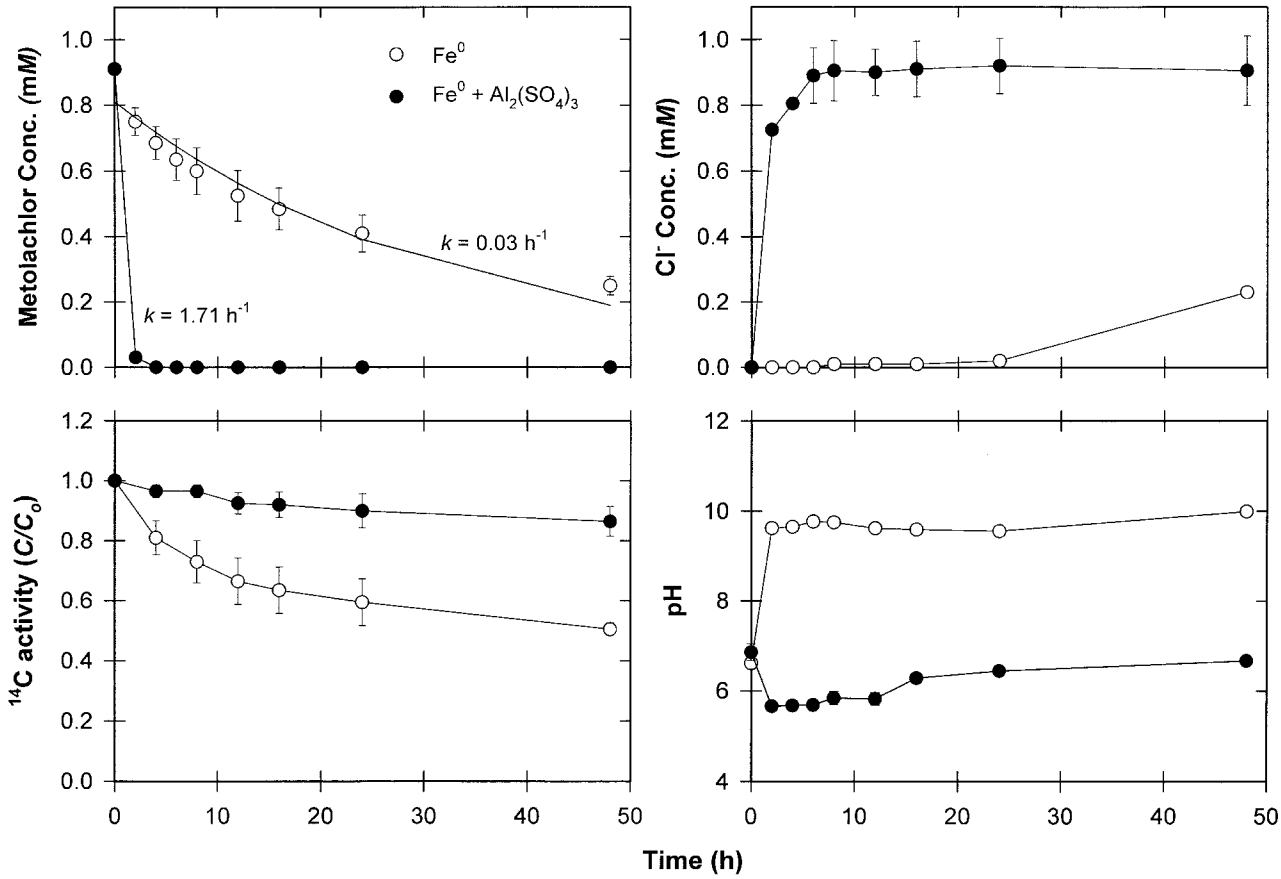

Fig. 1. Changes in metolachlor concentration, ^{14}C activity, pH, and production of Cl^- following the addition of Fe^0 and Fe^0 + $Al_2(SO_4)_3$ under batch conditions. Bars on symbols represent sample standard deviations; where absent, bars fall within symbols.

we believe that the facilitating effect of $Al_2(SO_4)_3$ is related to Fe(II) release and the nature of oxide coatings formed and not solely the result of a more acidic pH.

Efforts were made to optimize the concentration of $Al_2(SO_4)_3$ needed for efficient metolachlor destruction in the iron barrier. By varying $Al_2(SO_4)_3$ concentration and holding the mass of Fe^0 constant, we found that the optimum percentage of $Al_2(SO_4)_3$ for metolachlor destruction was between 1 and 4% (w/w) of the Fe^0 weight (Fig. 2). At 1 and 2% $Al_2(SO_4)_3$, we observed a near stoichiometric recovery of dechlorinated metolachlor. At 4% $Al_2(SO_4)_3$, metolachlor was completely removed from solution but the concentration of the dechlorinated product did not account for a complete mass balance, indicating that either further transformation of the dechlorinated product had occurred, and/or adsorption of the dechlorinated products was occurring at the higher $Al_2(SO_4)_3$ concentrations.

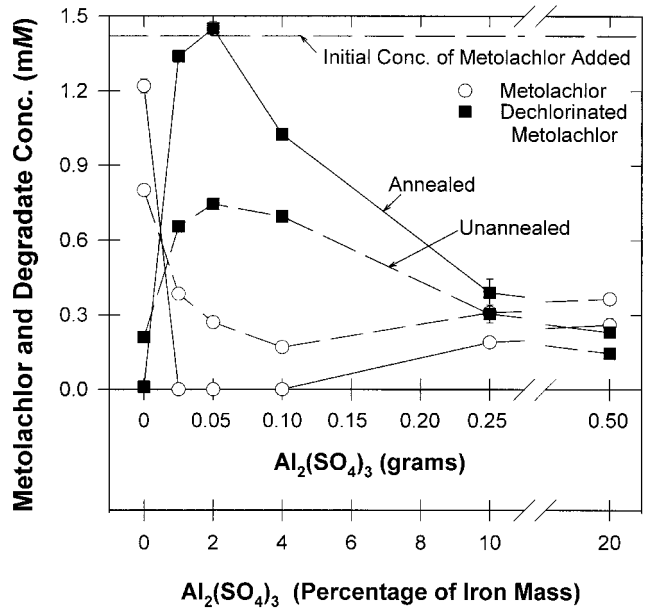

Fig. 2. Changes in metolachlor concentration and production of dechlorinated metolachlor following 2 h of treatment with various Fe^0 to $Al_2(SO_4)_3$ ratios under batch conditions. Bars on symbols represent sample standard deviations; where absent, bars fall within symbols.

Transport Experiments

When a 50:50 Fe^0–sand barrier was placed in the column, considerable differences in water and metolachlor transport were observed. Without the barrier, ^3H_2O transport essentially exhibited plug-type flow (minimal dispersion) (Column A, Fig. 3). With the barrier, some early and late arrival of ^3H_2O was noted, indicating that the barrier caused some deviation from plug-type flow due to differences in texture, dispersion, and H_2 production within the barrier (Fig. 3).

In the control column (no barrier), metolachlor and ^{14}C breakthrough curves (BTCs) were nearly identical, whereas the dechlorinated product and ^{14}C BTC were superimposed in the eluent of the column containing the 50:50 Fe^0–sand barrier. These results indicate complete (100%) metolachlor dechlorination in the PRB and show that the dechlorinated product was the primary degradate in the leachate (Fig. 3). Dechlorination was confirmed by the matching retention times and the UV spectrum of the column leachate with an authentic dechlorinated standard (inset, Fig. 3). Eykholt and Davenport (1998) studied the Fe^0–mediated dechlorination of the chloroacetanilide herbicides alachlor [2-chloro-2′,6′-diethyl-*N*-(methoxymethyl)acetanilide] and metolachlor. They found that Fe^0 was effective in transforming both compounds; terminal products after 5 d consisted of chloride (84% recovery for alachlor and a 68% recovery for metolachlor) and the dechlorinated acetanilides. Our observations demonstrate that Fe^0–mediated dechlorination of metolachlor, previously observed in stirred batch reactors, can also occur during unsaturated transport.

Transport experiments using a 25:75 Fe^0–sand barrier revealed results similar to the 50:50 Fe^0–sand barrier (Fig. 4). In general, less backside tailing of ^3H_2O was observed, indicating that the higher sand content of the 25:75 Fe^0–sand barrier resulted in less altering of water flow (Fig. 4). Both annealed and unannealed iron sources effectively reduced the concentration of metolachlor leaching through the columns but considerably more ^{14}C was retained in the unannealed barrier. The importance of $Al_2(SO_4)_3$ in the barrier was readily apparent in these experiments (Columns C vs. D, E vs. F, Fig. 4). Less metolachlor leaching occurred and more dechlorinated metolachlor was produced when $Al_2(SO_4)_3$ was added. Iron source was also important. More ^{14}C was adsorbed by the unannealed iron than the annealed iron and less metolachlor leached through the barriers containing annealed iron [with and without $Al_2(SO_4)_3$] than in those with unannealed iron (Fig. 4). Annealing is a manufacturing process that indirectly heats the iron under a hydrogen–nitrogen atmosphere. Raman spectroscopy of the two iron sources used in this study revealed that the annealed iron was largely coated with a thin layer of magnetite whereas the coating of unannealed iron was mostly hematite, maghemite, and magnetite. Similar observations have been reported by Odziemkowski and Gillham (1997). Spectra differences in the oxide and carbon regions for the two types of iron used in this study, however, indicate that annealed and unannealed iron probably came from different sources. That is, the annealed iron was not simply a heat-treated unannealed iron. Regardless, differences in oxide coatings between the iron sources distinctly influenced retention (Fig. 4) and corrosion rates. When submerged in water and left open to the atmosphere for several months, we observed that annealed iron was much more resistant to rusting, maintained a lower dissolved O_2 concentration in the water, and generated considerably more H_2 gas bubbles at the iron surface. In contrast, the iron–water interface of the unannealed iron was passivated within a few days. Based on these visual observations and results from the miscible displacement experiments, the magnetite-coated annealed iron may be preferred for vadose zone applications.

Subsequent transport experiments used metolachlor-contaminated soil (instead of the ^{14}C-metolachlor pulse)

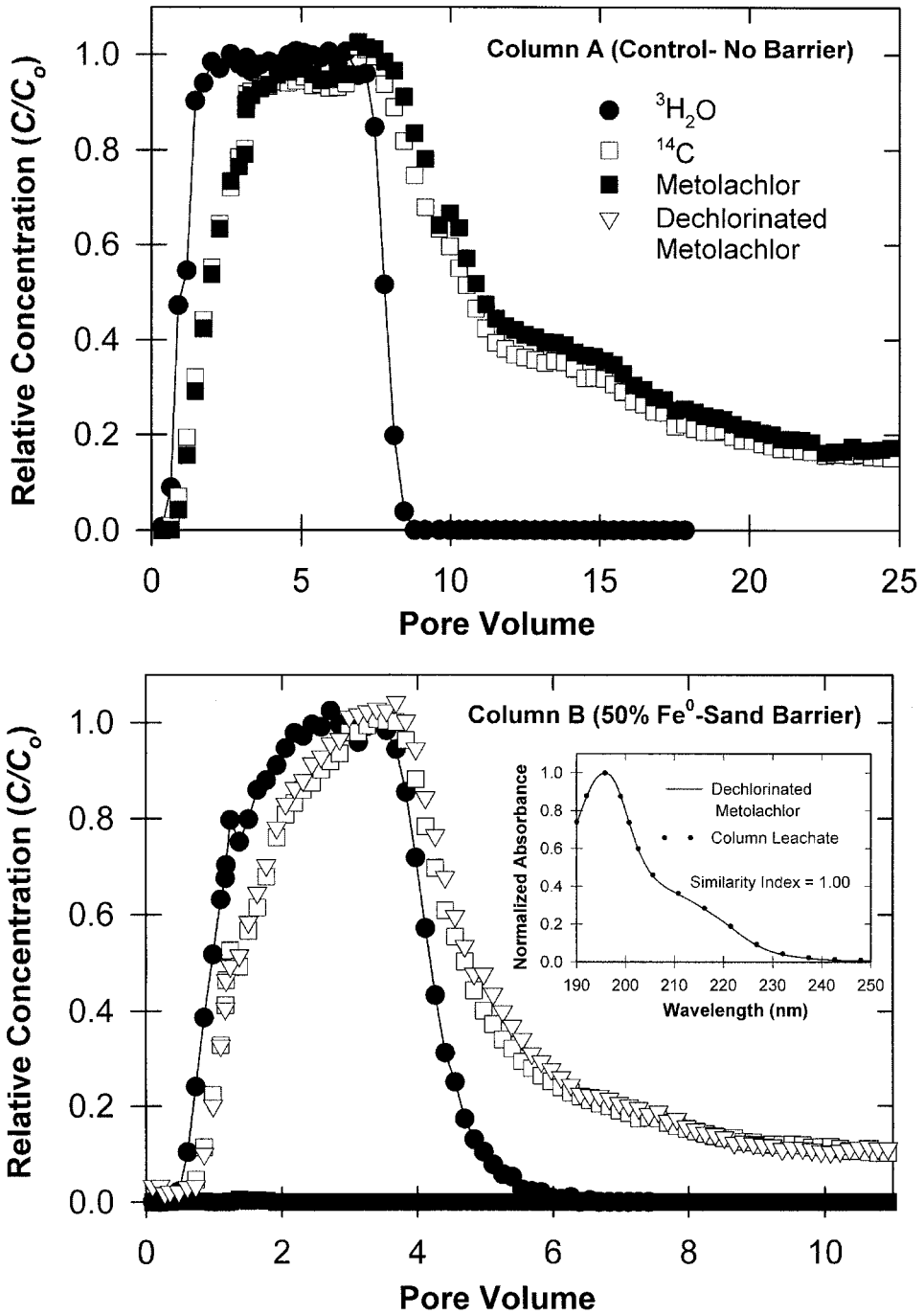

Fig. 3. Metolachlor breakthrough curves (BTCs) during unsaturated transport through soil columns assembled with and without 50:50 iron [Fe^0 + $Al_2(SO_4)_3$]–sand barriers.

from a metolachlor spill site in southwestern Nebraska. Results indicated that the unannealed iron barrier was effective in decreasing metolachlor concentration in the leachate by approximately 50% compared with the untreated contaminated soil (Fig. 5). It is noteworthy that under our experimental conditions, the resident time of the solute in the barrier was <0.5 d and that longer times would probably occur in the field and result in more efficient destruction. This would ultimately depend upon the thickness of the iron barrier and pore water velocity.

DISCUSSION

The high cost of some soil remedial treatments has kept some chemical dealers and end-users from revealing spills that may be point sources of ground and surface water contamination. Incineration costs for contaminated soil can range from \$261 to \$1961 per m^3 of soil (USEPA, 1990). These high costs have motivated researchers to seek straightforward and low-cost approaches to handling point sources of pesticide contamination. For PRB to be effective in the vadose zone,

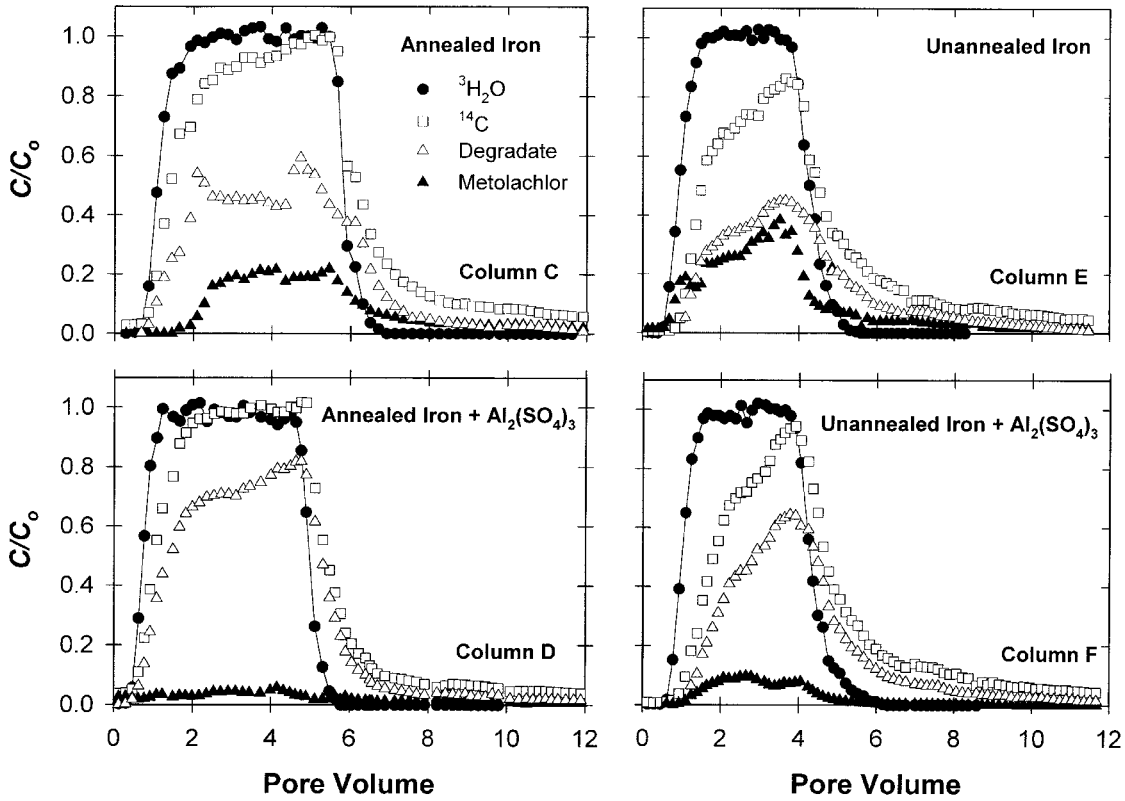

Fig. 4. The effects of $Al_2(SO_4)_3$ and iron source on metolachlor breakthrough curves (BTCs) during unsaturated transport through soil columns assembled with 25:75 iron–sand barriers.

several criteria must be met. The barrier must react with the target contaminants and not produce toxic effluent. Our current work demonstrates that Fe^0–sand barriers can dechlorinate metolachlor under unsaturated flow, while previous work demonstrated that Fe^0–treated metolachlor is more biodegradable than the parent compound (Comfort et al., 2001). It is noteworthy that the metolachlor degradate observed in our experiments has been reported to occur naturally as a result of abiotic degradation in soil and sediment under anaerobic conditions (Chesters et al., 1989).

Potential drawbacks of the 50:50 barrier are the relatively high concentration of iron used and its associated costs. In addition, the potential change in hydraulic conductivity of the barrier with time could cause application problems. After the transport experiments were terminated and the columns dismantled, the barrier had solidified from corrosion of the iron. Similarly, Mackenzie et al. (1999) described a section of their iron column, which was run under saturated conditions, as hardened solid masses cemented together with ferric oxyhydroxides. Therefore, even though our barrier was highly effective in dechlorinating metolachlor under unsaturated flow, the ability of the barrier to conduct water under natural drainage needs to be evaluated. It is likely that construction of the PRB would require engineering to facilitate solute transport through the barrier with time. This may be accomplished by using more sand in the barrier or perhaps by configuring the barrier to minimize horizontal water movement (i.e., vertical barriers or cone of depression).

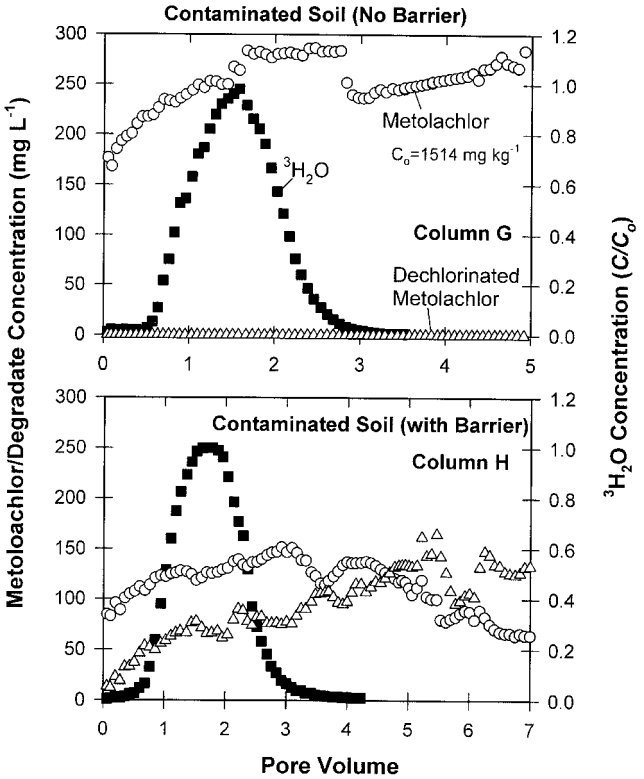

Fig. 5. Metolachlor and dechlorinated metolachlor breakthrough curves (BTCs) eluted from columns containing 25:75 iron–sand barriers and packed with metolachlor-contaminated soil.

A striking difference between PRB use in ground water and vadose zone applications is that PRBs are often designed to last 10 or more years when properly sized and placed in an aquifer. Whether a horizontally placed PRB will perform long enough within the vadose zone to handle a particular point source is contingent upon several factors. Although we demonstrated that $Al_2(SO_4)_3$ additions to Fe^0 can create a more reactive media, this may result in a shorter effective lifetime, especially when aging effects are considered. An obvious deterrent for using an iron barrier in the vadose zone is accelerated iron aging resulting from O_2 in the soil atmosphere and its subsequent influence on the pore fluid surrounding the iron surfaces. Only recently have researchers begun to examine mineral precipitates and corrosion effects on the longevity of PRBs. Phillips et al. (2000) provided excellent mineralogical characterization (X-ray diffraction [XRD] and scanning electron microscopy–energy dispersive X-ray [SEM–EDX]) of core samples taken from a 15-mo-old PRB. Their results indicated that iron oxyhydroxides were prevalent throughout, while aragonite ($CaCO_3$), siderite ($FeCO_3$), and FeS predominated in the more aerobic portions of the barrier.

Dissolved oxygen, as well as CO_3^{2-} and HCO_3^- in the pore fluid, will be driving factors influencing reaction rates by increasing oxide formation on the metal surface and decreasing reactivity (Mackenzie et al., 1999; Phillips et al., 2000). Subsoil atmosphere composition depends upon respiration rates of microorganism and plant roots, the solubility of O_2 and CO_2 in water, and the rate of gaseous exchange with the atmosphere (Jury et al., 1991). The degree to which O_2 will diffuse into the subsoil is also contingent on soil texture and aggregation, bulk density, soil water content, and depth. Considering these factors, it is unlikely that PRB efficacy would be sustained if placed at a shallow depth in a sandy soil. By contrast, if the barrier was placed near the capillary fringe of the water table in a clay or clay loam soil, its longevity would probably be enhanced due to less gaseous diffusion.

Equal consideration must also be given to temporal changes in hydraulic conductivity of the barrier during aging. Permeable reactive barrier failures in ground water have occurred from improper length or unrecognized heterogeneities in ground water flow paths, resulting in the contaminated plume bypassing the PRB (Laase et al., 2000). When placed in aquifers, PRBs are designed to have hydraulic conductivities that are greater than or equal to the surrounding aquifer so as not to impede ground water flow. Unlike saturated systems, where the least permeable layer often has the greatest influence on transport processes, water flow through unsaturated, layered soils can be quite different and heterogeneities in conductivity between horizons may have profound effects. For example, if the Fe^0–sand barrier is placed beneath a fine-textured soil, the discontinuities in pore sizes between the soil and the PRB could cause water to be held at the soil–Fe^0–sand interface until the hydraulic head increases to a point where the pores or channels in the Fe^0–sand begin to fill with water. This could result in ponding above the PRB followed by rapid channeling through the PRB, or bypass flow around the PRB (if vertical barriers were not used). It is essential that water continue to flow through the barrier with time. In the absence of artificial horizontal barriers that would force this issue, barrier composition (Fe^0–sand) must consider the hydraulic conductivity of the PRB relative to the surrounding soil. Despite these important considerations, which warrant further study and field testing, our initial observations indicate that iron barriers can function under unsaturated flow and may have a niche in containing solute leaching from point sources of contamination.

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REFERENCES

Chesters, G., G.V. Simsiman, J. Levy, B.J. Alhajjar, R.N. Fathulla, and J.M. Harkin. 1989. Environmental fate of alachlor and metolachlor. Rev. Environ. Contam. Toxicol. 110:11–74.

Comfort, S.D., P.J. Shea, T.A. Machacek, H. Gaber, and B.-T. Oh. 2001. Field-scale remediation of a metolachlor-contaminated spill site using zerovalent iron. J. Environ. Qual. 30:1636–1643.

Eykholt, G.R., and D.T. Davenport. 1998. Dechlorination of the chloroacetanilide herbicides alachlor and metolachlor by iron metal. Environ. Sci. Technol. 32:1482–1487.

Jury, W.A., W.R. Gardner, and W.H. Gardner. 1991. Soil physics. John Wiley & Sons, New York.

Laase, A.D., N.E. Korte, J.L. Baker, P.D. Dieckman, J.L. Vogan, and R.L. Focht. 2000. Evaluation of the Kansas City plant iron wall. p. 417–424. *In* G.B. Wickramanayake et al. (ed.) Chemical oxidation and reactive barriers. Battelle Press, Columbus, OH.

Loyaux-Lawniczak, S., P. Refait, J.-J. Ehrhardt, P. Lecomte, and J.-M.R. Genin. 2000. Trapping of Cr by formation of ferrihydrite during the reduction of chromate ions by Fe(II)–Fe(III) hydroxysalt green rusts. Environ. Sci. Technol. 34:438–443.

Mackenzie, P.D., D.P. Horney, and T.M. Sivavec. 1999. Mineral precipitation and porosity losses in granular iron columns. J. Hazardous Mater. 68:1–17.

Minnesota Department of Agriculture. 1997. Results of 1996 soil sampling of pesticides on crop production retailer facilities. Agron. and Plant Protection Serv., St. Paul, MN.

Norwood, V.M., and M.E. Randolph. 1990. A literature review of biological treatment and bioremediation technologies which may be applicable at fertilizer/agrichemical dealer sites. Natl. Fertilizer and Environ. Res. Center, Muscle Shoals, AL.

Odziemkowski, M.S., and R.W. Gillham. 1997. Surface redox reactions on commercial grade granular iron (steel) and their influence on the reductive dechlorination of solvent. Micro Raman spectroscopic studies. 213th ACS National Meeting, San Francisco, CA. Extended abstracts. Div. Environ. Chem. 37:177–180.

O'Hannesin, S., and R. Gillham. 1998. Long-term performance of an in-situ iron wall for remediation of VOCs. Ground Water 36:164–170.

Phillips, D.H., B. Gu, D.B. Watson, Y. Roh, L. Liang, and S.Y. Lee. 2000. Performance evaluation of a zerovalent iron reactive barrier:

Mineralogical characterizations. Environ. Sci. Technol. 34:4169–4176.

Pignatello, J.J., and K. Baehr. 1994. Ferric complexes as catalysts for Fenton degradation of 2,4-D and metolachlor in soil. J. Environ. Qual. 23:365–370.

Singh, J., S.D. Comfort, and P.J. Shea. 1998a. Remediating RDX-contaminated water and soil using zero-valent iron. J. Environ. Qual. 27:1240–1245.

Singh, J., P.J. Shea, L.S. Hundal, S.D. Comfort, T.C. Zhang, and D.S. Hage. 1998b. Iron-enhanced remediation of water and soil containing atrazine. Weed Sci. 46:381–388.

Sun, Y., and J.J. Pignatello. 1992. Chemical treatment of pesticide wastes. Evaluation of Fe(III) chelates for catalytic hydrogen peroxide oxidation of 2,4-D at circumneutral pH. J. Agric. Food Chem. 40:322–327.

Taylor, R.M. 1980. Formation and properties of Fe(II)Fe(III) hydroxy-carbonate and its possible significance in soil formation. Clay Minerals 15:369–382.

Tyre, B.T., R.J. Watts, and G.C. Miller. 1991. Treatment of four biorefractory contaminants in soils using catalyzed hydrogen peroxide. J. Environ. Qual. 20:832–837.

USEPA. 1990. Engineering bulletin: Mobile/transportable incineration treatment. EPA/540/2-90/014. Office of Emergency and Remedial Response, Washington, DC, Office of Res. and Development, Cincinnati, OH.

Wilson, E.K. 1995. Zero-valent metals provide possible solution to groundwater problems. Chem. Eng. News 73:19–22.

Van Genuchten, M.Th., and P.J. Wierenga. 1986. Solute dispersion coefficients and retardation factors. p. 1025–1054. *In* A. Klute (ed.) Methods of soil analysis. Part 1. Physical and mineralogical methods. 2nd ed. Agron. Monogr. 9. ASA and SSSA, Madison, WI.