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Field-Scale Remediation of a Metolachlor-Contaminated Spill Site Using Zerovalent Iron

S. D. Comfort*, P. J. Shea, T. A. Machacek, H. Gaber, and B.-T. Oh

ABSTRACT

Pesticide spills are common occurrences at agricultural cooperatives and farmsteads. When inadvertent spills occur, chemicals normally beneficial can become point sources of ground and surface water contamination. We report results from a field trial where approximately 765 m^3 of soil from a metolachlor [2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl) acetamide] spill site was treated with zerovalent iron (Fe^0). Preliminary laboratory experiments confirmed metolachlor dechlorination by Fe^0 in aqueous solution and that this process could be accelerated by adding appropriate proportions of $Al_2(SO_4)_3$ or acetic acid (CH_3COOH). The field project was initiated by moving the stockpiled, contaminated soil into windrows using common earth-moving equipment. The soil was then mixed with water (0.35–0.40 kg H_2O kg^{-1}) and various combinations of 5% Fe^0 (w/w), 2% $Al_2(SO_4)_3$ (w/w), and 0.5% acetic acid (v/w). Windrows were covered with clear plastic and incubated without additional mixing for 90 d. Approximately every 14 d, the plastic sheeting was removed for soil sampling and the surface of the windrows rewetted. Metolachlor concentrations were significantly reduced and varied among treatments. The addition of Fe^0 alone decreased metolachlor concentration from 1789 to 504 mg kg^{-1} within 90 d, whereas adding Fe^0 with $Al_2(SO_4)_3$ and CH_3COOH decreased the concentration from 1402 to 13 mg kg^{-1}. These results provide evidence that zerovalent iron can be used for on-site, field-scale treatment of pesticide-contaminated soil.

Pesticide spills and accidents involving farm chemicals take place each year on farmsteads and cooperatives. When these events occur, normally beneficial chemicals become sources of contamination for ground and surface water. Although the soil–water environment has an enormous potential to naturally attenuate xenobiotic compounds, this capacity can be exceeded when chemicals are either deliberately or inadvertently released to localized areas. To combat these point sources of contamination, treatments are needed that can alter the chemical structure of the contaminant so that natural attenuation can proceed.

The realization that many pollutants normally considered persistent in aerobic environments may be less persistent under anaerobic conditions has generated considerable interest in engineering a reducing environment in soils, sediments, and aquifers for remediation purposes. Under reducing conditions, detoxification of many contaminants can occur through reductive dehalogenation reactions. Although there are exceptions, as when vinyl chloride, a human carcinogen, is produced from reduction of more highly chlorinated compounds (Suflita et al., 1982), there is ample evidence to indicate that reducing or removing electron-withdrawing moieties from parent structures can result in more biodegradable products (Hundal et al., 1997; Singh et al., 1998a; Fathepure and Tiedje, 1999). Based on this premise, one technology gaining widespread acceptance is the use of zerovalent metals for remediating ground water contaminated with chlorinated solvents. Zerovalent iron (Fe^0, E_h^o = −409 mV; Weast, 1978) is an avid electron donor and has a high capacity to reduce a wide array of organic compounds. Under aerobic conditions, oxygen is the usual electron acceptor, while in anoxic environments, electron release from the reaction of Fe^0 with water can be coupled to the reduction of chlorinated and nitroaromatic compounds (Gillham and O'Hannesin, 1994; Agrawal and Tratnyek, 1996).

Current research has focused on the use of zerovalent metals for in situ treatment of contaminated ground water, with less research on using zerovalent metals for treating contaminated soils. Earlier work with zerovalent zinc demonstrated the utility of metals to treat soils contaminated with dichlorodiphenyltrichloroethane (DDT) (Staiff et al., 1977), methyl parathion (Butler et al., 1981), and polychlorinated biphenyls (Cutshall et al., 1993). More recent research indicates the tremendous potential of Fe^0 to remediate soils contaminated with 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) (Hundal et al., 1997; Singh et al., 1998a, 1999), and atrazine (Singh et al., 1998b). Despite encouraging results, this work has yet to evolve into routine large-scale treatment of contaminated spill sites.

Our objective was to use zerovalent iron to remediate a metolachlor-contaminated field site. We report laboratory observations demonstrating the capacity of Fe^0 to dechlorinate metolachlor in aqueous solution, then demonstrate the effectiveness of Fe^0 to decrease metolachlor concentrations in static soil microcosms and at the field scale in soil windrows.

MATERIALS AND METHODS

Metolachlor Spill Site

The metolachlor spill site was at a farm cooperative in southwestern Nebraska. This cooperative had been using a half-acre bentonite clay-lined lagoon to contain potentially contaminated storm runoff water and other excess wastewater. In 1995, an accidental release of metolachlor from a storage tank resulted in 2858 L of unrecovered product, some of which ran into the sump that drains into the lagoon. The spill resulted in approximately 765 m^3 (1000 yd^3) of contaminated soil that was excavated from the lagoon, stockpiled into two large windrows, and held for remedial treatment. The targeted contaminant was metolachlor, which was present at concentrations in excess of 1400 mg kg^{-1}, but soil analysis revealed additional pesticides such as atrazine (6-chloro-N^2-ethyl-N^4-isopropyl-1,3,5-triazine-2,4-diamine; initial concentration >250 mg kg^{-1}), alachlor [2-chloro-2′,6′-diethyl-*N*-(methoxymethyl)acetanilide;

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Abbreviations: HPLC, high-performance liquid chromatography.

>90 mg kg^{-1}], pendimethalin [*N*-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine; >90 mg kg^{-1}], and chlorpyrifos [*O*,*O*-diethyl *O*-(3,5,6-trichloro-2-pyridyl) phosphorothioate; >25 mg kg^{-1}].

Laboratory Solution Experiments

Aqueous solutions of metolachlor were prepared from the commercial product Dual 8E (Syngenta, Greensboro, NC) and spiked with [^{14}C-U-phenyl] metolachlor (28.6 μCi mg^{-1}) to produce a final concentration of 32 Bq mL^{-1}. Experimental units consisted of 250-mL Erlenmeyer flasks filled with 150 mL of metolachlor solution. All flasks were covered with Parafilm-coated stoppers and agitated on a reciprocating shaker at ambient temperature (23°C).

Two sets of companion batch experiments were conducted with zerovalent iron. The first set compared the destructive capacity of Fe^0 with and without $Al_2(SO_4)_3$; the second used Fe^0 with and without acetic acid. Initial metolachlor concentration was 1.09 m*M* for the Fe^0–$Al_2(SO_4)_3$ experiment and 1.00 m*M* for the Fe^0–acetic acid experiment. Each treatment (including controls) was replicated three times. Each treatment flask (containing 150 mL of metolachlor solution) received 18.75 g of unannealed Fe^0, with and without 0.75 g commercial-grade $Al_2(SO_4)_3$ or 0.75 mL glacial acetic acid. At 0, 2, 4, 6, 8, 12, 16, 24, and 48 h, 1.5-mL aliquots were removed and transferred to 1.7-mL polypropylene microcentrifuge tubes, centrifuged at 13 000 × *g* for 10 min, and analyzed by high-performance liquid chromatography (HPLC) for metolachlor and dechlorinated metolachlor. Carbon-14 in the aqueous solution was also monitored using the same sampling scheme by mixing 1 mL of uncentrifuged sample with 6 mL of Ultima Gold cocktail (Packard, Meriden, CT) and analyzed by liquid scintillation counting (LSC) using a Packard 1900TR liquid scintillation counter (Packard Instrument Co., Downers Grove, IL). Chloride analysis was also conducted on the samples taken for HPLC analysis with a Dionex (Sunnyvale, CA) DX-120X ion chromatograph using an AS14 IonPac column and a sodium carbonate (3.5 m*M*)–sodium bicarbonate (1.0 m*M*) eluent at a flow rate of 1.2 mL min^{-1}.

To determine differences in biodegradability between metolachlor and the Fe^0–treated metolachlor products (primarily dechlorinated metolachlor), 25 mL of 0.35 m*M* metolachlor solution (spiked with ^{14}C-metolachlor) was treated with and without 4.5 g Fe^0 and mixed with 24 mL of double strength *Pseudomonas* minimum media (without glucose; Hundal et al., 1997). Solutions were transferred to sterilized glass jars, then inoculated with 1 mL of a consortium obtained from the metolachlor-contaminated soil. This inoculum was extracted by shaking 4 g soil with 20 mL of saline solution for 48 h. The saline solution contained (g L^{-1}) NaCl (8.5), KH_2PO_4 (0.3), Na_2HPO_4 (0.6), and peptone (0.1). Evolved $^{14}CO_2$ was captured by placing 10 mL of 0.5 *M* NaOH in a 20-mL scintillation vial and suspending it inside the sealed glass jar and over the inoculated media. Carbon dioxide traps were changed approximately every 5 d. Captured $^{14}CO_2$ was determined by removing 0.5 mL from the CO_2 traps, mixing with scintillation cocktail, and determining total ^{14}C activity by liquid scintillation counting.

Laboratory Soil Incubation Experiments

Because solution experiments provided evidence that small additions of CH_3COOH or $Al_2(SO_4)_3$ facilitated Fe^0–mediated destruction of metolachlor, we subsequently conducted batch studies with the metolachlor-contaminated soil to determine optimum concentrations needed for efficient metolachlor destruction in static soil microcosms. This was accomplished by incubating 20 g (oven dry) soil with 5% Fe^0 (w/w) in 40-mL Teflon centrifuge tubes at 30°C and a soil water content of 0.40 kg kg^{-1}. Aluminum sulfate additions were between 0 and 5% (w/w) [0–1.0 g $Al_2(SO_4)_3$ to 20 g soil]. Acetic acid additions were between 0 and 2.5% (0–0.5 mL to 20 g soil). Soil treated with Fe^0 + $Al_2(SO_4)_3$ was incubated for 2 d; soil treated with Fe^0 + CH_3COOH was incubated for 7 d. Following incubation, the soil was extracted with 20 mL of CH_3CN and analyzed by HPLC (procedure described in Soil Analysis, below).

Field Experiment

The stockpiled soil was moved with a front-end loader into seven windrows, five of which were used in the field experiment. Windrow dimensions were 3.35 to 3.65 m wide by 1.07 to 1.37 m high and 25.91 to 60.66 m in length. The soil in each windrow was mixed three times within 24 h by using a tractor-pulled, high-speed soil mixing and fractionation implement (Frontier Industrial Corp., Salem, OR), sold under the trade name Microenfractionator (H&H Eco Systems, North Bonneville, WA). This implement is similar in appearance to a conventional composter but differs in that its components have been augmented and redesigned to handle windrows containing 100% soil. This is facilitated by a John Deere (Moline, IL) 6068T 170-horsepower diesel engine that propels a large 32-cm (diam.) stainless steel rotating drum with 50 fan-knife blades (30.8-cm length). This implement also allows simultaneous injection of liquids (i.e., water and CH_3COOH in this experiment) into the mixing tunnel via pressurized lines connected to a water tank, which is pulled along with the Microenfractionator (Fig. 1).

Following initial soil mixing, windrows were sampled approximately halfway up each side by using a hand-held soil probe (2.5-cm i.d., 53-cm length). Three cores were taken every 6.1 m and composited. Samples were placed in an insulated cooler and transported to the laboratory. Each composite sample was analyzed for metolachlor and average concentrations per windrow were calculated.

Once the initial samples were obtained, five treatments were initiated, one per windrow. Treatments included: (i) control (no Fe^0), (ii) Fe^0–only, (iii) Fe^0 + CH_3COOH, (iv) Fe^0 + $Al_2(SO_4)_3$, and (v) Fe^0 + CH_3COOH + $Al_2(SO_4)_3$. Treatments were added as a percentage of the oven-dry soil mass, which was estimated by multiplying the volume of each windrow times a soil bulk density of 1.4 g cm^{-3}. The Fe^0 was added at 5% (w/w), CH_3COOH at 0.5% (v/w), and commercial grade $Al_2(SO_4)_3$ at 2% (w/w). Expressing these percentages in the

Fig. 1. Soil mixer and water tank being pulled through a soil windrow.

Table 1. Soil physicochemical properties before (t = 0 d) and after (t = 90 d, mixed) treatment with zerovalent iron.

Soil property	Unit	Initial concentration	Control	Fe^0	Fe^0 + CH_3COOH	Fe^0 + $Al_2(SO_4)_3$	Fe^0 + CH_3COOH + $AL_2(SO_4)_3$
		t = 0 d	t = 90 d				
Phosphorus (weak Bray)	mg kg^{-1}	171 (23)†	186 (6)	215 (14)	182 (3)	98 (31)	26 (2)
Nitrate N	mg kg^{-1}	996 (231)	981 (25)	271 (14)	85 (12)	62 (6)	58 (2)
Ammoniacal N	mg kg^{-1}	5894 (902)	5745 (338)	4075 (954)	3677 (256)	4396 (249)	2901 (121)
Total N	%	1.11 (0.13)	1.17 (0.02)	0.97 (0.04)	0.82 (0.03)	0.85 (0.06)	0.55 (0.01)
Organic matter	%	2.6 (0.4)	2.5 (0.1)	3.1 (0.5)	2.6 (0.1)	1.9 (0.2)	1.9 (0.1)
Cation exchange capacity	$cmol_c$ kg^{-1}	7.5 (1.1)	12.1 (0.3)	11.5 (0.8)	12.4 (0.0)	20.4 (0.8)	25.0 (0.7)
Chloride	mg kg^{-1}	71 (13)	165 (7)	244 (30)	191 (5)	237 (9)	174 (6)
Sulfate	mg kg^{-1}	622 (21)	586 (16)	553 (57)	464 (7)	8646 (256)	8278 (65)
Iron (DTPA‡)	mg kg^{-1}	40 (12)	97 (17)	368 (19)	379 (2)	325 (12)	264 (1)
Zinc (DTPA)	mg kg^{-1}	66 (18)	91 (3)	72 (5)	61 (0)	45 (2)	58 (0)
Manganese (DTPA)	mg kg^{-1}	53 (18)	78 (4)	82 (3)	90 (5)	105 (4)	105 (1)
Copper (DTPA)	mg kg^{-1}	3.0 (1.2)	5.0 (1.9)	29.2 (2.0)	40.5 (1.4)	27.0 (1.2)	28.4 (0.4)
Boron	mg kg^{-1}	1.0 (0.2)	1.4 (0.1)	2.0 (0.1)	1.8 (0.0)	1.7 (0.1)	1.6 (0.0)
pH		6.6 (0.1)	6.4 (0.1)	7.6 (0.1)	8.1 (0.0)	7.1 (0.1)	7.5 (0.0)
Aluminum	mg kg^{-1}	2 (1)	1 (1)	4 (2)	3 (2)	2 (1)	2 (1)
Sand	%	38 (7)	43 (15)	53 (8)	54 (5)	61 (10)	62 (5)
Silt	%	33 (6)	35 (10)	24 (9)	37 (2)	33 (8)	33 (5)
Clay	%	30 (6)	22 (5)	23 (1)	9 (4)	6 (2)	5 (1)

† Parenthetic values indicate sample standard deviation of means (n = 5 for initial, n = 3 for treatments).
‡ DTPA = diethylenetriaminepentaacetic acid.

more conventional unit of mass of chemical added per cubic yard (1 yd^3 = 0.765 m^3) of soil (1070 kg or 2360 lb, assuming a 1.4 g cm^{-3} bulk density), our treatment rates were equivalent to 53.5 kg (118 lb) of Fe^0, 21.4 kg (47.1 lb) of $Al_2(SO4)_3$, and 5.4 L (1.42 gal) of acetic acid per 0.765 m^3 (yd^3) of contaminated soil.

The Fe^0 was unannealed iron purchased from Peerless Metal Powders (Detroit, MI) in 22.7 kg unlined paper bags. This Fe^0 had a specific surface area of 2.55 m^2 g^{-1} (Micromeritics, Norcross, GA). Aluminum sulfate (commercial grade) was purchased in 22.7-kg bags from Van Waters & Rogers (Omaha, NE). Glacial acetic acid was obtained in 208-L barrels from Celanese Chemicals (Dallas, TX), diluted with H_2O and added during the mixing operations.

The required amounts of iron and $Al_2(SO_4)_3$ (in 22.7-kg unlined paper bags) were placed on top of the windrows and directly mixed in with the Microenfractionator a minimum of three times. Water and acetic acid were also added during the mixing process until the soil gravimetric water content was between 0.35 and 0.40 kg kg^{-1}, which was determined at the field site by weight loss following repeated cycles of heating in a microwave oven. An added benefit of adding H_2O during mixing was that it greatly reduced the amount of Fe^0 dust released into the atmosphere during the first pass.

Once the desired soil water content was obtained, the windrows were covered with clear plastic that was held in place with wooden pallets. Windrows were sampled as described above at 1, 14, 28, 42, 60, 75, and 90 d. After sampling at 14, 28, 42, 60, and 75 d, additional water was applied to the top of the windrows (without mixing) to rewet the surface soil. Two sets of 90-d samples were taken, one before and one after mixing the windrows.

Soil Analysis

Soil samples obtained from the windrows were inventoried and stored at 4°C. For each sample, we determined soil water content, pH, and metolachlor concentration. Soil water content was determined on three 10-g subsamples by determining weight loss after drying in a microwave oven. Soil pH was determined on 20-g soil samples (oven-dry basis) using a 1:1 soil to H_2O ratio.

Metolachlor was extracted from 4.75 to 5.25 g soil (oven-dry basis) in a 40-mL Teflon centrifuge tube by adding 20 mL CH_3CN and shaking overnight (≥8 h) on a reciprocating shaker at ambient temperature. The tubes were then centrifuged at 5000 × g for 10 min and 1.5 mL was removed and microcentrifuged at 13 000 × g for an additional 10 min. After centrifuging, 1 mL of supernatant was stored in a glass HPLC vial at 4°C until analysis.

Metolachlor and its dechlorinated product were measured by HPLC by injecting 20 μL of the CH_3CN extract 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 acetonitrile and water at 1.0 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.

Standard soil nutrient and metal analyses (Table 1) were conducted by Midwest Analytical Laboratories (Omaha, NE) on initial (t = 0 d) and t = 90 d (mixed) samples.

Statistical comparisons of metolachlor concentrations and soil pH among treatments were conducted using Tukey's multiple comparison procedure (Steel and Torrie, 1980) with a 5% probability of a Type I error (α = 0.05).

RESULTS AND DISCUSSION

Laboratory Solution Experiments

Adding $Al_2(SO_4)_3$ alone had no effect in altering metolachlor concentration. By contrast, when $Al_2(SO_4)_3$ was added with Fe^0, first-order destruction rates were greatly increased (0.24 vs. 0.08 h^{-1}; Fig. 2). Assuming removal of one mole of Cl^- per mole of metolachlor, we recovered >80% of the Cl^- from the Fe^0 treatments. A near stoichiometric recovery of Cl^- coupled with the production of the dechlorinated product confirmed that dechlorination was the primary transformation occurring. Given that approximately 20% of the ^{14}C activity was lost within the first 2 h from solutions receiving Fe^0, some adsorption of metolachlor and/or its dechlorinated product(s) onto the Fe^0 occurred (Fig. 2). A decline in the dechlorinated product in the Fe^0 + $Al_2(SO_4)_3$ treatment after 12 h, without further loss in solution ^{14}C activity, indi-

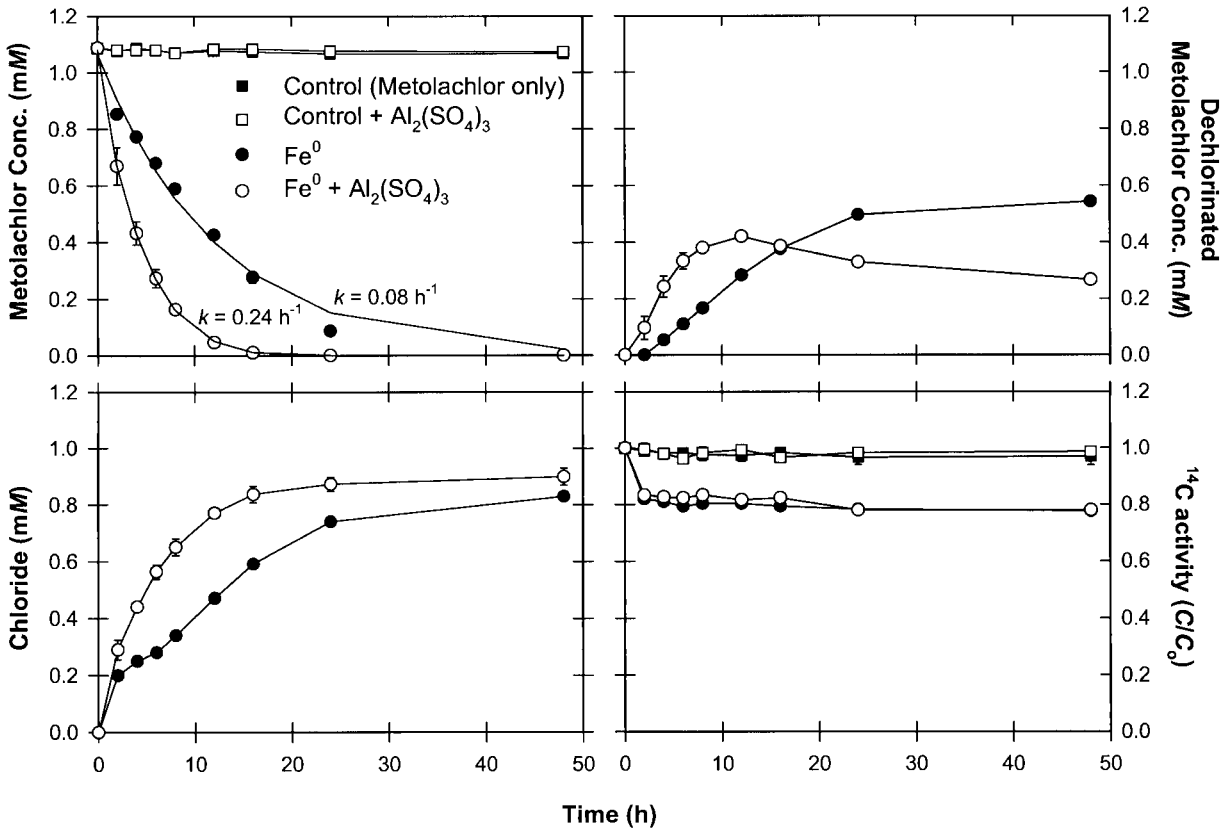

Fig. 2. Changes in metolachlor concentration, ^{14}C activity, and production of Cl^- and dechlorinated metolachlor following addition of Fe^0 or $Fe^0 + Al_2(SO_4)_3$ to aqueous solutions containing 1.09 m*M* metolachlor spiked with ^{14}C-metolachlor.

cates further transformation of the dechlorinated product. The companion experiment, which tested the effects of acetic acid on metolachlor transformation, produced similar results (Fig. 3), with acetic acid having an even more profound effect on the transformation rate (k = 0.39 h^{-1}). In this experiment, dechlorinated product was also produced (Fig. 3); Cl^- could not be quantified due to interference from the acetic acid.

Iron metal added to aqueous solutions of metolachlor efficiently dechlorinated this chloroacetamide herbicide. The dechlorinated product [*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl)acetamide] is formed when metolachlor accepts electrons released from oxidation of the Fe^0 to Fe^{2+} and Fe^{3+}. This reaction is promoted under acidic conditions and limited oxygen content. In summarizing the pathways of metolachlor degradation, Chesters et al. (1989) indicated that the same dechlorinated metolachlor product occurs naturally as a result of abiotic degradation in soil and sediment under anaerobic conditions.

Our results are consistent with previous reports of metolachlor dechlorination by iron metal in water (Eykholt and Davenport, 1998). Mass balance experiments using ^{14}C-metolachlor, with measurement of the dechlorinated compound and recovery of Cl^- released from metolachlor, indicated that the conversion is essentially complete, without the initial formation of other products.

Because dechlorination was the main destructive mechanism of the Fe^0 treatment, we compared the biodegradability of metolachlor with the Fe^0–treated metolachlor products in a mixed culture. The Fe^0–treated products were five times more utilizable as a sole carbon source than metolachlor (cumulative $^{14}CO_2$: 4.6 vs. 0.89%, Fig. 4), indicating that they are more biodegradable than the parent metolachlor. Singh et al. (1998b) similarly found in a 120-d study that adding Fe^0 to atrazine-contaminated soil increased cumulative mineralization from 4.1 to 11.2%.

Laboratory Soil Incubation Experiments

Although batch solution experiments indicated that $Al_2(SO_4)_3$ and acetic acid had a complementary effect on Fe^0–mediated metolachlor destruction, the optimum quantities required to treat the spill-site soil needed to be determined. Short-term soil incubations indicated that 2% $Al_2(SO_4)_3$ (w/w) and 0.5% acetic acid (v/w) effectively increased metolachlor destruction in static soil microcosms (Fig. 5). Because the greatest metolachlor destruction occurred within the first day of treatment (see below), these short-term incubations adequately determined the quantities of $Al_2(SO_4)_3$ and CH_3COOH required for field-scale treatment.

Metolachlor Spill Site

The metolachlor concentration declined dramatically within 1 d after treating the soil windrows. Concentrations decreased from 1789 to 972 mg kg^{-1} (a 46% decline) for the Fe^0–only treatment and from 1402 to 65 mg kg^{-1} (95% decrease) for the $Fe^0 + CH_3COOH + Al_2(SO_4)_3$

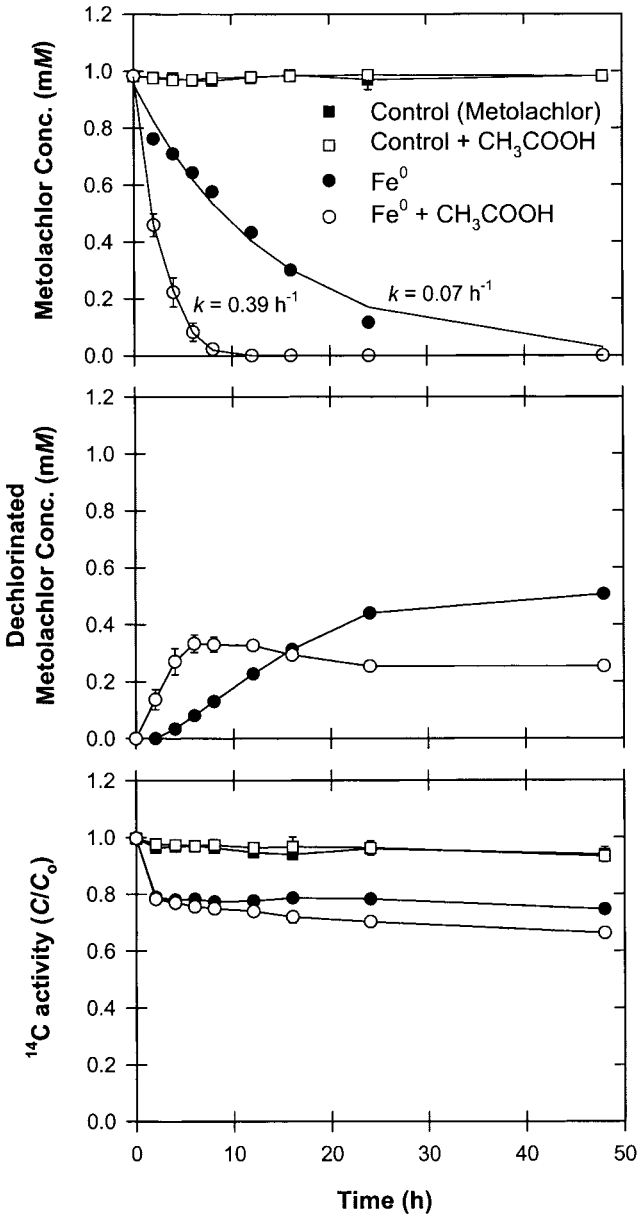

Fig. 3. Changes in metolachlor concentration, ^{14}C activity, and production of dechlorinated metolachlor following addition of Fe^0 or Fe^0 + acetic acid to aqueous solutions containing 1.00 m*M* metolachlor spiked with ^{14}C-metolachlor.

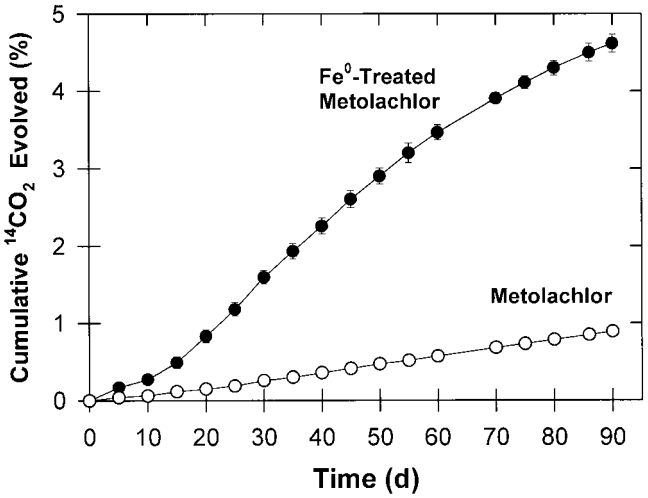

Fig. 4. Cumulative $^{14}CO_2$ evolved (percent of added ^{14}C) from inoculated solution media containing ^{14}C-labeled metolachlor or Fe^0–treated ^{14}C-labeled metolachlor as the sole C source.

treatment (Table 2). The remaining samplings showed a general decrease in concentrations with time but variability in metolachlor concentrations within the windrows prevented us from observing continuous incremental decreases (Table 2). After mixing the windrows again at t = 90 d, we observed the lowest concentrations of metolachlor obtained in this experiment, with final concentrations ranging between 504 mg kg^{-1} (72% decrease, Fe^0 only) and 13 mg kg^{-1} [99% decrease, Fe^0 + CH_3COOH + $Al_2(SO_4)_3$].

Notable observations from the field included dramatic changes in soil color following treatment. Within 1 d, the surface of the soil had begun to brown from the oxidation of the iron. Immediately below the surface (ca. 1 cm), the soil was gray to greenish gray, especially in windrows containing $Al_2(SO_4)_3$. This is probably due to the formation of green rust and reduced iron. Green rusts, often found as corrosion products of iron metal or as precipitates in anaerobic soils and sediments, are layered Fe(II)–Fe(III) hydroxides with anionic interlayers (CO_3^{2-}, Cl^-, and SO_4^{2-}) (Erbs et al., 1999). Green rusts have been shown to play a role in the reduction of NO_3^- (Hansen et al., 1996) and carbon tetrachloride (Erbs et al., 1999), which indicates that they may also promote the reduction of other nitrogenated and chlorinated compounds. In addition to their importance as reductants, green rusts can also be strong adsorbents due to the potential of their interlayers to sorb and exchange anions and polar uncharged molecules (Erbs et al., 1999).

With time, diffusion of oxygen into the windrow was inevitable and the brown oxidation layer at the surface gradually increased in size. Whereas the oxidation of green rust to goethite may also provide a source of electrons for reduction reactions, formation of a Fe(III) oxide layer passivates the iron surface. At the 14-d sampling, we took a vertical core in the Fe^0 + CH_3COOH + $Al_2(SO_4)_3$–treated windrow and segmented it into three 10-cm increments. The top (surface) segment, which was brown, had a metolachlor concentration of 34 mg kg^{-1} while the middle (brown-green) and bottom (green) sections (10–20, 20–30 cm) had concentrations ≤9 mg kg^{-1}. When the windrows were finally mixed at the end of the experiment (t = 90 d), the center and bottom of the windrows still exhibited a green rust color. Based on these observations, it is likely that anoxic conditions were maintained in the center and bottom of the windrows and by mixing the windrows, we exposed soil that had greater rates of metolachlor destruction to areas where the windrows were routinely sampled. This probably explains why metolachlor concentrations were lower after the post–90 d mixing.

Comparisons among treatments at each sampling date revealed that the Fe^0–only treatment significantly decreased metolachlor concentrations from the control (Ta-

Table 2. Extractable metolachlor concentrations following treatment with zerovalent iron.

Treatment	Initial (mixed)†	1 d	14 d	28 d	42 d	60 d	75 d	90 d	90 d (mixed)
	mg kg^{-1}								
Control	1813a‡	1976a	1766a	1638a	1555a	2035a	1867a	1826a	1522a
Fe^0	1789a	972b	769b	537b	467b	676b	651b	486b	504b
Fe^0 + CH_3COOH	1740a	403c	220c	162c	178c	375bc	418bc	158bc	90c
Fe^0 + $Al_2(SO_4)_3$	1656a	105c	107c	104c	98c	53c	59c	108c	40c
Fe^0 + CH_3COOH + $Al_2(SO_4)_3$	1402a	65c	41c	34c	52c	25c	34c	45c	13c

† Mixed: windrows were mixed three times immediately before sampling.
‡ Values with same letter within columns are not significantly different ($\alpha = 0.05$).

ble 2). Adding $Al_2(SO_4)_3$, acetic acid, or both with Fe^0 significantly increased metolachlor destruction. This was particularly apparent in treatments containing $Al_2(SO_4)_3$, which yielded the lowest metolachlor concentrations. Reasons for enhanced destruction by the addition of $Al_2(SO_4)_3$ and acetic acid are complex but can in part be attributed to alterations in soil solution pH, redox potential, and soil solution composition during corrosion of the Fe^0 surface. Decreasing pH will increase destruction rates by providing protons for reductive transformations and slow down Fe(II) oxidation and passivation of the iron surface. Although the $Al_2(SO_4)_3$ amendment significantly decreased soil pH in the windrows, the acetic acid treatment only slightly lowered the pH after application and residual effects were relatively short-lived (Table 3). After the first few samplings, pH tended to be higher in windrows receiving acetic acid than the comparable treatment [Fe^0 or Fe^0 + $Al_2(SO_4)_3$; Table 3].

The addition of acetic acid provided a readily utilizable carbon source that may have facilitated reductive transformations by producing an additional oxygen demand and source of electrons. It was also noted that individual grains of Fe^0 in windrows treated with acetic acid were less visible and the soil as a whole appeared to have a more uniform iron coating. Formation of metal–organic complexes on surfaces will increase iron dissolution (Sidhu et al., 1981, Schwertmann et al., 1986). Therefore, the acetic acid probably facilitated the initial dissolution and subsequent distribution of dissolved iron throughout the soil. High concentrations of organic acids can also inhibit crystallization of iron oxides, favoring less well-structured matrices (such as ferrihydrite, green rust, and magnetite) with greater surface area (Heck and Mermut, 1999).

Aside from lowering the pH, it is likely that the $Al_2(SO_4)_3$ played other roles in enhancing metolachlor destruction. An abundance of aluminum during Fe^0 oxidation promotes its incorporation into the oxidized iron structure (Schwertmann and Cornell, 1991). This is important because Al^{3+} has a smaller ionic radius that disrupts crystallization and favors formation of ferrihydrite (Fe_5HO_8) (Stucki et al., 1988). Ferrihydrite has a large surface area (>200 m^2 g^{-1}; Schwertmann and Cornell, 1991) and can serve as a reservoir for reduced iron (Baltpurvins et al., 1996). Klausen et al. (1995) demonstrated that Fe(II) bound to iron hydroxide surfaces or surface coatings plays an important role in reductive transformation of nitroaromatic compounds. Experiments conducted in our laboratory indicated that the presence of Fe(II), Fe(III), or Al(III) during Fe^0 corrosion can facilitate metolachlor destruction in aqueous solution. In these experiments, Al(III) was readily sorbed by, and/or incorporated into, the oxidizing iron and this corresponded with a release of Fe(II) into solution. Therefore, an indirect effect of adding $Al_2(SO_4)_3$ was likely its influence on Fe(II) concentration in the soil solution during the corrosion of Fe^0. Because sulfate was added as part of the $Al_2(SO_4)_3$, its presence must also be considered. Sulfate has been shown to sustain higher rates of iron corrosion (Reardon, 1995), apparently by dissolving the oxide film that coats the surface during oxidation (Gu et al., 1999). Under reducing conditions, sulfate also promotes formation of green rust II [$FeII_4FeIII_2(OH)_{12}SO_4 \cdot nH_2O$] (Refait et al., 1999).

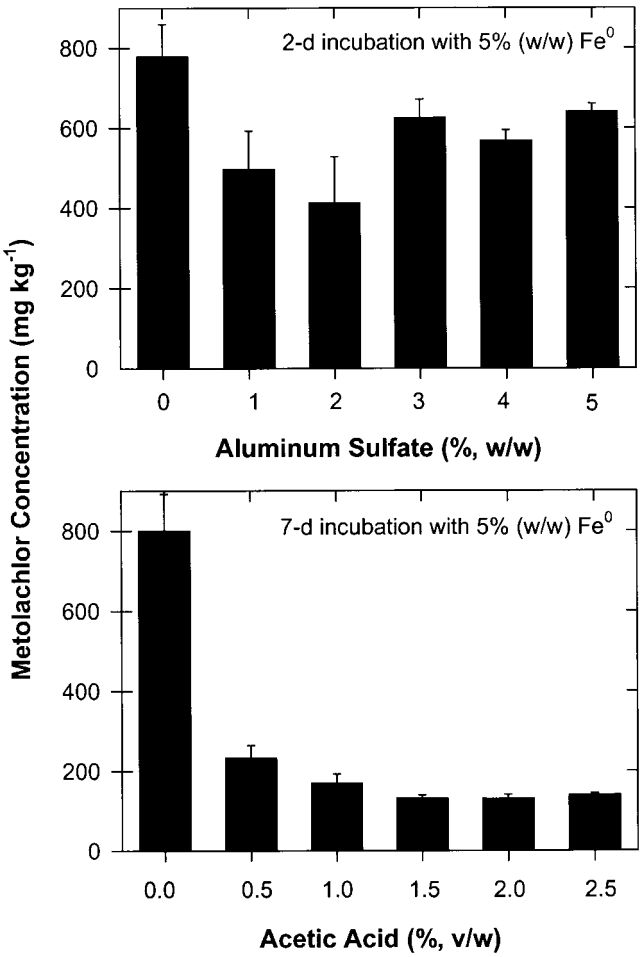

Fig. 5. Effects of $Al_2(SO_4)_3$ and acetic acid on metolachlor destruction in static soil microcosms treated with 5% (w/w) Fe^0.

Table 3. Soil pH following treatment with zerovalent iron.

Treatment	Initial (mixed)†	1 d	14 d	28 d	42 d	60 d	75 d	90 d	90 d (mixed)
Control	6.45b‡	5.44a	5.99a	6.03a	6.16a	6.03a	6.03a	6.13a	6.06a
Fe^0	6.55b	8.43d	8.29c	8.23c	8.17c	7.87c	7.84bc	7.74bc	8.22d
Fe^0 + CH_3COOH	6.43b	8.39d	8.36c	8.59c	8.49c	8.46d	8.38c	8.16c	8.75e
FE^0 + $AL_2(SO_4)_3$	6.45b	7.01c	7.43b	7.39b	7.44b	7.16b	7.23b	7.03b	7.22b
Fe^0 + CH_3COOH + $Al_2(SO_4)_3$	6.05a	6.37b	7.16b	7.27b	7.52b	7.46bc	7.53b	7.51bc	7.50c

† Mixed: windrows were mixed three times immediately before sampling.
‡ Values with same letter within columns are not significantly different ($\alpha = 0.05$).

Changes in Soil Chemical Properties

Initial analysis of the contaminated soil indicated that, in addition to metolachlor, this soil had very high concentrations of NO_3^-, NH_4^+, and P as well as diethylenetriaminepentaacetic acid (DTPA)–extractable metals (Zn, Mn, Fe, Cu) (Table 1). Following 90 d of treatment, some notable increases and decreases in soil chemical properties were observed (Table 1). Phosphorus concentrations decreased in windrows receiving $Al_2(SO_4)_3$. Aluminum sulfate has been traditionally used to remove phosphate from wastewater streams by forming $AlPO_4$ (Snoeyink and Jenkins, 1980). Hsu (1976) indicated the optimum pH for P removal by Al was 5.5 to 8.0, well within the range observed in the soil windrows (Table 3). Under acidic conditions (pH $<$ 6), $AlPO_4$ predominates, whereas at pH 6 to 8, an $Al(OH)_3$ forms, which removes P from solution by sorption of inorganic phosphate and entrapment of organic particles containing P (Cooke et al., 1986).

Nitrate concentrations were also reduced substantially by all Fe^0 treatments, corroborating previous research showing transformation of NO_3^- to NH_4^+ upon addition of Fe^0 (Cheng et al., 1997; Till et al., 1998). Other notable changes include an increase in Cl^-, which is probably attributable to dechlorination of metolachlor, as well as increases in SO_4^{2-} for treatments receiving $Al_2(SO_4)_3$ (Table 1). Although adding $Al_2(SO_4)_3$ with Fe^0 increased metolachlor destruction, the high SO_4^{2-} concentrations observed after treatment are a potential concern, especially in terms of salinity and subsequent influence on plant growth. It is also noteworthy that despite the large additions of Fe^0 and aluminum added to the soil, changes in DTPA-extractable iron increased only about eightfold (40 to ca. 300 mg kg^{-1}) and no increases in extractable aluminum were observed (Table 1).

The ability of aluminum to complex with acidic functional groups of soil humus has been well documented (McBride, 1994). This property was manifested in the soil extracts from windrows receiving $Al_2(SO_4)_3$, which were transparent, whereas the others were dark brown. Binding of the dissolved organic fraction by the Al oxides probably explains the decreases in extractable organic matter observed in the $Al_2(SO_4)_3$ treatments and corresponding increases in cation exchange capacity (CEC) (Table 1).

Treatment Costs

In many U.S. states, pesticide-contaminated soils are usually handled in one of three ways: the contaminated soil is reapplied to farmland at label rates or the soil is excavated and shipped to a certified landfill or incinerated (Paulson, 1998). Land-spreading is relatively easy if access to appropriate acreages is obtained and pesticide concentrations are low, but problems arise when the soil contains more than one pesticide (limiting cropping options) or is grossly contaminated and requires dilution. Incineration or landfill options are often too costly and neither treat the soil on-site. Given the multitude of pesticide-contaminated sites on individual farms and cooperatives throughout the USA, additional treatment options are needed that can be readily implemented and are inexpensive for end-users.

An important factor in evaluating remediation technologies is cost. Although factoring in labor, capital outlays, and equipment depreciation is complicated, listing chemical expenditures per mass of soil treated is relatively straightforward. Given that the soil was treated with 5% Fe^0 (w/w), and the unit cost of Fe^0 (bagged and delivered) was \$0.63 per kg, we calculated the cost of Fe^0 at \$44 per m^3 (\$34 per yd^3). Using a similar approach for the $Al_2(SO_4)_3$ (unit cost: \$0.37 per kg) and acetic acid (\$0.90 per L), the cost of these additions per cubic meter (m^3) of soil was \$10.35 (\$8 per yd^3) for $Al_2(SO_4)_3$ and \$6.33 (\$4.84 per yd^3) for acetic acid. Collectively, total chemical expenditures varied between \$44 and \$61 per m^3 (\$34–\$47 per yd^3). Additional costs were incurred for soil mixing, plastic sheeting, and analytical sampling. Unless personnel in charge of treating a contaminated site have access to their own mixing equipment, custom soil mixing would need to be factored into the overall costs. Soil mixing costs are often price-quoted on the volume of soil treated. H&H EcoSystems, the vendor of the soil mixing implement we used, estimated custom mixing charges of approximately \$33 per m^3 (\$25 per yd^3) for the volume of soil treated (T. Horn, H&H EcoSystems, personal communication, 2000). Therefore, chemical amendments plus mixing charges for treatment of the contaminated soil ranged between \$77 and \$94 per m^3 (\$59–\$72 per yd^3). This exceeds typical charges for land-spreading (ca. \$39 per m^3 or \$30 per yd^3) but is considerably less than what would be charged for removal and disposal by incineration (\$261–\$1961 per m^3, \$200–\$1500 per yd^3; USEPA, 1990). The quote from the local incinerator in Nebraska was \$790 per m^3 (\$604 per yd^3). Although land-spreading appears to be the most economical treatment currently available, this option may not be allowed for soils contaminated with the numerous pesticides that have been suspended or banned. Therefore, when land-spreading is not an option, results from our field trial support the

use of Fe^0 as a possible alternative for on-site treatment of pesticide-contaminated soil.

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