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Pilot-Scale Treatment of RDX-Contaminated Soil with Zerovalent Iron

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ABSTRACT

Soils in Technical Area 16 at Los Alamos National Laboratory (LANL) are severely contaminated from past explosives testing and research. Our objective was to conduct laboratory and pilot-scale experiments to determine if zerovalent iron (Fe^0) could effectively transform RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) in two LANL soils that differed in physicochemical properties (Soils A and B). Laboratory tests indicated that Soil A was highly alkaline and needed to be acidified [with H_2SO_4, $Al_2(SO_4)_3$, or CH_3COOH] before Fe^0 could transform RDX. Pilot-scale experiments were performed by mixing Fe^0 and contaminated soil (70 kg), and acidifying amendments with a high-speed mixer that was a one-sixth replica of a field-scale unit. Soils were kept unsaturated (soil water content = 0.30–0.34 kg kg^{-1}) and sampled with time (0–120 d). While adding CH_3COOH improved the effectiveness of Fe^0 to remove RDX in Soil A (98% destruction), CH_3COOH had a negative effect in Soil B. We believe that this difference is a result of high concentrations of organic matter and Ba. Adding CH_3COOH to Soil B lowered pH and facilitated Ba release from $BaSO_4$ or $BaCO_3$, which decreased Fe^0 performance by promoting flocculation of humic material on the iron. Despite problems encountered with CH_3COOH, pilot-scale treatment of Soil B (12 100 mg RDX kg^{-1}) with Fe^0 or Fe^0 + $Al_2(SO_4)_3$ showed high RDX destruction (96–98%). This indicates that RDX-contaminated soil can be remediated at the field scale with Fe^0 and soil-specific problems (i.e., alkalinity, high organic matter or Ba) can be overcome by adjustments to the Fe^0 treatment.

Soil and water contamination from munitions stockpiles and decommissioned production plants continues to be a serious environmental problem at many locations throughout the USA. Much of this pollution occurred from past discharges of explosive-tainted wastewater to settling ponds or impoundments, resulting in severe ground water contamination. This type of contamination is present at the Los Alamos National Laboratory (LANL, Los Alamos, NM) where ground water sampling has identified several high explosives. Ground water samples taken between 228 to 592 m verified that several high explosives and known degradates were present to a depth of 490 m. The high explosives most commonly found included hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazine (HMX), 2,4,6-trinitrotoluene (TNT), 4-amino-2,6-dinitrotoluene, 2-amino-4,6-dinitrotoluene, and 1,3,5-trinitrobenzene. Much of this ground water contamination can be linked to manufacturing activities that began in the 1940s at the southwestern edge of the laboratory known as Technical Area 16 (TA-16) (Environmental Restoration Project, 2001). Operations at TA-16 included high explosives research, development, testing, and manufacturing.

Soils located in TA-16 are grossly contaminated, with some soils containing high explosive concentrations of >20% (w/w). This magnitude of contamination is excessive and indicates that precipitated or solid-phase high explosives are present in the soil matrix. When soils contain solid-phase contaminants, soil solutions become saturated and natural attenuation processes are severely inhibited. Using ^{14}C-RDX, Singh et al. (1998a) demonstrated that the presence of solid-phase RDX in the soil matrix prevented the formation of bound (unextractable) residue. Consequently, remediating highly contaminated soils requires aggressive soil treatments that are sustainable and can continue to remove contaminants from the soil solution as the solid-phase residues dissolve.

Zerovalent iron (Fe^0) has an excellent potential to abiotically remediate RDX-contaminated water and soil (Hundal et al., 1997; Singh et al., 1998b, 1999). Hundal et al. (1997) found Fe^0 effectively destroyed RDX in aqueous solution and soil slurries. Aqueous batch experiments indicated that as little as 1% Fe^0 (w/v) effectively transformed 32 mg RDX L^{-1}. Moreover, transformation products (measured as ^{14}C activity) were water-soluble and not strongly sorbed to the iron surface. Producing non-adsorbing transformation products can be advantageous if these products are biodegradable. Singh et al. (1998b) tested this hypothesis by using ^{14}C-RDX in static microcosms and measuring mineralization by trapping evolved $^{14}CO_2$. Results showed that a single Fe^0 amendment increased RDX mineralization, with greater than 60% of the ^{14}C-RDX recovered as $^{14}CO_2$. Considering carbon use efficiencies for most organic compounds, these data indicate that the Fe^0–induced transformation products of RDX are highly biodegradable. Subsequent studies (Wildman and Alvarez, 2001; Oh et al., 2001; Oh and Alvarez, 2002) further support synergistic effects between Fe^0 treatment and enhanced biological degradation of RDX.

Although Hundal et al. (1997) observed that Fe^0 effectively transformed RDX in soil slurries, working with soil slurries is problematic for several reasons. The equipment required for continuous agitation is expensive and limits the volume of soil that can be treated at any given time. Dewatering of treated soil is also required. A desirable alternative to slurry treatment would be on-site treatment in soil windrows. Using soil windrows allows much greater volumes of soil to be treated and is constrained by only the size of the windrows and acreage available.

Initial work with RDX-contaminated soil from the

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Abbreviations: Fe^0, zerovalent iron; LANL, Los Alamos National Laboratory.

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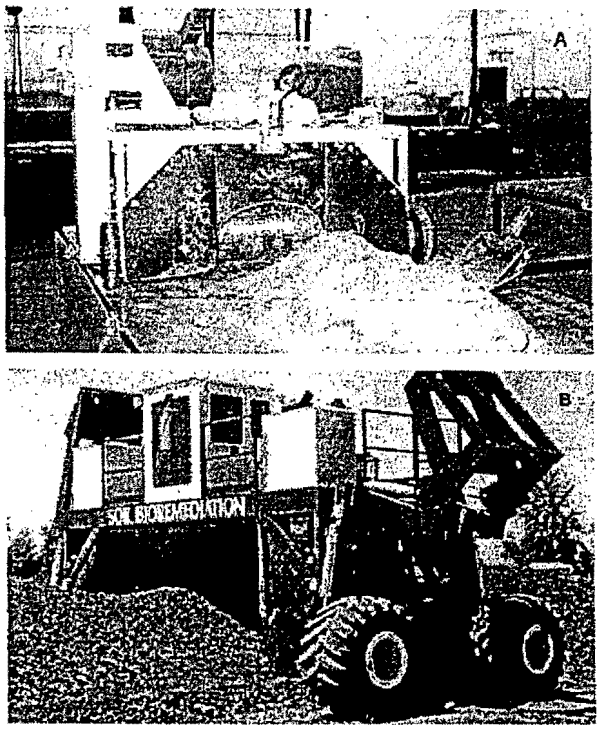

Fig. 1. Photographs of Microenfractionators. (*A*) Pilot-scale table-top unit (one-sixth scale of the field unit). (*B*) Field-scale Microenfractionator going through soil windrow; dimensions of the windrow are: base = 5.2 m, height = 1.98 m.

abandoned Nebraska Ordnance Plant (Mead, NE) indicated that Fe^0 could be effective in static unsaturated soil microcosms (Singh et al., 1998b). The effectiveness of Fe^0 in transforming RDX in unsaturated soils opened the door for field-scale applications. Using zerovalent iron at the field scale requires machinery that can thoroughly mix the iron and other amendments into the soil matrix. The Microenfractionator (H & H Eco Systems, North Bonneville, WA) is the trade name of a soil mixing implement that can treat large volumes of soil (400–1000 m^3 h^{-1}). This machinery can also simultaneously spray liquids into the soil windrows during mixing to achieve any desired water content.

Our objective was to combine Fe^0 treatment of RDX-contaminated soil with the machinery required for field-scale use. This was accomplished by conducting batch experiments in the laboratory to optimize Fe^0 applications and then testing these treatments at the pilot scale with a table-top version of the field-scale mixer (Fig. 1). Two high explosives–contaminated soils, indicative of the contamination found at LANL TA-16, were used for pilot-scale testing.

MATERIALS AND METHODS

Chemical Reagents and Soils

Technical-grade RDX was obtained from the U.S. Biomedical Research and Development Laboratory (Frederick, MD). Analytical standards of RDX were obtained from the Indian Head Division, Naval Warfare Center (Indian Head, MD) and AccuStandard (New Haven, CT). Two forms of Fe^0 were used. Degreased Fe^0 (40-mesh) was obtained from Fisher Scientific (Pittsburgh, PA). Analysis of similar iron (Fisher Scientific) by an outside laboratory determined a surface area of 1.87 m^2 g^{-1} using the Brunauer–Emmett–Teller (BET) method. The second Fe^0 source was unannealed iron from Peerless Metal Powders (Detroit, MI). This iron had a specific surface area of 2.55 m^2 g^{-1} (Micromeritics, Norcross, GA). Commercial-grade $Al_2(SO_4)_3$ and glacial acetic acid were used as received.

Two LANL soils were used for experimentation (hereinafter referred to as Soils A and B). Soil A used in the first batch and pilot-scale experiment was obtained from the center of a discharge pond approximately 100 m east of Building TA-16-260 at LANL TA-16. Soil B was from the same outwash pond but was mixed with material from the sides of the pond and discharge areas.

Soil A was sent to the University of Nebraska in a 208-L metal drum. Physical handling involved spreading the soil onto the stainless steel table of the pilot-scale mixer (Fig. 1A) and removing large stones (approximately >5 cm in diameter). A table-top fan was used to gently pass air across the soil surface to facilitate air-drying overnight. We then ran the Microenfractionator through the soil four times. The pilot-scale Microenfractionator is a one-sixth replica of the field-scale unit (Fig. 1B) and can mix 70 to 100 kg of windrowed soil in one pass. Much of the larger consolidated soil not removed by hand was broken apart and pulverized by the Microenfractionator, producing a homogeneous soil that was easy to handle. Once the soil had been mixed, it was divided into two piles and placed in plastic bins with covers. Five soil samples from each plastic bin were taken and analyzed for RDX. An additional subsample was sieved (<2 mm) before RDX analysis. Representative subsamples from each soil were also sent to Midwest Laboratories (Omaha, NE) for characterization (Table 1). Soil B was handled similarly using the same pilot-scale mixer but experiments were performed on-site at LANL.

Laboratory Experiments

Analysis of Soil A revealed an unexpected high pH (>9.9). Efforts were made to lower the pH of the soil slurry with acetic acid and determine the effectiveness of Fe^0. Five grams (oven-dry) soil was mixed with various amounts of 5% (v/v) acetic acid (total volume of acetic acid + H_2O = 11.75 mL) and allowed to equilibrate for 20 h. Solution pH was then determined with a meter and probe calibrated before each use with standard buffer solutions (Accumet, Fisher Scientific).

A separate experiment compared the effects of acids (HCl vs. CH_3COOH) on Fe^0-mediated destruction of RDX in aqueous solutions and soil washings under pH-stat conditions. The pH-stat experiments were conducted with a Metrohm Titrino (Model 718S; Brinkmann Instruments, Westbury, NY). Both the aqueous solutions of RDX (initial concentration = 20 mg L^{-1}) and aqueous soil washing of Soil A (concentration = 40 mg RDX L^{-1}) were treated with 1% (w/v) Fisher Scientific Fe^0. The pH was held at 4.5 with HCl or CH_3COOH and changes in solution RDX concentrations were determined at 2, 4, 8, and 24 h.

The effect of acidifying amendments on RDX destruction by Fe^0 in static soil microcosms was also investigated. In this experiment, triplicate samples from Soil A were incubated in Teflon centrifuge tubes at 30°C for 17 d at a gravimetric soil water content of 0.33 kg kg^{-1}. Treatments included: (i) Fe^0 + H_2O; (ii) Fe^0 + H_2SO_4; (iii) Fe^0 + $Al_2(SO_4)_3$; and (iv) Fe^0 + CH_3COOH. Controls (no Fe^0) were also included for each amendment [i.e., H_2O, H_2SO_4, $Al_2(SO_4)_3$, and CH_3COOH]. To increase soil water content to 0.33 kg kg^{-1}, 3 g of Soil A was

Table 1. Chemical and physical characteristics of Soils A and B from Los Alamos National Laboratory.

Soil property	Soil A	Soil B
RDX, mg kg^{-1}	2 700 (140)†	12 100 (814)
Organic matter, %	0.6 (0.1)	3.0 (0.2)
pH	9.9 (0.1)	7.0 (0.0)
Cation exchange capacity, cmol$_c$ kg^{-1}	20.0 (4.6)	6.7 (0.3)
Nitrate N, mg kg^{-1}	239.0 (63.6)	17.0 (1.2)
Sodium adsorption ratio	15.3 (0.4)	ND‡
Potassium, mg kg^{-1}	522.0 (15.6)	171.0 (14.7)
Magnesium, mg kg^{-1}	26.0 (2.8)	100.0 (5.0)
Calcium, mg kg^{-1}	3 223.0 (895.9)	1 070.0 (33.5)
Sodium, mg kg^{-1}	550.0 (15.6)	20.0 (1.0)
Sulfur, mg kg^{-1}	88.0 (12.0)	5.7 (0.6)
Zinc (DTPA)§, mg kg^{-1}	2.9 (0.2)	6.0 (1.0)
Manganese (DTPA), mg kg^{-1}	8.0 (0.7)	8.3 (1.5)
Iron (DTPA), mg kg^{-1}	17.0 (0.7)	14.0 (0.6)
Copper (DTPA), mg kg^{-1}	0.3 (0.0)	2.0 (0.1)
Boron, mg kg^{-1}	5.1 (6.9)	0.5 (0.1)
Barium¶, mg kg^{-1}	14.8	372
Sand, %	64.0 (2.8)	60.0 (4.0)
Silt, %	27.0 (1.4)	30.0 (4.0)
Clay, %	9.0 (1.0)	10.0 (0.0)

† Mean and sample standard deviation.
‡ Not determined.
§ Diethylenetriaminepentaacetic acid (DTPA)–extractable.
¶ Acetic acid in water (5%)–extractable (single measurement).

treated with 0.15 g Fe^0 (5%, w/w) and 1 mL of H_2O, acidified water (H_2SO_4, pH 2.0), H_2O + $Al_2(SO_4)_3$ (6 mg), or CH_3COOH (10%, v/v).

Pilot-Scale Experiments

Study I (Soil A)

Pilot-scale experiments were conducted with 70 kg (oven-dry) soil. The initial study was conducted with Soil A using two treatments: Fe^0 + CH_3COOH and a control (H_2O only). The soil was placed on the stainless steel table of the mixer (Fig. 1) and Fe^0 added to a V-shaped indentation along the top ridge of the soil windrow. Iron (3.5 kg) was added to the 70 kg of soil to yield a concentration of 5% (w/w). The soil and iron were then mixed by the Microenfractionator three times. The Fe^0–amended soil was evenly divided into five 16.25-kg volumes and placed in layers in a large plastic bin where 2.65 L of water–CH_3COOH was sprinkled onto the soil to raise the gravimetric water content to 0.30 kg kg^{-1}. Glacial acetic acid (1.05 L) was mixed with water and added to the soil to theoretically yield an initial concentration of 5% CH_3COOH (v/v) in the soil solution. This was determined by measuring the initial water content of the soil (0.11 kg kg^{-1}), calculating the additional water needed to bring the soil water content to 0.30 kg kg^{-1} (13.25 L), and adding the acetic acid to the water. The control treatment (no Fe^0) was handled similarly but only water was added. Soil bins were covered and placed in a controlled environment chamber at 30°C in the dark.

Sampling consisted of pushing a hand-held soil probe (i.d. = 1.905 cm; length = 30.48 cm) perpendicularly into the soil. The location of each soil core taken by date and replicate was recorded on a grid coordinate. Four soil cores were taken from each bin at 0, 10, 20, 40, 60, 80, and 110 d after treatment. Soil samples were held in plastic whirl top bags at 4°C until analysis. Soil analysis included pH (1:1 soil to H_2O), RDX concentration, and soil water content. Once gravimetric soil water content fell below 0.25 kg kg^{-1}, additional water and/or CH_3COOH were added to the soil and allowed to infiltrate. This resulted in adding water to the Fe^0 treatment on Day 10 (2.92 L) and water–CH_3COOH (3.33 L, 10% CH_3COOH, v/v) on Day 60. On Day 40, water (3.08 L) was added to the control.

Study II (Soil B)

A second pilot-scale experiment was conducted at the LANL using a second soil from the drainage pond (Soil B). In this experiment, procedures similar to Study I were followed but the number of treatments was expanded. These included: (i) control (H_2O only); (ii) Fe^0; (iii) Fe^0 + CH_3COOH; (iv) Fe^0 + $Al_2(SO_4)_3$; and (v) Fe^0 + CH_3COOH + $Al_2(SO_4)_3$. In this experiment, Fe^0 (5%, w/w) and acetic acid (1.05 L per 70 kg) were added at the same rate used in Study I and $Al_2(SO_4)_3$ was added at 2.0% (w/w). Soil samples were taken at 0.5 h and 10, 20, 40, 60, 80, 100, and 120 d after treatment. The soil water content was increased to 0.34 kg kg^{-1} in Soil B and the soil bins were incubated in the dark at approximately 28°C.

Batch Experiments Using Witherite and Acetic Acid

When acetic acid was added as an amendment, differences in RDX destruction were observed between Soil A and B (see Results). Acetic acid extracts of Soil A and B revealed large differences in Ba concentrations. Subsequent batch experiments were conducted to determine the effects of Ba and acetic acid on Fe^0 performance. This was accomplished by treating 100 mL of aqueous RDX (20 mg RDX L^{-1}) and RDX in a humic acid matrix (50 mg L^{-1}, International Humic Substances Society Reference #1R102H) with Fe^0 and various additions of acetic acid and Ba. Treatments included: (i) Fe^0 (2%, w/v); (ii) Fe^0 + 0.1 g witherite ($BaCO_3$); (iii) Fe^0 + CH_3COOH (0.5%, v/v); and (iv) Fe^0 + witherite + CH_3COOH. To test the effects of these treatments on long-term Fe^0 performance, experiments were conducted in three cycles where treatment solutions were sampled during the first 24 h and then decanted, and fresh RDX solutions (with $BaCO_3$ and CH_3COOH treatment additions) were added to the original Fe^0 followed by sampling for another 24 h. To test the residual effects of each treatment on Fe^0 performance, only aqueous RDX or RDX + humic acid (without $BaCO_3$ or CH_3COOH) was added in the third cycle.

Chemical and Physical Analyses

RDX was extracted from soil (3 g) with 15 mL CH_3CN by sonicating for 18 h at 30°C, centrifuging at 5000 × g, removing the supernatant, and centrifuging (12 000 × g) before analyz-

ing with high performance liquid chromatography (HPLC). Acetonitrile extracts (10–25 μL) were injected onto a Keystone Betasil NU(R) or NA column (Keystone Scientific, Bellefonte, PA) with an isocratic (50:50 or 30:70) mixture of methanol and H_2O at a flow rate of 1.0 mL min^{-1} and quantified spectrophotometrically at 220 or 254 nm. In the second pilot-scale experiment (Study II, Soil B), TNT was also quantified using the same HPLC procedure.

Acetic acid extracts of Soil A and B were prepared by shaking 25 g soil with 50 mL of CH_3COOH (5%, v/v) for 24 h and centrifuging at 5000 × *g* for 30 min. The supernatant was analyzed for Ba by inductively coupled plasma (ICP) (Midwest Laboratories).

RESULTS

Soil Analysis

Analysis of Soil A revealed an average RDX concentration of 2700 ± 140 mg kg^{-1} (n = 10) following mixing (Table 1). After passing the mixed soil through a 2-mm sieve, the sieved soil had a RDX concentration of 3150 ± 84.4 mg kg^{-1} (n = 4) indicating that contamination is mainly associated with the finer soil fraction. Additional chemical analyses revealed that Soil A was very high in Na, Ca, and K. A discrepancy was noted in soil pH between the commercial laboratory (pH 9.9) and our laboratory (11.1, n = 5). These very high pH values are probably a result of the high Na concentration. Based on the sodium adsorption ratio (SAR = 15.3), Soil A would be classified as either sodic or sodic-saline (the electrical conductivity of a paste extract was not measured).

The unexpected high pH of Soil A was in part the impetus for a second study using Soil B. Analysis of Soil B revealed a near-neutral pH with lower K, Ca, and Na concentrations but considerably greater RDX contamination (12 100 ± 814 mg kg^{-1}). Soil B also contained more organic matter (Table 1).

Laboratory Experiments

Initial efforts to remove RDX from Soil A with Fe^0 failed and it was believed that the high soil pH was rapidly passivating the Fe^0 and reducing electron transfer from the iron surface. We hypothesized that the soil pH needed to be lowered before Fe^0 would be effective. To accomplish this, various concentrations of acetic acid were added to a soil slurry. Following 20 h of equilibration, the initial pH of the slurry declined from 11.1 (no CH_3COOH added) to 4.7 (2.13% CH_3COOH, v/v). To determine how lowering pH would affect RDX destruction by Fe^0, we used a pH-stat to maintain constant pH (4.5) and determined destruction kinetics. We observed that for both pure aqueous solutions and aqueous extracts of Soil A (soil washings), RDX destruction was faster when CH_3COOH was used to control pH rather than the mineral acid HCl (Fig. 2).

Additional acidifying amendments were then evaluated to determine RDX destruction in static soil microcosms incubated for 17 d. This experiment demonstrated that the acidifying amendments improved the effectiveness of Fe^0 to remove RDX from Soil A (Table 2). The

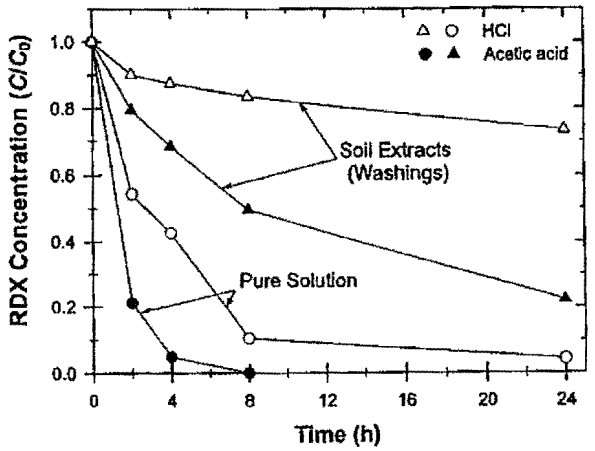

Fig. 2. Comparison of RDX destruction rates at constant pH 4.5 using HCl and CH_3COOH. Fisher Scientific Fe^0 was used at a rate of 1% (w/v). Aqueous soil washing was prepared from Soil A by creating a 20% (w/v) soil slurry, removing the soil, and treating the supernatant. Soil extract C_0 = approximately 40 mg RDX L^{-1}; pure solution C_0 = approximately 20 mg RDX L^{-1}.

RDX destruction with CH_3COOH and $Al_2(SO_4)_3$ was 99%. Controls verified that these acidifying solutions had little to no effect on RDX concentrations in the absence of Fe^0.

Pilot-Scale Experiments

Study I (Soil A)

Temporal changes in soil RDX concentrations revealed RDX destruction in both treatments (control and Fe^0–CH_3COOH, Table 3). At each sampling, less RDX was present in the Fe^0–CH_3COOH treatment than the control. At 110 d, 50 mg RDX kg^{-1} remained in the Fe^0-treated soil (98% destruction) versus 313 mg kg^{-1} in the control. Monitoring pH revealed that the CH_3COOH was somewhat effective in lowering the pH to <9 while the control soil pH remained ≥10.5 (Table 3).

Loss of RDX in the control treatment was unexpected and probably resulted from the unusually high soil pH observed throughout most of the experiment (pH 10.4–11.1; Table 3). RDX is known to undergo alkaline hydrolysis through bimolecular elimination of HNO_2, leading to a cyclohexenyl derivative intermediate (Hoffsommer et al., 1977; Croce and Okamoto, 1979). Further decomposition can lead to HCN, HNO_2, NO_2, HCHO, and N_2O (Hawari, 2000). Heilmann et al. (1996) also demonstrated rapid RDX hydrolysis (within 300 min) in solution at pH 11 and 50°C.

Monitoring soil water status during the experiment revealed that gravimetric water content was maintained between 0.25 and 0.30 kg kg^{-1} (data not shown). It is noteworthy that treatments were initiated by mixing the soil with the high-speed mixer but no mixing was performed when additional H_2O and/or CH_3COOH was added. Rather, the solutions were added to the top of the soil and allowed to infiltrate. In the field, this

Table 2. Batch experiments demonstrating changes in RDX concentrations in Soil A following treatment with Fe^0 and acidifying amendments. Static microcosms were incubated 17 d at 0.30 kg kg^{-1} and 30°C.

Treatment	RDX concentration	Reduction†
	mg kg^{-1}	%
Initial concentration (C_i)	2860 (101)‡	
	Iron treatments	
$Fe^0 + H_2O$	2240 (621)	22
$Fe^0 + H_2SO_4$	520 (190)	82
$Fe^0 + Al_2(SO_4)_3$	21 (1.5)	99
$Fe^0 + CH_3COOH$	37 (24)	99
	Controls	
H_2O (pH = 5.33)§	2520 (147)	12
H_2SO_4 (pH = 2.02)	2870 (192)	0
$Al_2(SO_4)_3$ (pH = 3.48)	2860 (175)	0
CH_3COOH (pH = 2.29)	2740 (138)	4

† Percent reduction = [1 − (RDX concentration/initial RDX concentration)] × 100.
‡ Values in parentheses represent sample standard deviations (n = 4).
§ pH values of solutions added to Soil A samples.

procedure would be recommended to minimize aeration of the soil windrow and accelerated aging (passivation) of the Fe^0.

One qualitative difference between the treatments was the abundant growth of fungal hyphae on the Fe^0–CH_3COOH-treated soil. This occurred within a few days after treatment and continued throughout the course of the experiment. No fungal growth was observed on the control soil.

We also noticed that the Fe^0–CH_3COOH-treated soil became more dense and difficult to probe for sampling. Because of the added acidity, some of the carbonates dissolved and effervesced following CH_3COOH addition. Consolidation and cementation of the precipitates probably resulted in a denser soil matrix. Additional mixing with the Microenfractionator following treatment would probably eliminate this problem.

Study II (Soil B)

High explosive concentrations in the control treatments (control and control + H_2O) indicated fairly constant RDX concentrations throughout the experiment with an average RDX concentration of 12 300 ± 634 mg kg^{-1} (Table 4). TNT concentrations, however, slowly declined with time indicating TNT degradation in the control. The variability and fluctuation in RDX concentrations is a function of the heterogeneity of contamination, which included solid-phase RDX intermixed throughout the soil matrix. Comparing results between the controls and the Fe^0–based treatments revealed that TNT and some RDX were transformed shortly after mixing (t = 0.5 h; Table 4). This demonstrates that abiotic transformations induced by Fe^0 can occur fairly quickly even in static, unsaturated soils. Moreover, relative declines in TNT concentration versus RDX immediately after Fe^0 treatment support that TNT is a preferential electron acceptor and more prone to reductive transformation by Fe^0.

Acidifying amendments were more effective in lowering and maintaining the pH of Soil B. The pH of the control ranged from 6.6 to 7.0 while the addition of Fe^0 increased pH from 7.2 (t = 0.5 h) to 8.6 (t = 120 d). Adding $Fe^0 + CH_3COOH$ decreased the pH, which remained low throughout the incubation [pH 4.5 (t = 0.5 h), 5.0 (t = 120 d)]. Similar results were observed with $Fe^0 + Al_2(SO_4)_3$ [4.8 (t = 0.5 h) to 6.3 (t = 120 d)] and $Fe^0 + CH_3COOH + Al_2(SO_4)_3$ [3.9 (t = 0.5 h), 4.8 (t = 120 d)]. Previous research has shown that RDX solubility is essentially constant between pH 4.2 and 6.2 (Lynch et al., 2001).

Results from the second pilot-scale experiment were not consistent with the first study (using Soil A) or laboratory batch studies. Using Soil B, we found that the largest destruction of RDX (and TNT) occurred with the Fe^0–only and $Fe^0 + Al_2(SO_4)_3$ treatments. Using Fe^0 alone, RDX concentrations decreased to 540 mg kg^{-1} (t = 120 d) resulting in a 96% reduction from the average initial concentration of the control (12 100 mg RDX kg^{-1}). The $Fe^0 + Al_2(SO_4)_3$ treatment was also equally effective and produced the lowest average concentration after 120 d (210 mg kg^{-1}, 98% decline; Table 4). Adding CH_3COOH, which had a positive effect on Fe^0–induced RDX destruction in solution (Fig. 2) and static soil microcosms (Soil A, Table 2), negatively affected RDX and TNT loss compared with Fe^0 alone in the second pilot-scale experiment (Table 4). When CH_3COOH was added, decreases in RDX and TNT concentrations occurred only within the first 10 d. This is in contrast to the Fe^0 and $Fe^0 + Al_2(SO_4)_3$ treatments where RDX loss continued to decline after 20 d. While a beneficial effect was observed by adding $Al_2(SO_4)_3$, this effect was negated when CH_3COOH was also added.

To determine why acetic acid had an inhibitory effect on Fe^0 performance in Soil B, an acetic acid extract of both soils was analyzed by inductively coupled plasma. This analysis revealed large differences in Ba concentra-

Table 3. Changes in RDX and pH following pilot-scale treatment of Soil A.†

Treatment	Days after application						
	0	10	20	40	60	80	110
				RDX concentration, mg kg^{-1}			
Control (H_2O only)	2320 (222)‡	1600 (94)	1230 (117)	1020 (106)	709 (132)	624 (113)	313 (119)
$Fe^0 + CH_3COOH$	2310 (222)	1150 (321)	890 (77)	600 (40)	623 (403)	158 (145)	50 (10)
				pH			
Control (H_2O only)	10.35	11.00 (0.13)	11.10 (0.03)	10.80 (0.03)	10.60 (0.05)	10.60 (0.18)	10.50 (0.11)
$Fe^0 + CH_3COOH$	9.99	9.12 (0.26)	8.96 (0.21)	8.60 (0.30)	8.74 (0.17)	8.00 (0.40)	8.80 (0.18)

† Initial treatments were added at Day 0. Soil was incubated at 30°C and soil water content was maintained between 0.25 and 0.30 kg kg^{-1}.
‡ Values in parentheses indicate standard deviation of subsample mean.

Table 4. Changes in RDX and TNT concentrations following pilot-scale treatment of Soil B with zerovalent iron.

Soil treatment	High explosive	Time after application							
		0.5 h	10 d	20 d	40 d	60 d	80 d	100 d	120 d
		mg kg^{-1}							
Control (dry soil)	RDX	10 940 (1 082)†	12 700 (512)	12 580 (2 285)	12 300 (812)	12 930 (1 377)	11 320 (1 327)	ND‡	ND
	TNT	844 (131)	810 (84)	762 (223)	700 (8)	560 (56)	500 (63)	ND	ND
Control (H_2O only)	RDX	12 700 (352)	12 500 (633)	13 000 (320)	12 800 (617)	12 200 (742)	11 800 (543)	12 600 (251)	11 600 (959)
	TNT	900 (20)	770 (72)	750 (34)	660 (29)	560 (38)	430 (24)	430 (27)	430 (27)
Fe^0	RDX	9 940 (735)	3 194 (3 084)	1 400 (1 500)	471 (529)	26 (25)	763 (518)	250 (76)	540 (270)
	TNT	150 (30)	40 (40)	20 (2)	15 (6)	10 (3)	8 (4)	30 (5)	20 (5)
Fe^0 + CH_3COOH	RDX	7 920 (413)	3 180 (416)	3 850 (2 460)	2 958 (2 493)	3 100 (680)	3 060 (292)	3 110 (1 370)	5 120 (674)
	TNT	81 (12)	20 (8)	41 (21)	30 (30)	23 (11)	10 (4)	20 (7)	20 (7)
Fe^0 + $Al_2(SO_4)_3$	RDX	10 200 (598)	1 600 (230)	210 (210)	846 (298)	126 (158)	248 (489)	372 (366)	210 (140)
	TNT	370 (22)	15 (2)	20 (4)	20 (6)	10 (1)	10 (8)	20 (2)	20 (2)
Fe^0 + CH_3COOH + $Al_2(SO_4)_3$	RDX	9 820 (387)	5 430 (977)	3 439 (1 373)	3 950 (1 220)	3 492 (1 518)	2 720 (1 110)	3 890 (934)	4 414 (1 529)
	TNT	180 (18)	49 (18)	32 (14)	36 (13)	29 (18)	10 (8)	30 (7)	30 (7)

† Values in parentheses indicate standard deviation of subsample mean.
‡ Not determined.

tions (Table 1). Past activities in sector TA-16 at LANL indicate that the likely source of Ba was $Ba(NO_3)_2$, which was mixed with TNT to produce the explosive baritol. Analysis of soils at LANL by X-ray diffraction (XRD) and scanning electron microscopy (SEM) indicate that most of the Ba is now in the form of barite ($BaSO_4$) and witherite ($BaCO_3$) (Don Hickmott, LANL, personal communication, 2001). Because $BaSO_4$ and $BaCO_3$ are not readily soluble in water (28.5 mg L^{-1} for $BaSO_4$ and 24 mg L^{-1} for $BaCO_3$; Dean, 1992), we believe less Ba was present in the soil solution of the Fe^0–only treatment. One notable observation from the acetic acid extracts was differences in color. The extract from Soil A was amber while Soil B was clear. Aqueous extracts from both soils were also amber. This qualitative difference indicates precipitation of humic materials in the acetic acid extract of Soil B.

Batch Experiments with Barium and Humic Acid

Our batch experiments confirmed that Ba (witherite) did not directly interfere with the Fe^0 treatment in an aqueous matrix because small additions of $BaCO_3$ actually increased RDX destruction. In the humic acid matrix, however, Ba decreased the effectiveness of Fe^0 (Cycle 1, Fig. 3). Acetic acid facilitated RDX destruction in both the aqueous and humic acid matrices during the first two cycles but RDX destruction was hindered when fresh acetic acid was not added to the humic acid matrix (Cycle 3, Fig. 3). Following Cycle 2, a brown floc (slime) was observed on the iron surface in the acetic acid treatments, which we believe was precipitated humic material. Without the addition of more acetic acid this precipitated material probably remained with the iron and prevented efficient RDX destruction. There is some evidence that the combination of Ba and CH_3COOH was also inhibitory. Results from Cycle 3 showed a residual effect of witherite + CH_3COOH, which was least effective in removing RDX while CH_3COOH alone was the most effective (Cycle 3, Fig. 3). Another notable observation is increased RDX destruction by Fe^0 and Fe^0 + witherite in the humic acid matrix compared with the aqueous matrix (Cycle 1, Fig. 3).

These batch results corroborate our pilot-scale data because as evidenced by our sampling scheme, acetic acid did not hinder RDX destruction until after 10 or 20 d, when no further RDX loss was detected (Table 4). Based on our batch results, we believe the time when RDX destruction stopped in our pilot-scale experiment (Table 4) probably corresponded with the time the acetic acid concentration had declined and was no longer effective in preventing the precipitation or buildup of humic materials on the iron surface.

DISCUSSION

The results of our pilot-scale experiments are consistent with previous work (Singh et al., 1998b) and confirm RDX transformation by Fe^0 in static unsaturated soil. Because of the high RDX concentration in the soils, low sorption (Singh et al., 1998a), and a solubility of approximately 40 mg kg^{-1} at the 28 to 30°C incubation temperatures (Bier et al., 1999), the soil water content (0.30–0.34 kg kg^{-1}) was sufficient for RDX dissolution and movement to the surfaces of incorporated iron granules.

Addition of H_2SO_4, $Al_2(SO_4)_3$, and CH_3COOH significantly improved RDX destruction (82–99%) compared with Fe^0 alone (22%). Although all three amendments lowered soil pH, which would favor reductive transformations, it is unlikely that they all acted similarly in improving RDX destruction. While the initial effect of H_2SO_4 is probably due to acidification, a high sulfate concentration may favor formation of ferrihydrite over goethite (Brady et al., 1986), which can produce green rust as the pH increases (Taylor and McKenzie, 1980). Our previous research with Fe^0 and $Al_2(SO_4)_3$ indicated that $Al_2(SO_4)_3$ in the soil solution during iron corrosion can facilitate metolachlor dechlorination by increasing the concentration of available Fe(II) and favoring green rust formation (Comfort et al., 2001). The early work of Taylor and Schwertmann (1978) also revealed that a high concentration of aluminum slows down the oxidation of Fe(II) and results in precipitation of an Al-ferrihydrite, which can then transform to green rust.

Acetic acid can facilitate RDX destruction either in solution or in a soil matrix if Ba contamination is not a problem. As demonstrated in the pH-stat experiment (CH_3COOH vs. HCl), the beneficial effect of CH_3COOH

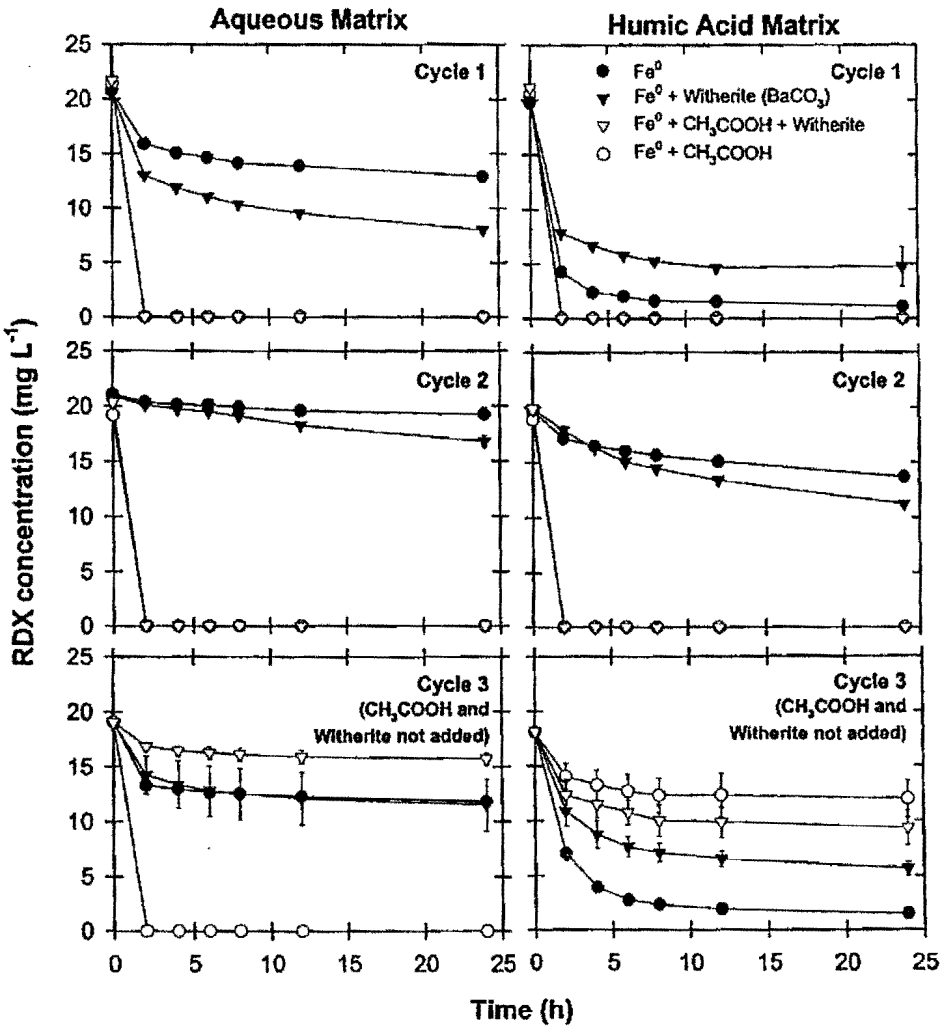

Fig. 3. RDX destruction by Fe^0 treatments in an aqueous matrix and humic acid (50 mg L^{-1}) matrix. Witherite and CH_3COOH were added to the matrices as indicated treatments in Cycles 1 and 2 but not in Cycle 3.

appears to be more than simple acidification of the RDX solution. Studies have shown that the reduction of compounds that have a weak interaction with the iron surface can be blocked by strong ligands (e.g., catechol, ascorbate, citrate) occupying surface sites (Cornell and Schwertmann, 1979; Johnson et al., 1998). The surface complexation model suggested by Scherer et al. (1999) indicates that if ligand competition is operative, destruction kinetics should rapidly decline toward zero as ligand concentration increases. However, this was not observed for CCl_4 dechlorination by Fe^0 in the presence of acetate (Johnson et al., 1998) nor in our experiments (RDX destruction increased). Because our experimental units were open to the atmosphere, formation of Fe(III) oxides was inevitable. Considering that the acetate ligand will complex with Fe^{2+} ($\log K_1 = 3.2$, $\log K_2 = 6.1$, $\log K_3 = 8.3$; Dean, 1992), this complex appears more resistant to oxidation. Visual evidence for this was observed in Fe^0–RDX–CH_3COOH mixtures where less Fe(III) species (i.e., rusting) occurred. High concentrations of CH_3COOH were used in our treatments; high concentrations of organic acids are known to inhibit crystallization of Fe(III) oxides (Cornell and Schwertmann, 1979). Acetic acid will also inhibit precipitation of $Fe(OH)_2$ and may promote formation of electron-conducting magnetite ($Fe_2^{III}Fe^{II}O_4$) on the iron surface through reaction of Fe^{2+} with amorphous Fe (hydr)oxides or γ-FeO(OH) (Tamaura et al., 1981, 1984). Unlike citrate and phosphate, acetate does not appear to suppress the crystal growth of magnetite (Sidhu et al., 1978). Thus by slowing down ferric oxyhydroxide formation on the iron surface and promoting magnetite formation, acetate would indirectly facilitate electron transfer from the iron. In addition, the increased microbial activity of Soil A after acetic acid addition (evidenced by fungal growth) may have further promoted RDX degradation.

Although Soil B had a high concentration of Ba ($BaSO_4$ or $BaCO_3$), it is unlikely that Ba alone reduced the effectiveness of the Fe^0 treatment because RDX destruction increased when witherite was added with

Fe^0 in an aqueous solution. Adding $BaCO_3$ may have promoted the carbonate form of green rust and slowed down Fe^0 corrosion because Ba does not readily hydrolyze (log K = 0.5; Dzombak and Morel, 1990, p. 105, 187) and adsorbs to the >FeOH surface as $>FeOHBa^{2+}$ (log K = 5.46; Dzombak and Morel, 1990, p. 105, 187). Adding acetic acid promoted dissolution of witherite and saturation of the iron surface with Ba. When acetic acid was no longer present in the matrix (Cycle 3), the witherite + CH_3COOH treatment removed the least RDX. This residual effect may be due to passivation of the iron surface.

Our solution experiments indicate that RDX destruction by Fe^0 was greater in the humic acid matrix than in aqueous solution (Cycle 1). Weber (1996) similarly observed that a Suwannee humic acid isolate acted as an electron transfer mediator in Fe^0 treatment of 4-aminoazobenzene. This mediating effect, however, may be compound specific because natural organic matter (NOM) had an inhibiting effect on Fe^0–mediated reduction of CCl_4 (Tratnyek et al., 2001). In our experiments, Fe^0 was less effective when $BaCO_3$ was added to the humic acid matrix. Considering that Ba is commonly used to determine soil acidity by displacing hydrogen on organic functional groups and results in flocculation of organic matter, we believe an indirect effect of high Ba in Soil B was precipitation of humic material at or near the iron surface, resulting in physical blocking and hindrance of electron transfer. Competition for surface sites on the iron may also be occurring, as observed between trichloroethylene and NOM (Tratnyek et al., 2001).

Because of the equilibrium between the soil solution and solid or crystalline phase, remediating soils containing solid-phase RDX will not only require treatments that demonstrate rapid destruction kinetics in solution but also those that continue to remove RDX as the solid phase dissolves. Dissolution of solid-phase RDX will depend on temperature and surface area (Lynch et al., 2002), crystal size and concentration gradients (Stumm and Morgan, 1996), as well as soil water content and saturation–desaturation cycles. Consequently, days to months may be required for all of the solid-phase RDX to enter the soil solution. For Fe^0 to be effective, it must continue to act as a reductant and engage in electron transfer reactions. Our experiments demonstrated that acetic acid greatly facilitated Fe^0–mediated RDX destruction but this destruction rate may not be sustainable in all soils. Based on differing results with Soils A and B, we found that soil physicochemical properties can profoundly affect Fe^0 performance, necessitating site-specific soil characterization before treatment. Alkaline soils such as Soil A will probably require pH adjustment whereas precipitation of humic material must be minimized in soils containing high concentrations of humic matter and/or Ba (as in Soil B). Moreover, variability arising from the nonuniform deposition of explosives and soil heterogeneity must be considered when treating munitions-contaminated soils.

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