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Remediating explosive-contaminated groundwater by in situ redox manipulation (ISRM) of aquifer sediments

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Received 25 May 2007; received in revised form 31 October 2007; accepted 1 November 2007

Available online 20 December 2007

Abstract

In situ chemical reduction of clays and iron oxides in subsurface environments is an emerging technology for treatment of contaminated groundwater. Our objective was to determine the efficacy of dithionite-reduced sediments from the perched Pantex Aquifer (Amarillo, TX) to abiotically degrade the explosives RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine), HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine), and TNT (2,4,6-trinitrotoluene). The effects of dithionite/buffer concentrations, sediments-solution ratios, and the contribution of Fe(II) were evaluated in batch experiments. Results showed that reduced Pantex sediments were highly effective in degrading all three high explosives. Degradation rates increased with increasing dithionite/buffer concentrations and soil to solution ratios (1:80–1:10 w/v). When Fe(II) was partially removed from the reduced sediments by washing (citrate-bicarbonate buffer), RDX degradation slowed, but degradation efficiency could be restored by adding Fe(II) back to the treated sediments and maintaining an alkaline pH. These data support in situ redox manipulation as a remedial option for treating explosive-contaminated groundwater at the Pantex site.

Published by Elsevier Ltd.

Keywords: Dithionite; Sediments; Degradation; RDX; HMX; TNT

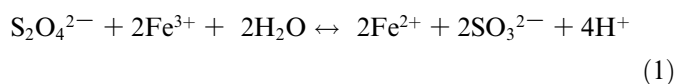
1. Introduction

The US Department of Energy's Pantex Plant at Amarillo, TX was constructed during World War II to produce conventional ordnances. In the 1950s, Pantex operations began using high explosives (HE) for manufacturing and assembling nuclear weapons. During production of conventional and nuclear weapons, HE-containing wastewater was routinely discharged into unlined ditches that eventually drained into an aquifer-recharging playa (Comfort, 2005). This practice ultimately contaminated the vadose zone and underlying perched aquifer with RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine), TNT (2,4,6-trinitrotolu-

ene), HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine), and several other contaminants (e.g., trichloroethylene (TCE), chromate). Among the three explosives, most attention has focused on RDX because it constitutes the majority of the plume that currently covers approximately 13 km² (Comfort, 2005). A groundwater pump and treatment system is in place to capture contaminants of concern in a section of the perched aquifer but site characteristics necessitate additional remedial technologies. The perched aquifer is ~90 m below the surface and only 30 m above the High Plains Aquifer, a major source of drinking water. Moreover, most of the perched aquifer is relatively thin (<4.5 m) and not amendable to a pump-and-treat remedial system. Collectively, these aquifer characteristics (depth and thickness) require an in situ remediation technology that can be implemented through injection wells.

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Several chemical and biological treatments have been proposed for remediating explosives-contaminated groundwater (Heijman et al., 1995; Van Aken and Agathos, 2001; Park et al., 2005). In situ redox manipulation or in situ chemical reduction is an emerging technology in which pH-buffered sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$) is injected into the aquifer. Because dithionite is a strong reductant, particularly in alkaline solutions (standard reduction potential = -1.12 V), it abiotically reduces and dissolves amorphous and some crystalline Fe(III) oxides (Amonette et al., 1998; Szecsody et al., 2004), producing several Fe(II) species including structural Fe(II) in clays, adsorbed Fe(II), siderite (FeCO_3) precipitates, and iron sulfides (FeS) (Hofstetter et al., 2003; Szecsody et al., 2004). Chemically reducing native Fe(III) in soils is faster than a biological approach (Amonette et al., 1994), but for this treatment to gain acceptance, the chemical reductant must be efficient and environmentally safe. Gan et al. (1992) found dithionite was most effective among various reductants evaluated in reducing structural iron in smectite. The overall reaction describing iron reduction by dithionite is



Dithionite and its reaction products (thiosulfate, sulfite, sulfate) are considered relatively nontoxic (Nzengungu et al., 2001) and thus offer an environmentally suitable means of treating contaminated groundwater. The overall success of in situ redox manipulation (ISRM), however, is contingent upon the aquifer containing enough iron oxides and iron-bearing clay minerals for the treated zone to remain effective (Amonette et al., 1994). Once the aquifer solids are reduced, subsequent oxidation of the adsorbed and structural ferrous iron in the reduced zone (i.e., redox barrier) occurs passively by the inflow of dissolved oxygen and contaminants that serve as electron acceptors (e.g., RDX, Cr(VI), TCE) (Szecsody et al., 2004).

Considerable research on ISRM has been conducted with chlorinated solvents and Cr(VI) (Fruchter et al., 2000; Szecsody et al., 2004) but only recently has this technology been investigated for high explosives. Initial testing by Pacific Northwest National Laboratory demonstrated that RDX was quickly degraded (within minutes) in batch and column studies by dithionite-treated sediments from the Pantex aquifer (Szecsody et al., 2001). As observed with zerovalent iron reduction of RDX (Singh et al., 1998), dithionite-reduced sediments also produced nitroso derivatives of RDX but these products were further reduced to ring fragments that were not strongly adsorbed (based on ^{14}C data; Szecsody et al., 2001). Subsequent biodegradation studies showed that the products of ^{14}C -RDX reaction with reduced sediments were readily biodegradable under aerobic conditions, with approximately 50% of the ^{14}C recovered as $^{14}\text{CO}_2$ after 100 d (Adam et al., 2005). Consequently, sequential abiotic reduction of RDX by a redox barrier followed by biodegradation of the transformed

products may provide a very efficient treatment for groundwater contaminated with HE.

To expand on previous observations between RDX and dithionite-reduced sediments (Szecsody et al., 2001), our objective was to determine degradation rates and products from the three HE present in the Pantex aquifer (i.e., TNT, HMX, and RDX). This was accomplished by evaluating treatment parameters such as dithionite/buffer concentrations, sediments-solution ratios, and the contribution of Fe(II) on degradation rates. The feasibility of regenerating the reductive capacity of the sediments following continued exposure to HE and oxygen was also determined.

2. Materials and methods

2.1. Chemicals and aquifer sediments

Technical grade RDX and TNT were obtained from the US Biomedical Research and Development Laboratory (Frederick, MD). HMX was obtained from Sandia National Laboratories (Albuquerque, NM). Reagent grade $\text{Na}_2\text{S}_2\text{O}_4$ and sodium citrate dihydrate crystals ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$) were purchased from Aldrich Chemical Co. (Milwaukee, WI) and sodium bicarbonate (NaHCO_3) from J.T. Baker (Phillipsburg, NJ). Ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) was obtained from Mallinckrodt Baker Inc. (Paris, KY), and K_2CO_3 and Optima™ grade methanol were purchased from Fisher Scientific (Fair Lawn, NJ). Deionized deoxygenated water (prepared by sparging with nitrogen) was used to prepare the aqueous solutions.

Nitrogen (N_2 , oxygen-free) and $\text{N}_2 + \text{H}_2$ (oxygen-free) gases were also required for the study. An O_2 -free environment was maintained within an anaerobic chamber (Coy Laboratory Products, Grass Lake, MI) by purging with O_2 -free N_2 (95% N_2 :5% H_2).

Sediments cores obtained from the perched Pantex aquifer (~90 m) were kept in a cold room (4.5 °C) until processed by sieving (<4-mm size fraction). Physicochemical characteristics of the aquifer sediments were determined by Midwest Laboratories (Omaha, NE) (Table 1). Soil pH was measured in water (1:1) using a combination electrode (Eckert, 1988). Organic matter was determined colorimetrically by chromic acid oxidation using Walkley-Black

Table 1
Physicochemical characteristics of sediments from the perched Pantex aquifer (Amarillo, TX)

Soil property	Unit	Value
Soil pH (1:1 solids, H_2O)		8.91 – 9.03
Organic matter	%	0.1 ± 0.0 ^a
Cation exchange capacity	meq 100 g ⁻¹	8.7 ± 0.21
DTPA-extractable Fe	mg kg ⁻¹	16.0 ± 7.5
Sand	%	90.7 ± 2.3
Silt	%	3.3 ± 1.2
Clay	%	6.0 ± 2.0

^a Sample standard deviation of means ($n = 3$).

method (Schulte, 1988). Cation exchange capacity was determined by saturating the soil with ammonium acetate, displacing it with NaCl and titrating with HCl (Rhoades, 1982). Extractable Fe was analyzed by extracting soil with DTPA and detecting Fe with inductively coupled argon plasma (Whitney, 1988). The particle size analysis was done by the hydrometer method (Gee and Bauder, 1986). Although mostly sand (91%), visual observations of the Pantex sediments during handling revealed that the perched aquifer sediments contained small pebble-size occlusions of clay.

2.2. Dithionite reduction of sediments

Fe(III) phases in Pantex sediments were reduced using $\text{Na}_2\text{S}_2\text{O}_4$ in an anaerobic chamber. This was accomplished by combining sediments (0.5–4 g) with 40 ml of deoxygenated water in 45-ml Teflon tubes and agitating overnight on a reciprocating shaker at room temperature. Ten to 100 mM of dithionite and 20–400 mM of K_2CO_3 were then added to each suspension. The mixture was kept on a reciprocating shaker for 24 h, centrifuged and the supernatant (containing dithionite and its degradation products thiosulfate, sulfate, and bisulfite) was discarded. The reduced sediments were washed twice with deoxygenated water to remove excess and entrained dithionite and the other sulfur compounds before using in batch studies. Controls were prepared in a similar manner without the addition of dithionite.

2.3. HE degradation kinetics

Protocols used in batch experiments generally consisted of mixing 2 g of reduced Pantex sediments with 40 ml of aqueous solution containing the HE of interest (RDX, HMX, or TNT). Treatments included various dithionite (10–100 mM) and K_2CO_3 (20–200 mM K_2CO_3) concentrations at a dithionite- K_2CO_3 molar ratio of 1:2. All experiments were conducted in the anaerobic chamber.

In another experiment, the mass of Pantex sediments (0.5–4.0 g) reduced with 100 mM dithionite and 400 mM K_2CO_3 was adjusted to yield solid-to-solution ratios that varied from 1:80 to 1:10. The reduced sediments were then used to treat 40 ml solutions of RDX (20 mg l^{-1}).

Because four moles of H^+ are generated per mole of dithionite during iron reduction (Eq. (1)), a buffer is usually added in a 1:4 ratio (dithionite:buffer) to maintain pH (Szecsody et al., 2004). To determine the effects of varying buffer concentrations, HE degradation kinetics were compared under unbuffered and buffered conditions. Dithionite (100 mM) alone, and combined with 200 and 400 mM K_2CO_3 , was used to reduce 2 g Pantex sediments in 40 ml water. The reduced sediments were then used to treat 40 ml of aqueous solution containing 20 mg RDX l^{-1} , 3.5 mg HMX l^{-1} and 65 mg TNT l^{-1} in three experiments. At selected times, multiple aliquots were removed to determine temporal changes in HE concentrations.

2.4. Transformation of RDX by Fe(II) and dithionite-treated sediments

Dithionite-citrate-bicarbonate (DCB) is commonly used to extract and quantify crystalline Fe(III) oxides in soils by reducing Fe(III) to Fe(II) (Heron et al., 1994). Extracting sediments with DCB partially removes Fe(II) and amorphous and crystalline Fe(III) oxides from the reduced sediments. For subsurface applications, this poses the hypothetical problem of removing Fe(II) by the migrating solutions and diminishing the overall reductive capacity of the sediments with time. To determine the effect of removing DCB-extractable Fe(II) and of its subsequent regeneration in the sediments through the addition of Fe^{2+} , Pantex sediments were reduced with DCB and then supplemented with Fe^{2+} . Pantex sediments (2 g) and 25 ml of deoxygenated water were added to 45-ml Teflon tubes and agitated overnight on a reciprocating shaker at room temperature. Fifteen milliliters of citrate-bicarbonate buffer (8 parts 0.3 M citrate and one part 1 M bicarbonate, pH 8.5) were mixed with 25 ml of 100 mM dithionite and added to each suspension. The mixture was kept on a reciprocating shaker for 24 h, centrifuged and the supernatant discarded. One set of experimental units ($n = 3$) was then washed twice with deoxygenated water to remove excess dithionite, soluble Fe(II) and other sulfur anions; for comparison, another set was not washed (unwashed). Fe^{2+} (as FeSO_4 , 0.35 mM) was added back into DCB-treated, washed samples and the pH left unadjusted (6.8) or increased to 8.25 with 0.5 N NaOH. A set of RDX solutions treated with 0.35 mM Fe^{2+} (pH 8.25) without sediments served as a control. Sample aliquots were then periodically collected and temporal changes in RDX concentrations determined by HPLC.

2.5. Capacity of reduced sediments to degrade RDX

The capacity of the dithionite-treated sediments to continuously degrade RDX was evaluated. This was accomplished by treating 40 ml of 20 mg RDX l^{-1} solution with 2 g of reduced soil (100 mM dithionite, 400 mM K_2CO_3 , washed twice with deoxygenated water) and measuring changes in RDX concentration at 0, 1, 2, 4, 8, and 24 h. After the last sampling, the solutions were centrifuged and the supernatants removed. Fresh RDX (20 mg l^{-1}) solution was reseeded into the same experimental unit (i.e., reduced soil) and the sampling cycle was repeated at 24, 48, 72, 96, and 120 h (five cycles). Changes in the RDX concentration were monitored between reseeded cycles.

Because the reduced sediments continuously exposed to RDX eventually lost their reductive capacity, we determined whether the reductive capacity of sediments could be regenerated (i.e., re-reducing the sediments) following exposure to the HE and oxygen. Two g of perched aquifer sediments were reduced with 100 mM dithionite in 400 mM K_2CO_3 . The reduced sediments were then used to treat

40 ml of solution containing 20 mg RDX l⁻¹ and 65 mg TNT l⁻¹ in two separate experiments. After 5 d, the tubes were centrifuged at 5000g for 20 min and the supernatants removed and analyzed for HE concentrations. The sediments were extracted with methanol (10 ml) to remove and quantify adsorbed RDX and TNT. The methanol was removed and the sediments were allowed to re-oxidize outside the chamber for 2 d. The sediments were then treated (reduced) with dithionite again and used to treat fresh solutions of RDX and TNT. This process was repeated for a total of six cycles.

2.6. Chemical analysis and Fe fractionation

RDX, TNT, and HMX analyses were performed by HPLC (Shimadzu, Kyoto, Japan) by injecting 20 µl of sample into a 4.6- by 250-mm Keystone Betasil NA column (Thermo Hypersil-Keystone, Bellefonte, PA). The mobile phase was 50:50 methanol:water at a flow rate of 1 ml min⁻¹ with spectrophotometric quantification at 220 nm. Selected aliquots were also analyzed by liquid chromatography-mass spectrometry to identify the reaction products. A BetaBasic C-18 column (Thermo Hypersil-Keystone) was used for separation on a Waters 2695 HPLC interfaced to a Micromass Quattro Micro triple quadrupole mass spectrometer with electrospray ionization (Waters Corp., Milford, MA). The isocratic mobile phase consisted of 80:20 water:isopropanol (0.5% ammonium formate) at pH 8.0.

Iron extractions were carried out in the anaerobic chamber. Solutions used for the extractions included: (a) 0.5 M HCl, (b) 5 M HCl, (c) 1 M CaCl₂ (ion exchangeable Fe(II)) (Heron et al., 1994), and (d) hydroxylamine (Lovley and Phillips, 1987). Each extraction was conducted in triplicate. Fe(II) in supernatant solutions and from various extractions was determined spectrophotometrically using the Ferrozine method (Stookey, 1970). Total Fe(II) was defined by the 5 M extraction. Total Fe in the 5 M HCl extract was quantified by reducing aqueous Fe(III) to Fe(II) with 0.025 M NH₂OH · HCl and Fe(III) was calculated from the difference between total Fe and Fe(II). FeCO₃ + FeS were determined from the difference between the 0.5 M HCl and 1 M CaCl₂ extractions (Heron et al., 1994). Amorphous Fe(III) oxyhydroxides were calculated from the difference between hydroxylamine and 0.5 M HCl extractions (Lovley and Phillips, 1987).

3. Results and discussion

3.1. Effect of dithionite/buffer concentrations on HE degradation

Using a 1:2 dithionite-K₂CO₃ ratio, 2 g of Pantex sediments were reduced with varying concentrations of dithionite/buffer. Increasing both dithionite and buffer concentrations (in a 1:2 ratio) significantly increased RDX degradation (Fig. 1). Given that the sediments mass

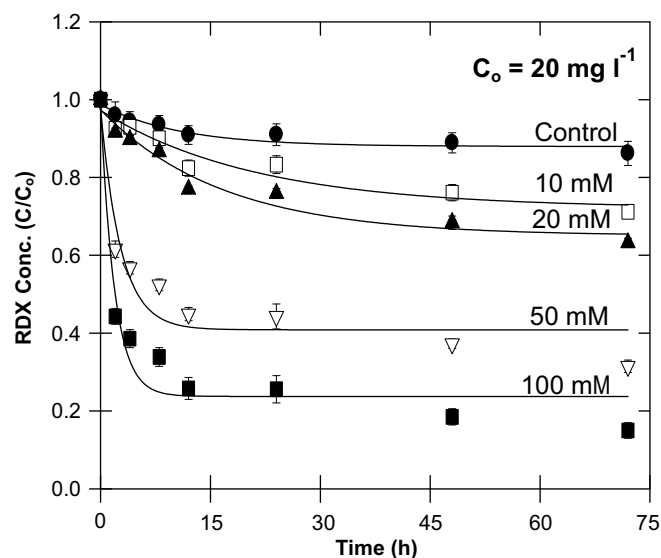


Fig. 1. Transformation of RDX in a batch system containing 2 g Pantex sediments reduced with varying amounts of dithionite buffered with K₂CO₃. The control consisted of RDX + 2 g unreduced sediments in K₂CO₃ buffer with no dithionite. Bars on symbols represent standard deviations; where absent, bars fall within symbols.

was fixed (2 g) and washed twice after reduction to remove entrained dithionite and dithionite products, the greater HE degradation observed with increased dithionite/buffer concentration can be attributed to a greater reduction of Fe(III) to Fe(II) (Table 2). Fractionation of the Fe phases revealed that increasing the dithionite concentration increased the concentration of various Fe(II) species and decreased the amount of Fe(III) (Table 2). The pH after 72 h was between 8.5 and 9.0. Although increasing the dithionite/buffer concentrations increased the rate and amount of RDX lost, none of the dithionite/K₂CO₃ concentrations resulted in 100% removal of the RDX (Fig. 1). By increasing the dithionite/K₂CO₃ ratio from 1:2 to 1:4 however, more Fe(II) was generated from the 2 g of Pantex sediments (100 mM:400 mM, Table 2) and RDX was completely removed (Fig. 2). Using the 1:4 dithionite/K₂CO₃ ratio and increasing the amount of sediments exposed resulted in reducing more Fe(III) to Fe(II) (Solid:Solution ratio 1:80 → 1:10, Table 2). This in turn, increased the rate of RDX degradation (Fig. 2).

The importance of the buffer on treatment efficacy was further demonstrated on all three HE. The explosives RDX, HMX, and TNT were more quickly degraded by the buffered, reduced sediments than the unbuffered, reduced sediments (Fig. 3). The pH of the reduced sediments buffered with K₂CO₃ ranged from 8.0 to 9.5 but was 7.2 in the absence of buffer. In the presence of buffer, the sediments turned black, likely due to formation of magnetite (Fe₃O₄) but in the absence of buffer, the sediments were light green. FeS and FeCO₃ were also formed (Table 2). Degradation of the three HE after 72 h of treatment increased from 10% to 50% when K₂CO₃ buffer was used with dithionite (Fig. 3). Differences in degradation rates

Table 2
Iron phases ($\mu\text{mol g}^{-1}$) during reduction of Pantex sediment with dithionite

Dithionite conc. (mM)	K ₂ CO ₃ conc. (mM)	Solid:solution ratio	Sorbed Fe(II)	Fe(II)CO ₃ and Fe(II)S	Total Fe(II)	Amorphous Fe oxides	Total Fe(III)	Total Fe [(Fe(II) + Fe(III))]	Fe(II) in supernatant (mg l^{-1})
Untreated		1:20	0.0 \pm 0.0 ^a	0.12 \pm 0.0	24.2 \pm 1.3	92 \pm 1.9	314 \pm 11	338	0.0 \pm 0.0
10	20	1:20	6.3 \pm 1.6	22.4 \pm 0.9	57.7 \pm 1.9	70 \pm 2.2	279 \pm 9.2	337	0.1 \pm 0.0
20	40	1:20	9.9 \pm 1.4	33.3 \pm 1.2	91.5 \pm 1.8	57 \pm 1.7	251 \pm 8.2	343	0.3 \pm 0.0
50	100	1:20	11.8 \pm 0.8	54.7 \pm 1.7	107 \pm 2.1	48 \pm 0.9	236 \pm 5.1	343	0.4 \pm 0.0
100	200	1:20	14.3 \pm 1.1	70.3 \pm 1.2	126 \pm 2.4	34 \pm 1.1	211 \pm 12	337	1.2 \pm 0.2
100	400	1:20	13.3 \pm 1.2	92.1 \pm 1.1	167 \pm 2.2	24 \pm 1.3	173 \pm 5.7	340	0.0
100	400	1:80	2.73 \pm 0.4	21.1 \pm 1.3	52.1 \pm 1.1	ND ^c	171 \pm 2.6	223	0.0
100	400	1:40	5.1 \pm 0.5	40.9 \pm 1.8	89.7 \pm 1.3	ND	197 \pm 4.9	287	0.0
100	400	1:10	18.3 \pm 2.7	102 \pm 2.1	211 \pm 2.9	ND	202 \pm 7.6	413	0.0
100	nil	1:20	31.5 \pm 3.8	30.2 \pm 0.9	72.7 \pm 1.9	33 \pm 1.8	203 \pm 13	276	74.0 \pm 3.2
100	C-B ^b buffer	1:20	11.6 \pm 0.5	39.7 \pm 1.2	110 \pm 0.8	49 \pm 2.4	174 \pm 2.1	284	74.2 \pm 4.1

^a Sample standard deviation of means ($n = 3$).

^b Citrate-bicarbonate buffer.

^c Not determined.

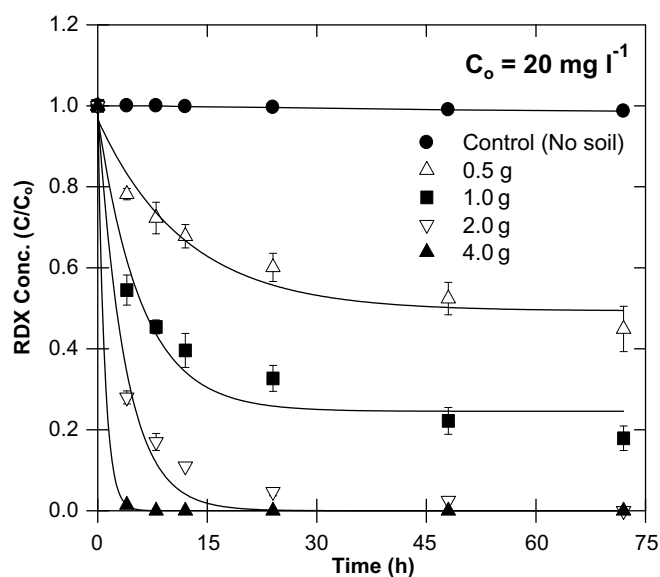


Fig. 2. Transformation of RDX in a batch system containing varying amounts of reduced sediments. The sediments were each reduced with 100 mM dithionite buffered with 400 mM K₂CO₃. The control consisted of RDX in K₂CO₃ buffer solution with no soil.

between buffered and unbuffered treatments are likely due to mobilization and removal of some Fe(II) in the supernatant at lower pH (Table 2). Moreover, the concentration of FeCO₃ + FeS was low in the absence of buffer but increased with added buffer, so adding more K₂CO₃ may favor FeCO₃ formation. TNT has previously been shown to be rapidly degraded by siderite and ferrous iron (Nefso et al., 2005).

Szecsody et al. (2004) previously observed that using less buffer during dithionite reduction resulted in a lower pH, which mobilizes iron via reductive dissolution and resulted in less Fe(III) reduction. Less Fe(III) reduction in unbuffered conditions may also be due to faster decomposition of dithionite at low pH. The degree to which less Fe(III) reduction in sediments may affect contaminant degradation

rates would be compound-specific and sediments-specific (dependent on Fe(II) phases produced). For example, the largest difference between buffered and unbuffered treatments was observed for RDX, with less treatment differences observed for HMX and TNT (Fig. 2). Similarly, Boparai et al. (2006) observed significant alachlor transformation by reduced sediments in the presence of buffer but very limited transformation in the absence of buffer. TCE degradation by highly reduced sediments (with buffer) had a half-life of 1.2–5.4 h whereas the half-life in partially reduced sediments (less buffer) was 200 to 400 h (Szecsody et al., 2004).

Treating equal molar concentrations (10 μM) of explosives with reduced sediments provided one means of evaluating electron acceptor preference and resulted in the following order of degradation: TNT ($k = 2.87 \text{ h}^{-1}$) > RDX ($k = 2.01 \text{ h}^{-1}$) > HMX ($k = 0.434 \text{ h}^{-1}$) (Fig. 4). RDX transformations by dithionite-reduced sediments produced the three commonly observed nitroso products hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine (MNX), hexahydro-1,3-dinitroso-5-nitro-1,3,5-triazine (DNX), and hexahydro-1,3,5-trinitroso-1,3,5-triazine (TNX), which subsequently disappeared within a few hours of the reaction (Fig. 5). As the reaction continued, an HPLC peak, eluting before the nitrosos and RDX, increased with time. The mass spectrum of this peak was consistent with methylenedinitramine (MDNA), with a molecular formula of CH₄N₄O₄ and nominal mass of 136. In the negative ion mode this compound would lose a proton to give a formate adduct $[\text{M}-\text{H}+\text{HCOO}^-]^-$ ion at m/z 180 and as a dimer of MDNA at m/z 271 (Fig. 6). MDNA is unstable in water and abiotically degrades to N₂O and HCHO (Fig. 5); HCHO is readily biodegraded to CO₂ (Halasz et al., 2002). MDNA was also observed during treatment of HMX with dithionite-reduced sediments. Likewise, the transformation products of TNT were 2-aminodinitrotoluene, 4-aminodinitrotoluene, 2,4-diaminonitrotoluene, and 2,6-diaminonitrotoluene (data not shown). These degradation products were further degraded

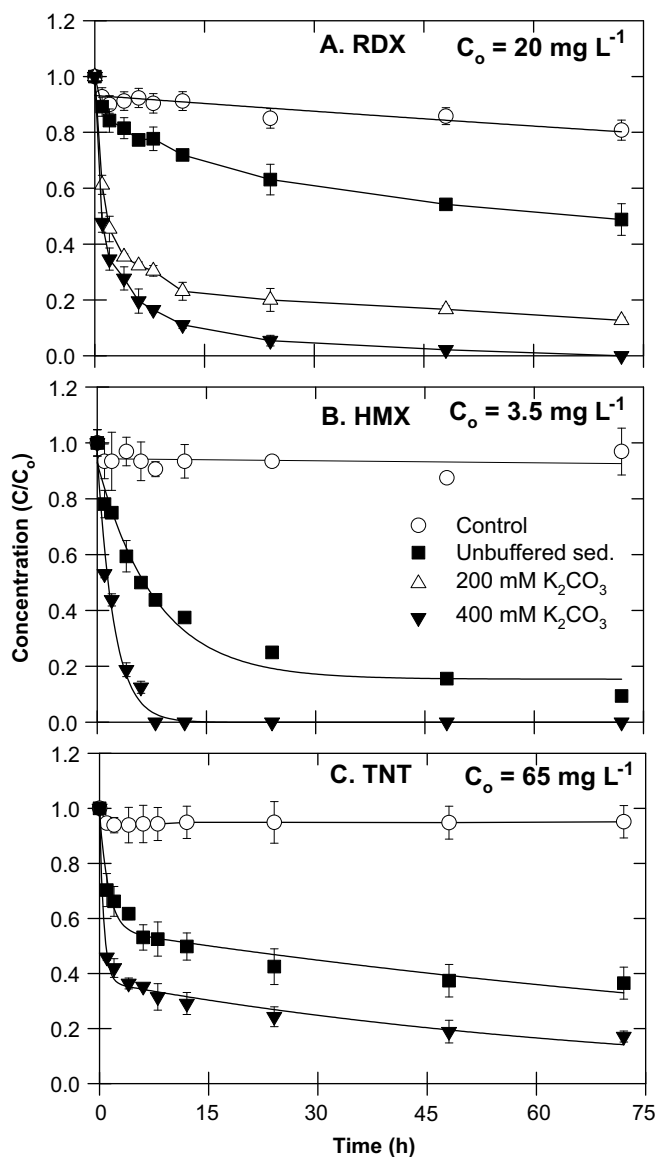


Fig. 3. Transformation of (A) RDX, (B) HMX, and (C) TNT in unbuffered and K_2CO_3 (200 or 400 mM) buffered Pantex sediments reduced with 100 mM dithionite. The controls consisted of explosive + 2 g sediments without buffer and dithionite.

to unidentified products. The degradation pathway of TNT by Fe(II) in reduced sediments is also presented (Fig. 5).

3.2. Transformation of RDX by Fe(II) and dithionite-treated sediments

When Pantex sediments treated with DCB were not washed with deionized H_2O , RDX degradation was fast with 100% removal observed within 6 h. This fast reaction was likely due to excess dithionite and its degradation products (sulfur compounds) entrained in the unwashed sediments (Fig. 7). By washing the reduced sediments, degradation slowed considerably and only 60% of the RDX was transformed within 72 h. Extracting sediments with DCB partially removes Fe(II) and amorphous and crystal-

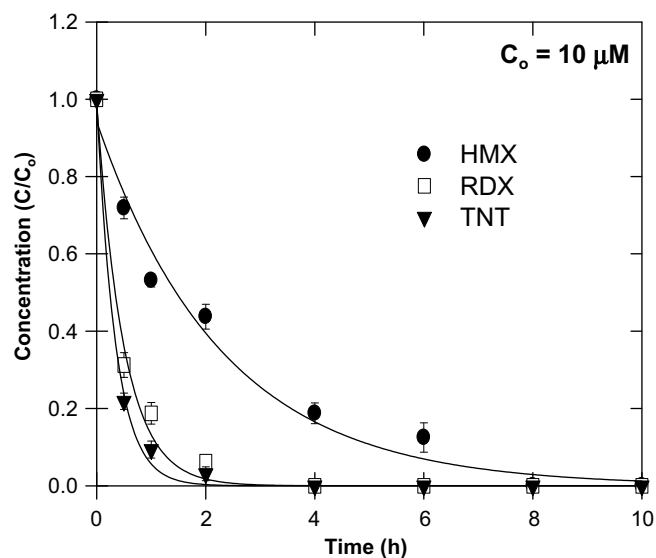


Fig. 4. Degradation of equimolar concentrations of high explosives (10 μM) with 2 g reduced sediments (100 mM dithionite + 400 mM K_2CO_3).

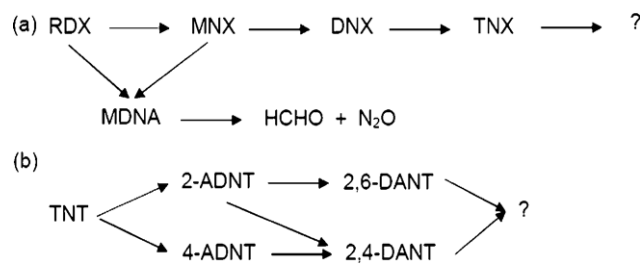


Fig. 5. Possible pathways for degradation of RDX and TNT by reduced sediments.

line Fe(III) oxides from the reduced sediments. To quantify the importance of the removed Fe(II), we added Fe(II) back into the system. When Fe(II) was added back to washed sediments without adjusting pH (pH 6.8), RDX degradation rates decreased further. However, when Fe(II) was added and the pH maintained at 8.25 (pH of the unwashed treatment), RDX degradation was greatly enhanced and approached rates observed in the unwashed sediments (Fig. 7). Because treatment by aqueous Fe(II) alone (pH 8.25) showed very little RDX degradation, the combination of (hydr)oxide surfaces, Fe(II), and alkaline pH appears critical for rapid degradation. Previous studies have shown that Fe(II) bound to iron (hydr)oxides (Pecher et al., 2002; Elsner et al., 2004), iron sulfides (Butler and Hayes, 1998), green rusts (Williams and Scherer, 2001), and mineral phases containing structural Fe(II) including phyllosilicates (Cervini-Silva et al., 2001; Hofstetter et al., 2003) can reduce chromates, nitroaromatics, and chlorinated organic contaminants. The effect of pH on contaminant reduction by sorbed Fe(II) has also been reported. Lee and Batchelor (2002) found an increase in the rate of TCE dechlorination by green rust when pH was increased from 6.8 to 8.1. They attributed this observation to the conver-

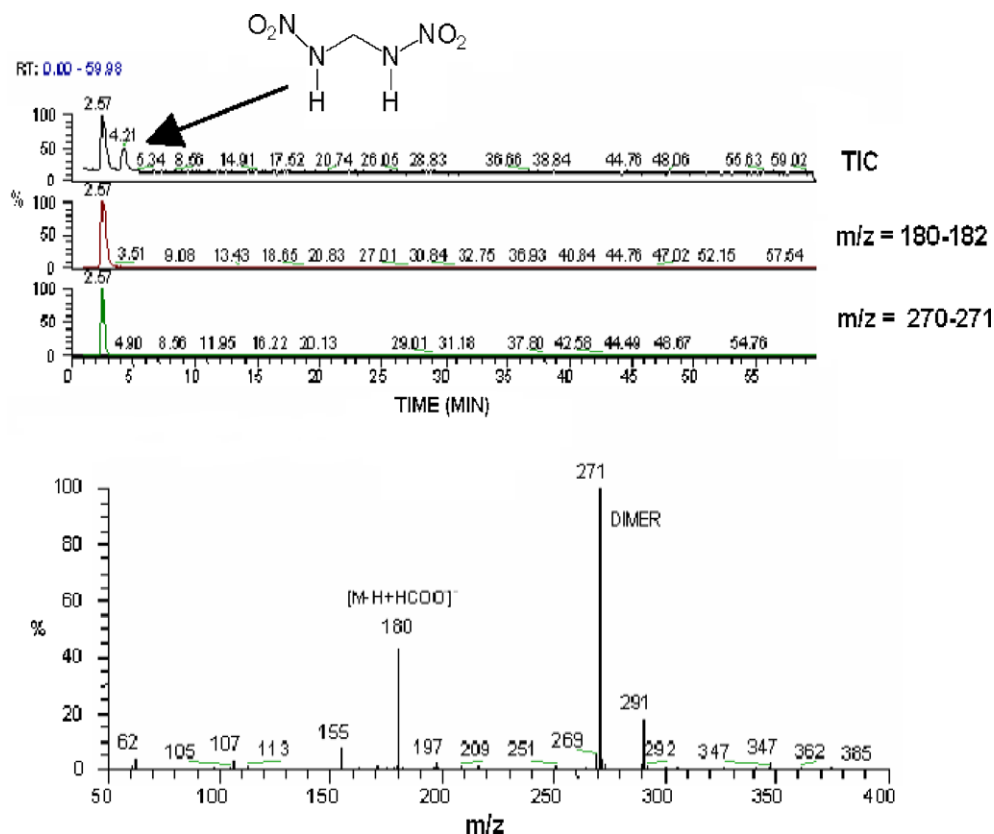


Fig. 6. Negative mode total ion chromatograms and spectra showing MDNA (transformation product of reduced sediments treated RDX).

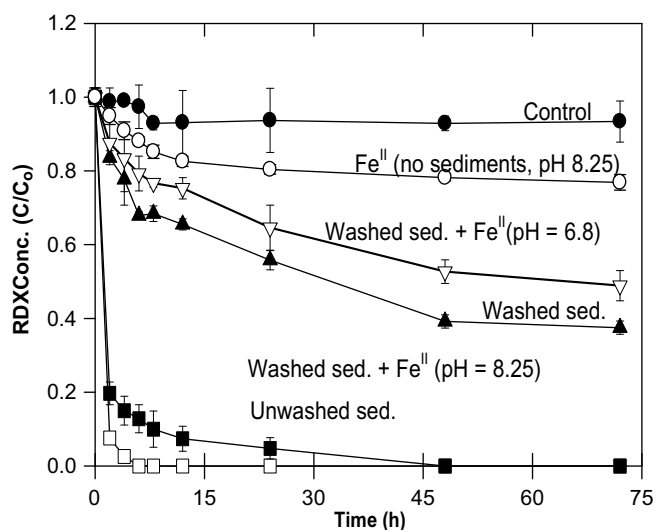


Fig. 7. Changes in RDX concentration following treatment with washed and unwashed Pantex sediments reduced with 100 mM dithionite, and washed Pantex sediments reduced with 100 mM dithionite + 0.35 mM Fe²⁺.

sion of unreactive sites to reactive Fe(II) sites and the higher electron density of unprotonated $\equiv\text{Fe(III)O-Fe(II)OH}^0$ than protonated $\equiv\text{Fe(III)OFe(II)OH}_2^+$ surface groups (Butler and Hayes, 1998; Lee and Batchelor, 2002). Pecher et al. (2002) also observed an exponential increase in CBr₃ (flourotribromomethane) degradation by goe-

thite and Fe(II) when the pH increased from 6 to 8.9 and attributed this to increased Fe(II)_{sorb} concentration.

3.3. Reductive capacity of reduced sediments to degrade HE

The longevity of redox barriers will depend on the redox capacity of the reduced sediments, volume or thickness of the redox zone, and the influx of dissolved oxygen and contaminants (i.e., electron acceptors). To determine the reductive capacity of a fixed mass of sediments, RDX was repeatedly added to 2 g of sediments and changes in degradation rates observed. All RDX was lost from solution within 24 h of initial exposure to the reduced Pantex sediments but the transformation rate decreased with successive RDX reseedings (third, fourth and fifth cycles) (Fig. 8). When RDX was reseeded in the fifth cycle, RDX loss from solution was only 22% after 24 h. Total mass of RDX transformed by the 2 g of reduced sediments was estimated at 9.72 μmol (4.86 $\mu\text{mol g}^{-1}$). Estimating the reductive capacity of the sediments based on RDX loss alone would be dependent upon how many electrons each μmol of RDX accepted (e.g., 2 e⁻ for MNX, 6 e⁻ for TNX). Considering the initial transformation of RDX to its nitroso products (i.e., MNX, DNX, TNX), the amount of Fe(II) provided by the reduced sediments was between 9.72 and 29.16 μmol of Fe(II) g⁻¹ sediments. Previous studies (Szecsody et al., 2001) using dissolved O₂ showed that the Pantex sediments had a reductive capacity of 71.6 μmol

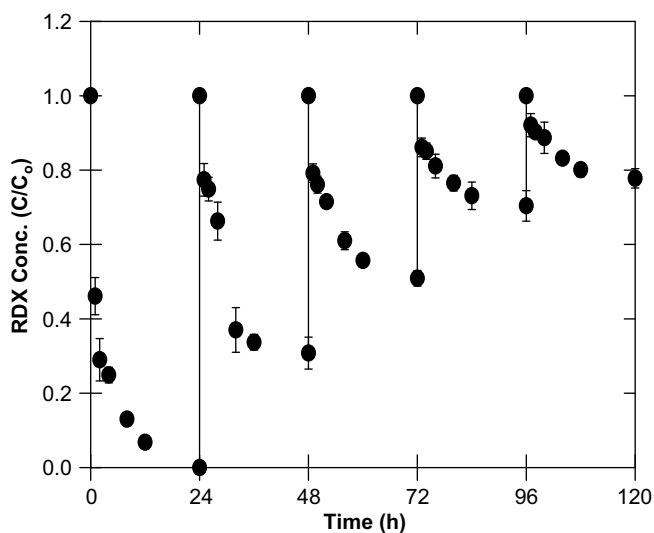


Fig. 8. RDX destruction in solutions containing dithionite-reduced sediments and after reseeded RDX (20 mg l⁻¹).

of Fe(II) g⁻¹ sediments. This difference in reductive capacity is likely attributable to the additional electrons needed to further reduce the nitroso products as well as the electron acceptor preference of dissolved O₂ versus RDX.

After losing its capacity to transform RDX, we found the reduced sediments could be regenerated by re-treating with dithionite. Results from six cycles of successive reduction-oxidation showed that both RDX and TNT were effectively transformed with no change in degradation rates (data not shown). The stability of the sediments to transform explosives following regeneration (i.e., reduction) indicates little to no loss in reductive capacity. Such stability would be important if the aquifer sediments were to be used as a barrier to remediate contaminated water (Lee and Batchelor, 2004). It is important to note that the HE concentrations used in the batch experiments were approximately 10-fold larger than observed in the Pantex aquifer and the soil:water ratios of the aquifer are 100-fold or more greater than those used in these batch studies. Column studies by Szecsody et al. (2001) indicated that reduced Pantex sediments can treat several hundred pore volumes of RDX-contaminated groundwater. Considering the hydrological characteristics of the Pantex site, it is estimated that the longevity of a redox barrier could be 30 years or more (Aquifer Solutions, Inc., 2002) before the redox zone may need to be regenerated.

4. Conclusion

Explosives (RDX, HMX, and TNT) can be successfully transformed by iron-rich sediments following treatment with dithionite. Reaction rates depend on the concentration of dithionite, solid-solution ratio, pH, and the buffering matrix. The transformation kinetics of explosives increased as the solid-solution ratio increased or as the dithionite/buffer concentration increased. Reduction of

Fe(III) with dithionite produces protons and lowers the pH of the system. Low pH results in less Fe(III) reduction as well as mobilization and removal of Fe(III). Thus unbuffered, reduced sediments showed slower kinetics than buffered, reduced sediments. The Pantex sediments can be successfully regenerated with little or no loss in reduction capacity to transform HE. Our results indicate that in situ redox manipulation can be used to remediate HE-contaminated groundwater at the Pantex site. Because various Fe oxides and Fe(II) species form during reduction of sediments by dithionite, identification of those forms responsible for HE transformation would help guide further applications of this technology.

Acknowledgements

Funding was provided in part by a grant from the Strategic Environment Research and Development Program (SERDP), Project ER-1376. Partial support was also provided by the University of Nebraska School of Natural Resources and Water Sciences Laboratory. This paper is a contribution of Agricultural Research Division Projects NEB-40-002 and 40-019.

References

- Adam, M.L., Comfort, S.D., Zhang, T.C., Morley, M.C., 2005. Evaluating biodegradation as a primary and secondary treatment for removing RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) from a perched aquifer. *Bioremed. J.* 9, 1–11.
- Amonette, J.E., Szecsody, J.E., Schaef, H.T., Templeton, J.C., Gorby, Y.A., Fruchter, J.S., 1994. Abiotic reduction of aquifer materials by dithionite: a promising in-situ remediation technology. In: Gee, G.W., Wing, N.R. (Eds.), *In-Situ Remediation: Scientific Basis for Current and Future Technologies. Part 2. Thirty-Third Hanford Symposium on Health and the Environment*, November 7–11, Pasco, WA. Battelle Press, Columbus, OH. pp. 851–881.
- Amonette, J.E., Fruchter, J.S., Gorby, Y.A., 1998. Method of Removing Oxidized Contaminants from Water. United States Patent 5,783,088.
- Aquifer Solutions, Inc., 2002. Conceptual Deployment Scenarios for In Situ Remediation of the Southeast Perched Aquifer Plume, Pantex Plant, Amarillo, Texas. Aquifer Solutions Inc., Evergreen, Colorado.
- Boparai, H.K., Shea, P.J., Comfort, S.D., Snow, D.D., 2006. Dechlorinating chloroacetamide herbicides by dithionite-treated aquifer sediment and surface soil. *Environ. Sci. Technol.* 40, 3043–3049.
- Butler, E.C., Hayes, K.F., 1998. Effect of solution composition and pH on the reductive dechlorination of hexachlorethane by iron sulfide. *Environ. Sci. Technol.* 32, 1276–1284.
- Cervini-Silva, J., Larson, R.A., Wu, J., Stucki, J.W., 2001. Transformation of chlorinated aliphatic compounds by ferruginous smectite. *Environ. Sci. Technol.* 35, 805–809.
- Comfort, S., 2005. Remediating RDX and HMX contaminated soil and water. In: Fingerman, M., Nagabhushanam, R. (Eds.), *Bioremediation of Aquatic and Terrestrial Ecosystems*. Science Publishers, Enfield, NH, pp. 263–310.
- Eckert, D.J., 1988. Recommended pH and lime requirement tests. In: Dahnke, W.C. (Ed.), *Recommended Chemical Soil Test Procedures for the North Central Region*. North Dakota Agric. Exp. Stn. Bulletin No. 499 (revised), North Dakota State Univ., Fargo, ND. pp. 5–8.
- Elsner, M., Schwarzenbach, R.P., Haderlein, S.B., 2004. Reactivity of Fe^{II}-bearing minerals toward reductive transformation of organic contaminants. *Environ. Sci. Technol.* 38, 799–807.

- Fruchter, J.S., Cole, C.R., Williams, M.D., Vermuel, V.R., Amonette, J.E., Szecsody, J.E., Istok, J.D., Humphrey, M.D., 2000. Creation of a subsurface permeable treatment zone for aqueous chromate contamination using in situ redox manipulation. *Ground Water Monit. Rem.* 20, 66–77.
- Gan, H., Stucki, J., Bailey, G.W., 1992. Reduction of structural iron in ferruginous smectite by free radicals. *Clays Clay Miner.* 40, 659–665.
- Gee, G.W., Bauder, J.W., 1986. Particle-size analysis. In: Klute, A. (Ed.). *Methods of Soil Analysis. Part 1: Physical and Mineralogical Methods*, 2nd ed. Agron. Monogr. 9, Am. Soc. Agron., Madison, WI. pp. 383–411.
- Halasz, A., Spain, J., Paquet, L., Beaulieu, C., Hawari, J., 2002. Insights into the formation and degradation mechanisms of methylenedinitramine during the incubation of RDX with anaerobic sludge. *Environ. Sci. Technol.* 36, 633–638.
- Heijman, C.G., Grieder, E., Holliger, C., Schwarzenbach, R.P., 1995. Reduction of nitroaromatic compounds coupled to microbial iron reduction in laboratory aquifer columns. *Environ. Sci. Technol.* 29, 775–783.
- Heron, G., Crouzet, C., Bourg, A.C., Christensen, T.H., 1994. Speciation of Fe(II) and Fe(III) in contaminated aquifer sediments using chemical extraction techniques. *Environ. Sci. Technol.* 28, 1698–1705.
- Hofstetter, T.B., Schwarzenbach, R.P., Haderlein, S.B., 2003. Reactivity of Fe(II) species associated with clay minerals. *Environ. Sci. Technol.* 37, 519–528.
- Lee, W., Batchelor, B., 2002. Abiotic reductive dechlorination of chlorinated ethylenes by iron-bearing soil minerals. 2. Green rust. *Environ. Sci. Technol.* 36, 5348–5354.
- Lee, W., Batchelor, B., 2004. Abiotic reductive dechlorination of chlorinated ethylenes by soil. *Chemosphere* 55, 705–713.
- Lovley, D.R., Phillips, E.J.P., 1987. Rapid assay for microbially reducible ferric iron in aquatic sediments. *Appl. Environ. Microb.* 53, 1536–1540.
- Nefso, E.K., Burns, S.E., McGrath, C.J., 2005. Degradation kinetics of TNT in the presence of six mineral surfaces and ferrous iron. *J. Hazard. Mater.* 123, 79–88.
- Nzengung, V.A., Castillo, R.M., Gates, W.P., Mills, G.L., 2001. Abiotic transformation of perchloroethylene in homogeneous dithionite solution and in suspensions of dithionite-treated clay minerals. *Environ. Sci. Technol.* 35, 2244–2251.
- Park, J., Comfort, S.D., Shea, P.J., Kim, J.S., 2005. Increasing Fe⁰-mediated HMX destruction in highly contaminated soil with didecyl-dimethylammonium bromide surfactant. *Environ. Sci. Technol.* 39, 9683–9688.
- Pecher, K., Haderlein, S.B., Schwarzenbach, R.P., 2002. Reduction of methane by surface-bound Fe(II) in aqueous suspensions of iron oxides. *Environ. Sci. Technol.* 36, 1734–1741.
- Rhoades, J.D., 1982. Cation exchange capacity. In: Page, A.L., Miller, R.H., Keeney, D.R. (Eds.). *Methods of Soil Analysis. Part 2: Chemical and Microbiological Methods*, Second Edition. Agron. Monogr. 9, Am. Soc. Agron., Madison, WI. pp. 149–151.
- Schulte, E.E., 1988. Recommended soil organic matter tests. In: Dahnke, W.C. (Ed.). *Recommended Chemical Soil Test Procedures for the North Central Region*. North Dakota Agric. Exp. Stn. Bulletin No. 499 (revised), North Dakota State Univ., Fargo, ND. pp. 29–31.
- Singh, J., Comfort, S.D., Shea, P.J., 1998. Remediating RDX-contaminated water and soil using zero-valent iron. *J. Environ. Qual.* 27, 1240–1245.
- Stookey, L.L., 1970. Ferrozine – A new spectrophotometric reagent for iron. *Anal. Chem.* 42, 779–781.
- Szecsody, J.E., Fruchter, J., McKinley, M.A., Resch, C.T., Gilmore, T., 2001. Feasibility of In Situ Redox Manipulation of Subsurface Sediments for RDX Remediation at Pantex. Pacific Northwest National Laboratory, Richland, WA, USA.
- Szecsody, J.E., Fruchter, J.S., Williams, M.D., Vermuel, V.R., Sklarew, D., 2004. In situ chemical reduction of aquifer sediment: Enhancement of reactive iron phases and TCE dechlorination. *Environ. Sci. Technol.* 38, 4656–4663.
- Van Aken, B., Agathos, S.N., 2001. Biodegradation of nitrosubstituted explosives by white-rot fungi: A mechanistic approach. *Adv. Appl. Microbiol.* 48, 1–70.
- Whitney, D., 1988. Micronutrient soil test for zinc, iron, manganese, and copper. In: Dahnke, W.C. (Ed.). *Recommended Chemical Soil Test Procedures for the North Central Region*. North Dakota Agric. Exp. Stn. Bulletin No. 499 (revised), North Dakota State Univ., Fargo, ND. pp. 20–22.
- Williams, A.G., Scherer, M.M., 2001. Kinetics of Cr(VI) reduction by carbonate green rust. *Environ. Sci. Technol.* 35, 3488–3494.