ER ID 95718

From: Bioremediation of Aquatic and Terrestrial Ecosystems (2005) p. 263-310.

Remediating RDX and HMX Contaminated Soil and Water

Steve Comfort

School of Natural Resources, University of Nebraska,
256 Keim Hall, Lincoln, Nebraska 68583-0915, U.S.A.

Introduction

RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) and HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) are two types of heterocyclic nitramine compounds that have been manufactured and used worldwide as military explosives. RDX was first synthesized in 1899 for medicinal purposes but later recognized for its value as an explosive in 1920 (Akhavan 1998). In the 1940s, the Bachmann synthesis was developed and used for large scale production of RDX during World War II (Bachmann and Sheehan 1949). At the time of its development, the Bachmann synthesis was considered an efficient reaction with high yields but the products of the reaction also contained an impurity (i.e., HMX) that was later recognized and utilized as an explosive (Akhavan 1998). By varying the temperature and reagent concentrations, the Bachmann synthesis could produce large yields of HMX (Urbanski 1984). This led to the introduction of octols in 1952, (mixtures of HMX and TNT), which increased HMX use by the military. Depending on where RDX was manufactured and used, it has also been known as Research Development eXplosive (U.S.), Research Department eXplosive (Britain), or Royal Demolition eXplosive (Canada). Other common names for RDX include cyclonite, hexogen, and cyclotrimethylenetrinitramine. HMX has a higher melting point than RDX and is thus known as High Melting explosive, octogen, or cyclotetramethyl-enetetranitramine (Urbanski 1984, Akhavan 1998).

RDX and HMX are classified as secondary explosives (also known as high explosives), which means they cannot be detonated readily by heat or shock but require a primary explosive for initiation. RDX and HMX have been used by the military for a variety of purposes. RDX is commonly used in press-loaded projectiles, cast loadings with TNT, plastic explosives, or

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base charges in blasting caps and detonators. As an explosive, HMX is superior to RDX because its ignition temperature is higher and has greater chemical stability. HMX is commonly used as a booster charge in mixtures or as an oxidizer in solid rocket and gun propellants (Island Pyrochemical Industries 2004). HMX is also used to implode fissionable material to achieve critical mass in nuclear devices (Yinon 1990). Like other energetic compounds, RDX and HMX possess multiple nitro groups but are structurally unique in that the nitro moieties of nitramines are bonded to the central ring via single nitrogen-nitrogen bonds (Fig. 1). This distinction is important because unlike aliphatic and aromatic nitro compounds that can be produced biosynthetically by some plant and microbial species (Turner 1971), nitramines appear to be true xenobiotics and occur in nature solely from human activities (Coleman *et al.* 1998).

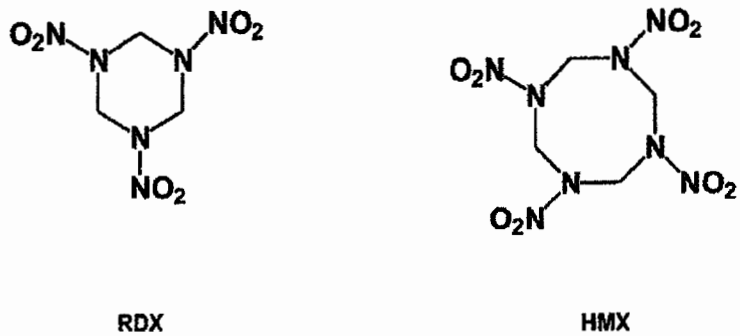

Figure 1. Chemical structures of RDX and HMX.

Examples of military activities that have contaminated many former and current defense sites include the improper disposal of wastewaters generated during the manufacturing and assembling of munitions or the repeated discharge of live ammunition at military training grounds. Training ranges have the additional problem of unexploded ordnances (UXOs), which are caused when munitions fail to explode or have incomplete detonations. These so-called "dud rates" can be as high as 10% (Defense Science Board 1998) and are a major concern because UXOs can potentially leak and cause high concentrations directly around the projectile, whereas incomplete detonation disperses undetonated materials around the impact site. The types of UXOs vary widely and include small arms ammunition, bombs, artillery rounds, mortars, air-craft cannon, tank-fired projectiles, rockets, guided missiles, grenades, torpedoes, mines, chemical munitions, bulk explosives, and pyrotechnics (MacDonald 2001).

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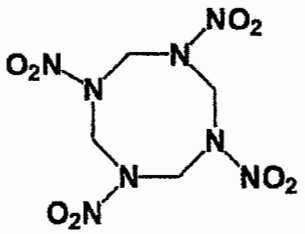

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Getting a precise figure on the number of sites contaminated with munitions is difficult because not all federal lands have been extensively sampled but it is known that at least geographically, the Department of Defense (DoD) has the largest cleanup program. Through fiscal year 1996, the DoD has spent $9.4 billion on environmental cleanup and identified 12,000 contaminated sites (not all munitions-contaminated) at 770 active or recently closed installations, plus 3,523 contaminated sites at 2,641 former facilities (Siegel 1998). Specific estimates on the number of sites with UXOs also vary. Data compiled by the EPA in 1999 indicated >7500 sites already transferred or slated for transfer from military control could contain UXOs (MacDonald 2001). The Defense Science Board (1998) on UXOs estimated 1500 sites existed but acknowledged this number is uncertain because of the absence of surveys. These sites ranged from small parcels of land to vast tracts covering thousand of acres. Consequently, the Department of Defense's cleanup challenges could cover somewhere between 10 to 20 million acres in the U.S. (Siegel 1998). The Defense Science Board projected that if only 5% of the acreage suspected of containing UXOs required remediation, cleanup costs could exceed $15 billion.

At sites where munitions were manufactured or assembled, soil contamination has typically resulted from the once common practice of releasing explosive-tainted wastewater to drainage ditches, sumps, settling ponds or impoundments. TNT manufacturing for example, required large volumes of water for purification. The aqueous waste produced from this process, known as red water, has been found to contain up to 30 additional compounds besides TNT (Urbanski 1984). Similar practices occurred at loading, packing and assembling plants, where wastewater (also known as pink water) generated during plant operations was routinely discarded outside into sumps and drainage ditches. Left untreated, surface soils laden with wastewater constituents eventually became point sources of ground water contamination. One study showed that of the numerous sites sampled, >95% contained TNT and 87% exceeded permissible ground water concentrations (Walsh *et al.* 1993).

Environmental risk assessments of military facilities have determined that contaminated soils often contain mixtures of energetic compounds rather than a single explosive. In addition to nitramines (RDX, HMX), other classes of contaminants commonly observed include nitroaromatics (TNT, dintro- and nitrotoluenes) and nitrate esters (nitroglycerin, nitrocellulose). Of these, TNT, RDX and HMX have been the most frequently detected largely because of their prevalence in manufacturing specific compositions (e.g., octol contains ~ 75% HMX and 25% TNT; Akhavan 1998, Composition C-4, 91% RDX, Smith-Simon and Goldhaber 1995) and synthesis impurities. The Bachmann synthesis of RDX (Bachmann and

Sheehan 1949) commonly results in HMX impurities of 8 to 12% (Fedoroff and Sheffield 1966) whereas the two grades of HMX used for military purposes contain between 2 and 7% (w/w) RDX (Island Pyrochemical Industries 2004). Consequently, to effectively remediate munitions-contaminated soil and water, treatment technologies must be robust enough to treat multiple energetic compounds rather than a single explosive.

Environmental Fate and Toxicity

Structural differences between energetic classes (i.e., nitroaromatics vs nitramines) are manifested in their recalcitrance and environmental fate. For example, when soils contain low to modest concentrations of TNT (e.g., <500 mg kg^{-1}), several biotic and abiotic transformations can promote natural attenuation and detoxification (Comfort *et al.* 1995, Hundal *et al.* 1997a, Peterson *et al.* 1996, 1998, Kreslavski *et al.* 1999). Microbial degradation of TNT has been demonstrated by aerobic, anaerobic, or combined pathways with practically every study observing amino degradation products (reduction of one or more nitro moieties; e.g., McCormick *et al.* 1976, Isbister *et al.* 1980, Schackmann and Müller 1991, Walker and Kaplan 1992, Funk *et al.* 1993, Marvin-Sikkema and de Bont 1994, Bradley and Chapelle 1995, Gilcrease and Murphy 1995, Bruns-Nagle *et al.* 1996, Pasti-Grigsby *et al.* 1996). The aromatic amines derived from TNT (e.g., 2,4-diaminonitrotoluene) can partition to soil organic matter and eventually irreversibly bind to soil humic matter through imine linkages resulting from condensation with carbonyl groups (Bartha and Hsu 1974, Hsu and Bartha 1976, Bollag *et al.* 1983). Also, the electron donating character of NH_2-substituents makes these products more prone to attack by dioxygenases and subject to further degradation (Dickel *et al.* 1993). Hundal *et al.* (1997a) studied the long-term sorption of TNT in soils and observed that after 168 d of equilibration, 32 to 40% of the sorbed ^{14}C-TNT was irreversibly bound (unextractable). In a detailed study using size-exclusion chromatography, Achtnich *et al.* (1999) showed that reduced derivatives of TNT formed during an anaerobic/aerobic soil treatment were irreversibly bound to a wide range of molecular size humic acids (>5,000 daltons).

By contrast, the reduction of the nitramines (i.e., RDX, HMX) typically produces nitroso rather than amino derivatives. Because RDX and its nitroso derivatives are stable under aerobic conditions, reports of irreversibly bound RDX have been less prevalent. Price *et al.* (2001) systematically studied the short-term fate of RDX and concluded that RDX was fundamentally different from TNT by being relatively more recalcitrant

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in aerobic soils slurries. Only under highly reducing conditions was RDX subject to extensive mineralization. Price *et al.* (2001) also concluded that under aerobic conditions, most RDX was associated with the solution phase and did not bind in unextractable forms. Sheremata *et al.* (2001), however, studied the long-term fate of RDX and reported that although RDX was not extensively sorbed by surface soils (Kd = 0.83 L kg^{-1}), what was sorbed was nearly irreversible with no appreciable difference between sterile and nonsterile soils. By contrast, Singh *et al.* (1998a) observed conditions under which unextractable RDX residues did and did not form and suggested soil concentration might be a determining factor. In a long-term soil slurry study, Singh *et al.* (1998a) observed that 34% of the added RDX (32 mg L^{-1}) was sorbed within 30 min, with sorption increasing to only 37% after 168 d. Approximately 84% of the sorbed RDX was readily extractable and only 8% of the initial ^{14}C was unextractable. Interestingly, no bound residue formed when the soils were highly contaminated and contained solid-phase RDX - a condition that is readily observed in surface soils surrounding loading and packing facilities. The presence of solid-phase RDX in a soil matrix would keep the soil solution saturated and severely limit microbial activity (i.e., biotic transformations). Oh *et al.* (2001) also observed bound-residue formation while treating RDX with zerovalent iron and hypothesized that upon ring fission, the amine-containing products (e.g., hydroxymethylnitramine) could bind to the carbonyl functional groups of humics to form unextractable residues. Therefore, it appears that transformation (biotic or abiotic) beyond the nitroso derivatives is needed before bound or unextractable residues of RDX will be observed but in many cases, RDX will remain recalcitrant in the solution phase and readily available for transport.

Although TNT, RDX, and HMX have been detected in ground water, RDX appears to pose the greater environmental concern for aquifers because of its prevalent use and sorption characteristics. Despite having a lower aqueous solubility than TNT (RDX = 34.4 mg L^{-1} at 25°C, TNT = 128.5 mg L^{-1}; Park *et al.* 2004; Table 1), RDX is more mobile in soils than TNT. This characteristic has resulted in the observance of larger RDX plumes than TNT beneath sites that have been heavily contaminated with both compounds (Spalding and Fulton 1988). In comparing RDX with HMX, both are structurally similar by consisting of multiples of the CH_2=N-NO_2 monomeric unit but these polynitramines differ with HMX being less water soluble than RDX (Table 1) and chemically more stable and resistant to attack by strong base (Akhavan 1998). Recent biodegradation studies have also confirmed that HMX is more resistant to microbial attack than RDX (Shen *et al.* 2000).

Brannon and Pennington (2002) compiled solubility and sorption

Table 1. Compiled solubility and adsorption coefficients for RDX and HMX.

Compound	Statistic	Solubility and Temperature	Solubility Reference[1]	Partition Coefficient	Total Organic Carbon	Organic Carbon Coefficient Koc	Partition Reference[1]
		(mg L^{-1})		(L kg^{-1})	(%)	(L kg^{-1})	
RDX		28.9(10°C)	Sikka *et al.* 1980	0.43	0.6	73	Tucker *et al.* 1985
		42.3 (20°C)	Sikka *et al.* 1980	0.16	0.5	32	Tucker *et al.* 1985
		38.4 (20°C)	Spanggord et al. 1983	0.93	0.5	186	Tucker *et al.* 1985
		59.9 (25°C)	Banerjee *et al.* 1980	1.21	1.4	85	Tucker *et al.* 1985
		59.9 (26.5°C)	Sikka *et al.* 1980	1.65	2.0	81	Tucker *et al.* 1985
		75.7 (30°C)	Sikka *et al.* 1980	2.39	6.0	40	Tucker *et al.* 1985
		27.2 (20°C)	Bier *et al.* 1999	0.81	0.5	150	Tucker *et al.* 1985
		34.5 (25°C)	Bier *et al.* 1999	2.42	6.3	38	Tucker *et al.* 1985
		43.8 (30°C)	Bier *et al.* 1999	7.30	3.1	235	Tucker *et al.* 1985
		89.7 (45°C)	Bier *et al.* 1999	0.74	1.2	61	Tucker *et al.* 1985
		113.9 (50°C)	Bier *et al.* 1999	0.57	1.0	58	Tucker *et al.* 1985
				0.87	0.7	132	Tucker *et al.* 1985
				1.20	1.0	125	Brannon *et al.* 1992
				3.50	2.4	146	Brannon *et al.* 1992
				0.95	2.4	40	Myers *et al.* 1998
				0.77	0.6	135	Myers *et al.* 1998
				0.97	1.7	57	Singh *et al.* 1998a
				6.38	4.9	130	Singh *et al.* 1998a
				1.40	3.3	42	Spanggord *et al.* 1980
				4.20	3.3	127	Spanggord *et al.* 1980
	Mean					99	
	Median					83	
	Std Dev.					58	
HMX		1.21 (10°C)	Spanggord *et al.* 1982	12.10	2.4	504	Brannon *et al.* 1999
		2.60 (20°C)	Spanggord *et al.* 1982	4.25	0.6	670	Brannon *et al.* 1999
		5.00 (22-25°C)	Glover and Hoffsommer 1973	1.60	2.4	67	Myers *et al.* 1998
		5.70 (30°C)	Spanggord *et al.* 1982	1.17	0.6	205	Myers *et al.* 1998
		6.60 (20°C)	McLellan *et al.* 1988b	8.70	1.3	669	McGrath 1995
		2.00 (20°C)	Park *et al.* 2004				
		8.00 (45°C)	Park *et al.* 2004				
		22.0 (55°C)	Park *et al.* 2004				
	Mean					423	
	Median					504	
	Std Dev.					275	

[1] Many references initially compiled and cited in Brannon and Pennington (2002).

	Mean	1.40	3.3	42	Spanggord *et al.* 1980	
	Median	4.20	3.3	127	Spanggord *et al.* 1980	
	Std Dev.					
HMX						
	1.21 (10°C)	Spanggord *et al.* 1982	12.10	2.4	504	Brannon *et al.* 1999
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coefficients of energetic compounds from several references and reported linear adsorption coefficients (Kd) between 0 and 8.4 L kg^{-1} for RDX and <1 to 18 L kg^{-1} for HMX. While previous studies have revealed that sorption of RDX and HMX appear to be governed more by clay content than organic matter (Sheremata *et al.* 2001, Monteil-Rivera *et al.* 2003), differences in organic carbon partition coefficients (Koc) among the nitramines can be ascertained. Using only Kd values where the organic carbon content of the sorbent was ≥0.5% and more representative of surface soils, the calculated average Koc value was 99 L kg^{-1} for RDX and 423 L kg^{-1} for HMX (Table 1). By comparison, the recently developed polycyclic nitramine CL-20 (2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane), which is being considered by the military for large scale production, had an average Koc of 745 L kg^{-1} (n=5) (Balakrishnan *et al.* 2004). Szecsody *et al.* (2004) compared the sorption characteristics of RDX and CL-20 on six different soils and observed mixed results in a 24-h batch experiment that monitored changes in solution phase concentrations. On three of the soils, RDX sorption was similar to two-fold greater than CL-20 but on the other three soils, CL-20 sorption was 3 to 9 fold greater than RDX. Calculated Koc values for CL-20 on soils with organic carbon contents ≥0.5% averaged 367 L kg^{-1} (range: 84 - 680 L kg^{-1}, n=4). The lower Koc for RDX indicates that it would be the first to migrate through the surface soil layers and underscores why it has been the most frequently observed nitramine in ground water.

The driving force behind all remedial efforts is a concern for the environment and human health. In this regard, RDX has been shown to adversely affect the central nervous system, gastro-intestinal tract and kidneys (Etnier 1989). Common symptoms of RDX intoxication include nausea, vomiting, hyperirritability, headaches, and unconsiousness (Kaplan *et al.* 1965, Etnier 1989, Etnier and Hartley 1990). Liver tumors have been reported in mice fed RDX for 3 months (ATSDR 1996) and the EPA has classified RDX as a possible human carcinogen. The EPA established a lifetime health advisory guidance level of 2 ug L^{-1} for RDX in drinking water for adults. Information on the adverse effects of HMX on humans is limited but the EPA has recommended that drinking water be less than 400 ug L^{-1} (ATSDR 1997).

In addition to human health concerns, the dissemination of nitramines into waterways and soil pose ecological concerns. Consequently, risk assessments and cleanup activities of munitions-contaminated sites require extensive exposure and effects data so that accurate and realistic decisions can be made (Steevens *et al.* 2002). Considerable research on this topic has been published in the last five years (see Steevens *et al.* 2002, Gong *et al.* 2001a, b, and Robidoux *et al.* 2002 and references cited within) and

includes work by Robidoux *et al.* (2002), who measured the sublethal and chronic toxicities of RDX and HMX on earthworms. They found that reproduction parameters such as number of juveniles and biomass for the earthworm species *Eisenia andrei* were significantly decreased by RDX (soil concentration ≥46.7±2.6 mg/kg) and HMX (≥15.6±4.6 mg/kg). Gong *et al.* (2001a, b) examined the ecotoxicological effects of RDX and HMX on indigenous soil microbial processes and concluded that extractable soil concentrations as high as 12500 mg HMX kg^{-1} did not significantly influence soil microorganisms whereas RDX showed significant inhibition on several microbial activities (e.g., potential nitrification, basal respiration). Because soil microorganisms will likely be more affected by what is in the soil solution rather than the total soil concentration (typically determined by acetonitrile extractions), differences in aqueous solubilities between RDX and HMX may explain their results. Using HMX at its solubility limit (<6.5 mg L^{-1}), Sunahara *et al.* (1998) observed no toxic effects to *Vibrio fisheri* (Microtox) and a green alga (*Selenastrum capricornutum*) whereas the cell density of the green alga was reduced by 40% at RDX concentrations near its solubility limit (40 mg L^{-1}). While nitroaromatic compounds (e.g., TNT) can adversely affect aquatic organisms, Lotufo *et al.* (2001) found that HMX and RDX had no significant effect in survival or growth of benthic invertebrates. Earlier research by Bentley *et al.* (1977a, b) also determined that RDX was more toxic than HMX to bluegills (*Lepomis macrochirus*), fathead minnows (*Pimephales promelas*) and aquatic algae (*S. capricornutum, A. flos-aquae*).

The recalcitrance of nitramines in contaminated soils combined with their capacity to leach and impart toxicity concerns underscore the importance of designing remedial treatments that rapidly transform RDX and HMX and render these compounds harmless. To this end, this chapter presents some site-specific examples of RDX and HMX contamination and reviews some laboratory, pilot, and field-scale remediation studies specifically aimed at mitigating soil and ground water contamination.

Examples of RDX and HMX Contamination at Military Sites

Soil and water contaminated with munitions have resulted from a variety of military operations. Examples included: (i) explosive manufacturing, (ii) load, assemble and packing facilities, (iii) munitions maintenance and demilitarization, and (iv) training ranges were firing of live ammunition from small arms, artillery mortar fire, and explosive detonation occurred over multiple acreages. To illustrate the environmental and financial ramifications of these past activities, three defense sites are highlighted

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with a brief overview of the contamination, cleanup costs, and the formidable challenges that lie ahead in remediating the contaminated soil and water.

Nebraska Ordnance Plant

The former Nebraska Ordnance Plant (NOP, Mead, NE) was a military loading, assembling, and packing facility that produced bombs, boosters, and shells during World War II and the Korean War. Ordnances were loaded with TNT, amatol (TNT and NH_4NO_3), tritional (TNT and Al), and Composition B (~60% RDX and 40% TNT) (Comfort *et al.* 1995). During ordnance production, process wastewater was routinely discharged into sumps and drainage ditches. These ditches became grossly contaminated with TNT and RDX with soil concentrations exceeding 5000 mg kg^{-1} near the soil surface (Hundal *et al.* 1997b). When rainfall exceeded infiltration rates, ponded water that formed in the drainage ditches literally became saturated with munitions residues (i.e., reached HE solubility limits) before percolating through the profile (Fig. 2). Considering this process proceeded unabated for more than 40 years, it is no surprise that the ground water beneath the NOP eventually became contaminated. Further complicating ground water concerns were the extensive use of trichloroethylene (TCE) to degrease and clean pipelines by the U.S. Air Force in the early 1960s. As a

Figure 2. Photograph of drainage ditch following heavy precipitation. Drainage ditch adjoined munitions load line building at former Nebraska Ordnance Plant (Mead, NE).

result, the RDX/TCE contaminant plume under the NOP facilities is estimated in the billions of gallons and covering several square miles (Fig. 3).

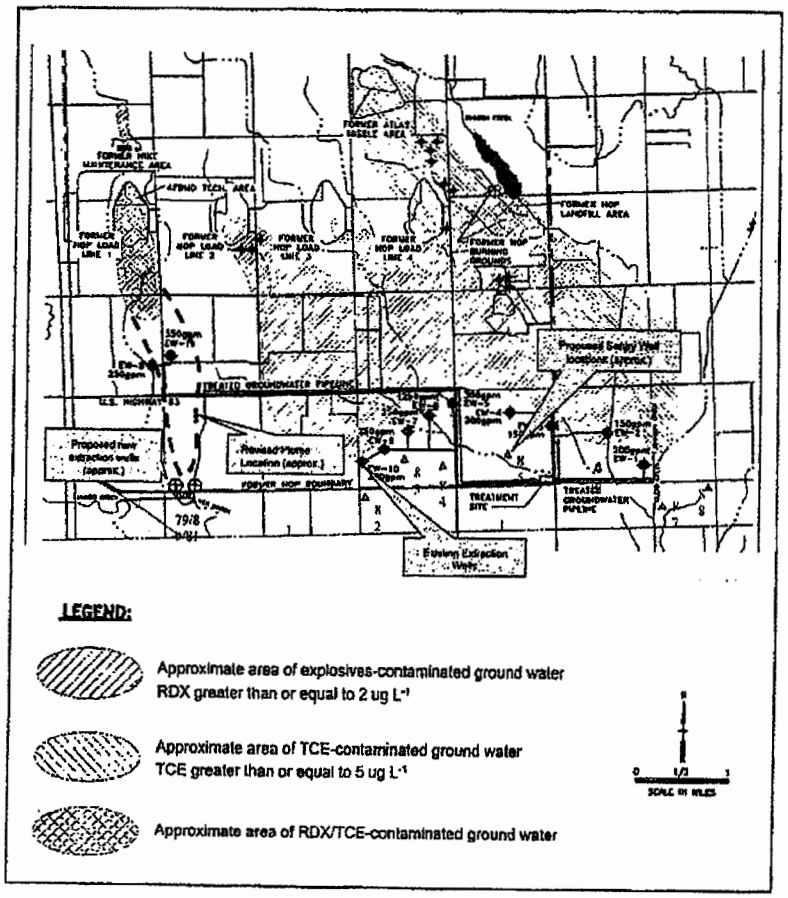

Figure 3 : RDX and TCE plumes beneath the Nebraska Ordnance Plant (Mead, NE).

To prevent the contaminated plume from migrating offsite and in the direction of municipal well fields, an elaborate series of eleven extraction wells and piping networks were constructed to hydraulically contain the leading edge of the RDX/TCE plume (Fig. 3). Currently this $33 million dollar facility treats approximately 4 million gallons of ground water per

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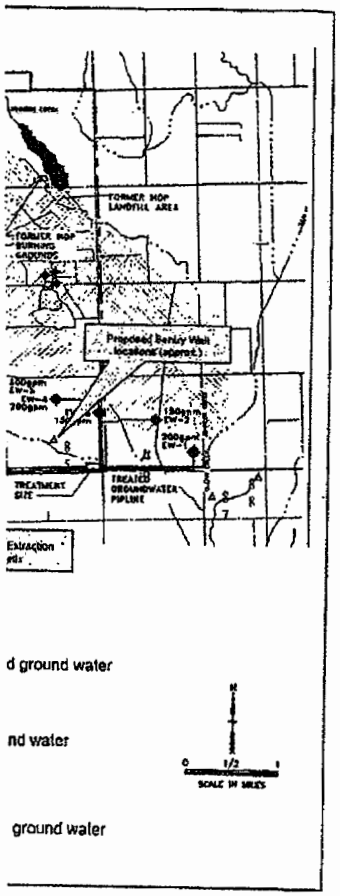

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day with granular activated carbon (GAC). Annual operating costs are approximately $800,000/year. Hydraulic containment plus additional remediation efforts may take 125 years to remadiate the ground water plumes. Future costs will also involve the installation of additional wells to contain a larger than originally anticipated plume under one of the load lines (Fig. 3). The ground water treatment costs are in addition to costs of incinerating the soils that were laden with TNT, RDX, and HMX. An incineration system consisting of rotary kiln followed by a secondary combustion chamber incinerated approximately 16,449 tons of contaminated soil at a technology cost of $6.5 million ($394/ton) and a total cost of $10.7 million ($650/ton). Additional costs were also incurred to remove the contaminated load line buildings and site restoration.

Department of Energy Pantex Plant

The U.S. Department of Energy's (USDOE) Pantex plant near Amarillo, Texas, was constructed during World War II by the U.S. Army for the production of conventional ordnances. In the 1950s, portions of the original plant were renovated and new facilities constructed so that HEs could be manufactured and used for assembly of nuclear weapons. Pre-1980 industrial operations included on-site disposal of high explosives and wastewater into unlined ditches. Surface runoff from these ditches into an aquifer-recharging playa (i.e., closed drainage basins that is periodically wet and dry during the year) has contaminated the perched aquifer beneath the Pantex Plant (Fig. 4). The perched aquifer is contaminated with RDX, HMX, TNT, TCE, 2,4-DNT (2,4-dinitrotoluene), 1,2-DCA (1,2-dichloroethane), PCE (tetrachloroethene) and chromium. Of these, considerable attention has focused on the high explosive RDX because it is the most widespread. The plume is estimated at 1.5 billion gallons and covers approximately 5 to 6 square miles (Fig. 4). While a ground water pump and treat system is currently in place to capture contaminants of potential concern in a section of the perched aquifer, hydrological characteristics of the site make implementing additional remedial technologies extremely formidable. Foremost is that the perched aquifer is ~90 m (300 ft) below the surface and 30 m (100 ft) above the High Plains aquifer, one of the largest aquifers in the world. Second, the saturated thickness of the perched aquifer is less than 4.5 m (15 ft) in many locations, making pump and treat systems ineffective. Migration of the contaminated plume beyond the bound of the Pantex site and into privately owned lands has further exacerbated the problem.

The USDOE Innovative Treatment and Remediation Demonstration (ITRD) program was initiated to evaluate emerging technologies that may potentially replace inefficient or ineffective technologies. In 1998, the ITRD

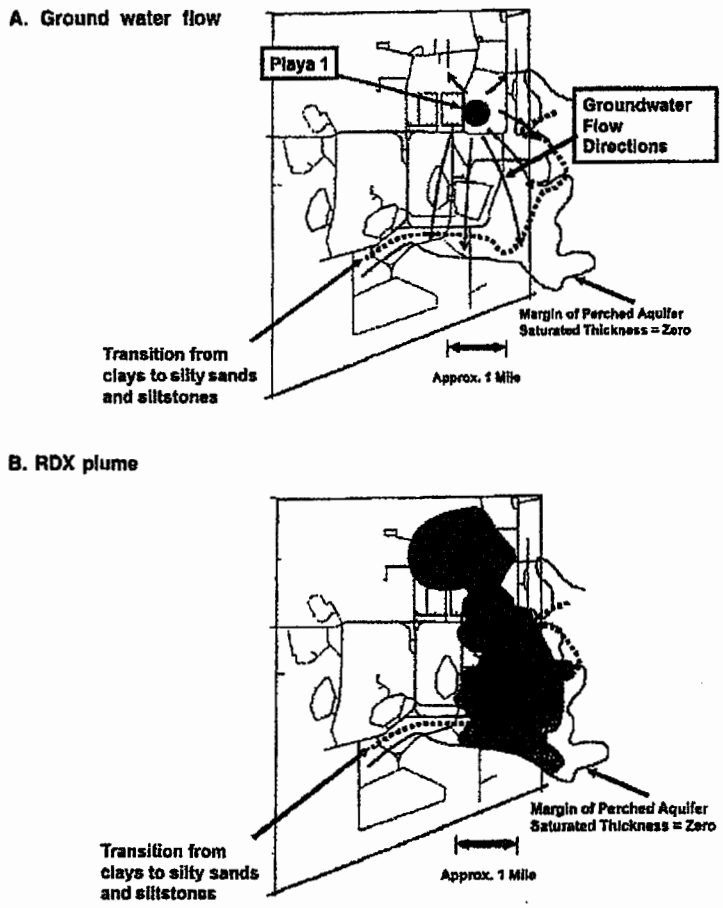
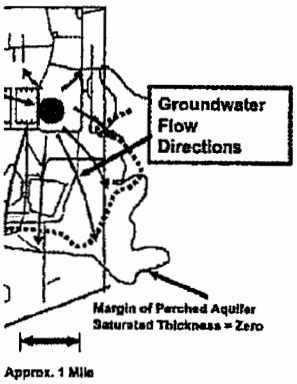
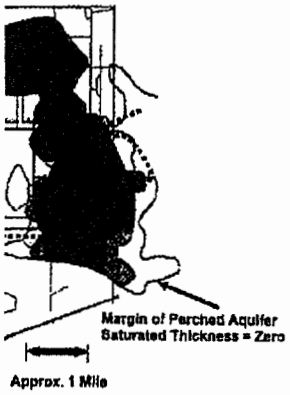


Figure 4. Ground water flow (A) and RDX plume (B) beneath the Pantex Plant (Amarillo, TX). Figure courtesy of Aquifer Solutions, Inc. (Evergreen, CO).

process for the Pantex Plant recommended three in situ technologies for further testing: (i) oxidation by $KMnO_4$; (ii) anaerobic biodegradation; and (iii) chemical reduction by dithionite-treated (reduced) aquifer material. Bench-scale feasibility studies of all three technologies have been conducted and deployment scenarios developed. Well construction costs and spacing are principal driving variables in cost estimates with a number of data gaps still present (Aquifer Solutions Inc. 2002).





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Massachusetts Military Reservation

Military testing and training grounds provide vital lands for preparing military troops for combat and maintaining readiness. While an important resource for military exercises, site commanders must delicately balance these lands so that training operations proceed without the environmental consequences associated with repeated release of energetic compounds. Decades of continuous discharge of live ammunition from small arms, artillery mortar fire, and explosive detonations have contaminated surface soils and impacted ground water at several locations across the U.S. This type of contamination is exemplified at the Massachusetts Military Reservation (MMR) where more than 40 years of military and law enforcement training has contaminated Cape Cod's sole aquifer with RDX. Additional investigations have uncovered propellants, metals, pesticides, volatile and semi-volatile organic compounds, and unexploded ordnances. By impacting 200,000 year-round residents and >500,000 summertime residents who rely on Cape Cod's aquifer for drinking water, the financial costs of cleaning up MMR, coupled with public and political outcry, have forced the Department of Defense to seek proactive remedial technologies that prevent situations like MMR from reoccurring, yet still allow the training grounds to be used for preparing U.S. troops.

Remediating military training ranges present unique challenges because they typically encompass thousands of acres that are under constant barrage from training exercises. For example, the training ranges at MMR cover approximately 144,000 acres, with multiple target areas. Recent records indicate that before the EPA halted military activities at MMR, 1,770,000 small arms and more than 3000 rounds of artillery and mortar were fired annually. Extensive investigations at military training grounds have determined that soil contamination is extremely variable with concentrations ranging from "no detect" to isolated "hot spots." In a recent study characterizing contamination at military firing ranges, Jenkins *et al.* (2001) found examples of contamination by showing that surface soils concentrations ranged between 458 and 175,000 ug 2,4-dintrotoluene kg^{-1} in front of a single 105-mm howitzer that had fired about 600 rounds within 30 d. This same study observed that soil samples collected below and adjacent to a 155-mm howitzer shell that had undergone low-order detonation were heavily contaminated with TNT and its biological degradation products (Jenkins *et al.* 2001). These reports as well as others (Thiboutot *et al.* 1998), confirm that military testing and training ranges, although vital to preparing Armed Forces, must be characterized for environmental contaminants and in many instances, remedial efforts taken to control the leaching of explosives and prevent ground water contamination.

The Nebraska Ordnance Plant, Pantex, and Massachusetts facilities

exemplify just three of the potentially thousands of munitions-contaminated sites currently in need of remediation. Clearly, the enormous environmental and financial ramifications associated with these facilities provide ample justification for the development of cost-effective and environmentally sound treatment technologies. To date, the most demonstrated remediation technology for explosive-containing soils is incineration. Although incineration is effective, it is expensive, produces an unusable ash byproduct, and has poor public acceptance due to safety concerns regarding air emissions (Lechner 1993). Incineration would also be impractical for impact ranges that may require treatment of thousands of acres. Likewise, the use of granular activated carbon in pump and treat systems for ground water is effective in removing a wide variety of HEs but at a considerable annual cost and, as demonstrated at the Nebraska Ordnance Plant, could take more than a century to complete. Furthermore, the spent activated carbon can usually not be reused and requires incineration (Sisk 1993). The hydrological characteristics of some sites (i.e., Pantex) also make GAC unfeasible and in-situ technologies more desirable. While many researchers have taken a biological approach to solving HE contamination (bioremediation, phytoremediation, composting, etc.), there is also a large contingency that have tried an abiotic or chemical approach. Chemical approaches are usually performed by adding one or more chemicals reagents (reductant, oxidant) or altering the physiochemical properties of the soil-water environment. Chemical methods offer several advantages to biological methods because they are often faster, can treat highly contaminated environments, and are less sensitive to ambient conditions. The goal of a chemical approach is to either transform the xenobioitc into carbon dioxide, H_2O and mineral elements or structurally transform the parent compound into a product that is more biodegradable (i.e., abiotic-biotic approach). Because excellent reviews of biological approaches to remediating munitions contaminated soil and water are currently available (Gorontzy *et al.* 1994, Hawari 2000, Hawari *et al.* 2000, Rosser *et al.* 2001, Spain 1995, Spain *et al.* 2000, Van Aken and Agathos 2001), this chapter focuses on reviewing some abiotic approaches that have been used to remediate RDX and HMX contaminated soil and water.

Abiotic Remediation Treatments for RDX/HMX-Contaminated Soil and Water

Chemical Reduction Using Zerovalent Iron

From a historical perspective, metals have been used to transform and synthesize organic chemicals since the late 1800s. The use of zerovalent metals in environmental research, however, did not surface until fifteen to

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twenty years ago when Sweeny (1979, 1981), followed by Senzaki and Kumagai (1988, 1989), reported that metallic iron could be used to degrade organic contaminants such as chlorinated solvents in water. The more recent idea that iron metal could be used for *in situ* remediation of subsurface contaminants grew primarily from work carried out at the University of Waterloo. In a project involving sorption of organic compounds to well casings, it was noted that the concentration of the halogenated compound, bromoform, declined when in contact with steel and aluminum casing materials. This 1984 observation was attributed to a dehalogenation reaction, but the environmental significance of this work was not realized until a few years later when the results were re-evaluated and published (Reynolds *et al.* 1990). Today, the use of zerovalent metals has become an alternative to the common pump-and-treat and air-sparging technologies, and the emergence of the so-called permeable reactive barriers (PRBs), consisting of scrap Fe^0 cuttings, has proven to be a highly cost effective treatment for contaminated ground water (Wilson 1995). Since these initial reports by the University of Waterloo, a flurry of research activity on the use of zerovalent metals in environmental research has ensued with more than 500 publications currently available (http://cgr.ese.ogi.edu/ironrefs/). Furthermore, >80 PRBs have been installed in the U.S. and 100 world-wide (EnviroMetal Technologies, Inc. 2004), with the majority of applications targeting chlorinated solvents. This heightened interest and field-scale deployment has helped to make Fe^0 the most widely studied chemical reductant for environmental applications (Tratnyek *et al.* 2003).

Iron is an effective remediation tool because when placed in water, metallic iron (Fe^0) becomes an avid electron donor and its oxidation (E^0_h = -0.409 V) can drive the reaction of many redox-sensitive contaminants. Researchers have used Fe^0 as the bulk reductant for the reduction of nitroaromatic compounds to anilines (Agrawal and Tratnyek 1996), which can be further degraded biologically (Dickel *et al.* 1993) or incorporated into natural organic matter via enzyme-catalyzed coupling reactions (Bollag 1992, Hundal *et al.* 1997a). Through studies on the dehalogenation of chlorinated methanes, Matheson and Tratnyek (1994) proposed three possible reduction mechanisms, with direct electron transfer at the iron interface as the most probable reaction pathway. Later, Scherer *et al.* (1999) expanded this theory by proposing that mineral precipitates formed during iron corrosion may influence the efficacy of iron to transform contaminants by acting as a physical barrier, semiconductor, or reactive surface. Others have shown that iron can work in conjunction with naturally occurring electron transfer mediators (quinone moieties in humic and fulvic acids) to facilitate contaminant destruction in contaminated soils and sediments (Weber 1996).

Several recent studies have also indicated the importance of surface-bound Fe(II)-species as electron donors in redox transformations of organic compounds (Klausen *et al.* 1995, Heijman *et al.* 1993, Heijman *et al.* 1995, Amonette *et al.* 2000, Satapanajaru *et al.* 2003a, b). The catalytic activity of Fe(II) in the presence of oxides is believed to be the result of complexation of Fe(II) with surface hydroxyl groups and the formation of inner-sphere bonds, which increases the electron density of the adsorbed Fe(II). Klausen *et al.* (1995) demonstrated that surface bound Fe(II) on iron (hydr)oxide surfaces or surface coatings plays an important role in the reductive transformation of nitroaromatic compounds. Gregory *et al.* (2004) observed complete transformation of RDX by adsorbed Fe(II) on magnetite with reaction rates increasing as a function of adsorbed Fe(II). While Klausen *et al.* (1995) observed that unbound Fe(II) species were not reactive for nitroaromatics, the lack of reactivity to unbound Fe(II) appears to be compound specific because Eary and Rai (1988) report chromate reduction by ferrous iron and Gregory *et al.* (2004) reported that 72 uM of RDX was transformed by 1.5 mM Fe(II) ($FeCl_2$) at pH 8.0. Our laboratory has also observed RDX degradation in aqueous solutions by Fe(II) alone (100 mg L^{-1} $FeSO_4 \bullet 7H_2O$) at pH 8.5 (unpublished data). A confounding factor in these experiments however, is that magnetite or green rusts can also form at alkaline pH and thus a homogenous solution of Fe(II) can become a mixed phase system (Fe(II) + magnetite or other precipitates).

In aerobic environments, oxygen is the normal electron acceptor during iron corrosion while under anaerobic conditions, such as those encountered in ground water or waterlogged soils, electron transfer during iron corrosion can be coupled to redox sensitive organic contaminants. For this reason, use of zerovalent iron is generally implemented under fully anoxic conditions because the presence of oxygen is expected to lower the efficiency of the process by competing with the target contaminants (Joo *et al.* 2004), accelerating iron aging (passivation), and cause loss of reactivity (Gaber *et al.* 2002). Ironically, examples exist where destruction kinetics of certain contaminants by Fe^0 have been accelerated by exposure to air. Tratnyek *et al.* (1995) observed a higher rate of CCl_4 degradation by Fe^0 in an air-purged system ($t_{1/2}$ = 48 min) than in a nitrogen-purged ($t_{1/2}$ = 3.5 h) or oxygen-purged environment ($t_{1/2}$ = 111 h). Satapanajaru *et al.* (2003a) found that Fe^0-mediated destruction of metolachlor [2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methyl ethyl) acetamide] was faster in batch reactors shaken under aerobic than anaerobic conditions and contributed this increase to the formation and facilitating effects of green rusts, mixed Fe(II)-Fe(III) hydroxides with interlayer anions that impart a greenish-blue color. Joo *et al.* (2004) also observed that the herbicide

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molinate (S-ethyl hexahydro-1H-azepine-1-carothioate) was much more readily transformed by Fe^0 when shaken in the presence of air than when purged with N_2. Interestingly, they showed that the transformation occurring was actually an oxidation caused by a two-electron reduction of oxygen to form hydrogen peroxide, which subsequently caused the formation of strongly oxidizing substrates (i.e., hydroxyl radicals). All these observations lend credence to using zerovalent iron in microaerophillic environments, such as those that might be encountered in treating soils.

Earlier work with zerovalent zinc demonstrated the utility of metals to treat soils contaminated with DDT (Staiff *et al.* 1977), methyl parathion (Butler *et al.* 1981) and polychlorinated biphenyls (Cuttshall *et al.* 1993). More recent research indicates the tremendous potential of Fe^0 to degrade high explosives (Hundal *et al.* 1997b, Singh *et al.* 1998b, 1999, Wildman and Alvarez 2001, Oh *et al.* 2001, Oh and Alvarez 2002, Comfort *et al.* 2003, Park *et al.* 2004) and a variety of pesticides (atrazine, Singh *et al.* 1998c; dicamba, Gibb *et al.* 2004; metolachlor, Comfort *et al.* 2001; Satapanajaru *et al.* 2003a, b).

RDX/HMX-Contaminated Soil. One of the biggest obstacles to treating contaminated soils at former loading, packing and manufacturing facilities (e.g., Nebraska Ordnance Plant) is the sheer magnitude of contamination present in the impacted surface soils. It is not uncommon for surface soils to contain energetic compounds in percentage concentrations and approach detonation potential (Crockett *et al.* 1996, Talmage *et al.* 1999, Comfort *et al.* 2003, Schrader and Hess 2004). Because of the equilibrium relationship between the soil solution and solid phase explosive, remediating soils containing solid-phase HEs will not only require treatments that demonstrate rapid destruction in solution but also those that continue to transform RDX/HMX as dissolution and desorption occurs from the soil matrix. To evaluate Fe^0 as a remedial treatment for RDX-contaminated soil, Singh *et al.* (1998b) began by initially determining the effectiveness of zerovalent iron to remove or transform RDX in a near-saturated solution. Treating a 32 mg L^{-1} RDX solution (144 uM) with 10 g Fe^0 L^{-1} resulted in complete RDX removal from solution within 72 h (Fig. 5A). Simultaneous tracking of ^{14}C in solution provided a carbon mass balance for the RDX. At Fe^0 concentrations ≤ 2 g Fe^0 L^{-1}, solution ^{14}C activity remained unchanged (Fig. 5B), indicating that RDX transformation products produced from the Fe^0 treatment (measured as ^{14}C activity) were watersoluble and not strongly sorbed by the Fe^0. At 100 g Fe^0 L^{-1}, 80% of initial ^{14}C activity was lost from solution. More than 95% of the ^{14}C lost, however, was recovered from the Fe^0 surface through a series of extraction and oxidation procedures. Oh *et al.* (2002) treated RDX with scrap iron and high-purity iron under anaerobic conditions. They observed that RDX was readily transformed by both iron

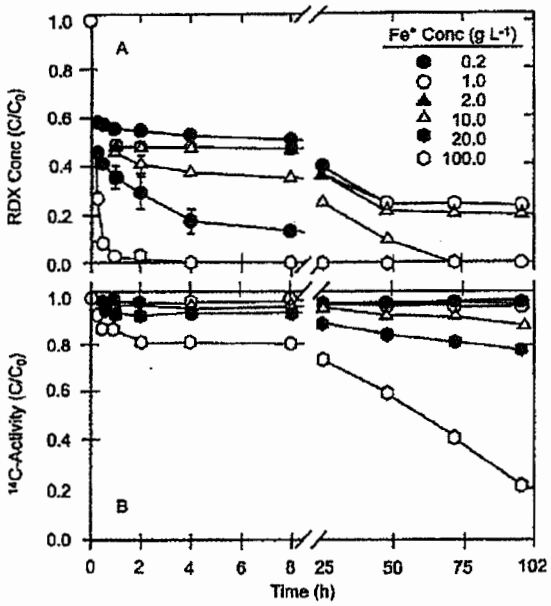

Figure 5. Changes in aqueous RDX (A) and ^{14}C (B) concentrations after tr
an aqueous solution containing 32 mg RDX L-1 with various Fe^0 concentra
Originally printed in *Journal of Environmental Quality* 27:1240-1245.

sources with no appreciable buildup of identifiable degradate
measuring changes in TOC they also confirmed that RDX transform
products were not sorbed to the iron surface.

Major biological reduction products of RDX include mono-, di, a
nitroso degradates of RDX, specifically MNX (1,3-dinitro-5-nitros
triazacyclohexane), DNX (1,3-dinitroso-5-nitro-1,3,5-triazacycloh
and TNX (1,3,5-trinitroso-1,3,5-triazacyclohexane) (McCormick *et a*
Singh *et al.* (1998b) monitored these compounds, as well as inor
species (NH_4^+, NO_2^-, and NO_3^-), in an experiment that treated 20 m
RDX with 10 g Fe^0 L^{-1}. Results indicated a rapid initial decrease
concentration that slowed by 24 h (Fig. 6A). While a buildup of MN
and TNX was observed and could be considered a potential conce
the general toxicity of N-nitroso compounds (Mirvish *et al.* 1976, d
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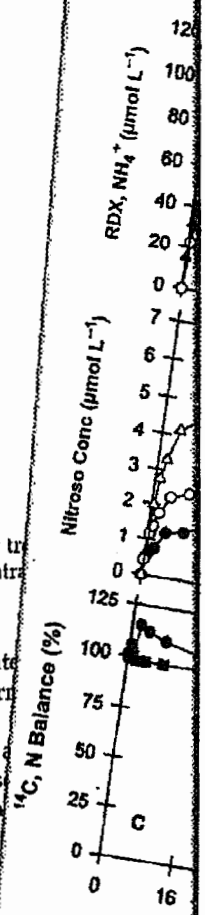

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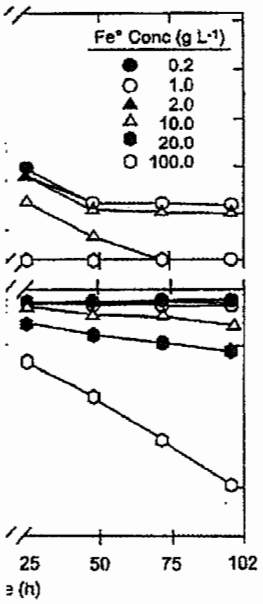

C (B) concentrations after treating
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RDX include mono-, di, and tri-
INX (1,3-dinitro-5-nitroso-1,3,5-
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Other researchers have observed a somewhat similar situation during Fe^0 treatments where destruction rates were initially slow for 12 to 24 h (i.e., lag

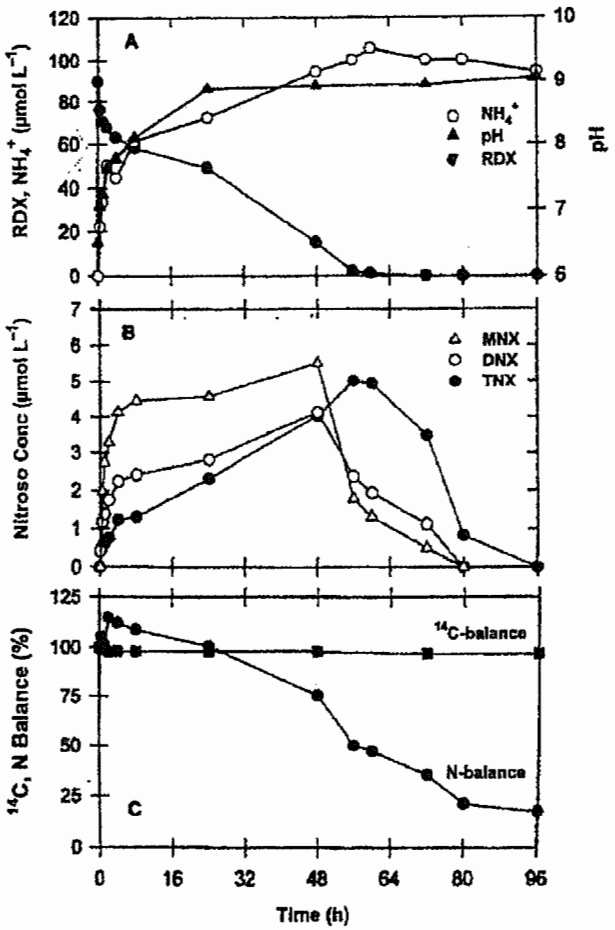

Figure 6. Changes in pH, RDX, and NH_4^+ (A) and MNX, DNX, and TNX (B) concentrations following treatment of 20 mg RDX L^{-1} (90 u*M*) with 10 g Fe^0 L^{-1}. Carbon-14 balance of added ^{14}C-RDX was determined by ^{14}C-activity remaining in solution (C); N-balance of added RDX-N was determined by summing RDX-N, NH_4^+-N, and N associated with nitroso degradation products (C). Originally printed in *Journal of Environmental Quality* 27:1240-1245.

time) before an increase in destruction was observed. These observations typically occur when the pH is alkaline (>8.0) and been attributed to the formation of reactive Fe(II) precipitates such as green rust, magnetite, and secondary reductants [Fe(II) or Fe(II)-containing oxides and hydroxides] coordinated on the oxides of the Fe^0 surface (Satapanajaru *et al.* 2003, Alowitz and Scherer 2002, Gregory *et al.* 2004).

Most research studies performed with Fe^0 have been aimed at potential applications to *in situ* permeable reactive barriers (PRB). As a result, the majority of laboratory experiments have been conducted inside an anaerobic chamber. While anaerobic conditions can be easily obtained inside a PRB, it will be more difficult to exclude oxygen when treating soils *ex situ*, even if treatments involve soil slurries. To optimize conditions under which zerovalent iron could be used, a few researchers have investigated Eh/pH conditions under which Fe^0 was most effective in transforming RDX (Price *et al.* 2001, Singh *et al.* 1999). By using an Eh/pH-stat, Singh *et al.* (1999) showed that RDX destruction kinetics by Fe^0 increased as the Eh and pH decreased with no appreciable increase in destruction rates when Eh <0 mV (Fig. 7).

Although numerous reports now confirm that Fe° can effectively transform RDX in solution and soil slurries (Hundal *et al.* 1997b, Singh *et al.* 1998b, 1999, Wildman and Alvarez 2001, Oh *et al.* 2001, Oh and Alvarez 2002, Comfort *et al.* 2003, Park *et al.* 2004), 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 *in situ* applications or 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 acreages available (Comfort *et al.* 2003). However, for Fe^0 to be effective in static soil windrows, contaminant destruction must occur in the soil solution before the intermixed iron in the soil matrix becomes passivated by exposure to air. As stated earlier, because strictly anoxic conditions are not required for Fe^0 to transform contaminants and examples exist where destruction kinetics were faster in microaerophillic than anaerobic conditions (Tratnyek *et al.*1995, Satapanajaru *et al.* 2003a, Joo *et al.* 2004), it is reasonable to assume that Fe^0 can be used as a soil treatment for remediation purposes. Initial laboratory work with RDX-contaminated soil from the Nebraska Ordnance Plant showed that Fe^0 intermixed with moist soil (0.30-0.40 kg H_2O kg^{-1} soil) could transform RDX under static unsaturated conditions (Singh *et al.* 1998b). Results showed that a single addition of 5% Fe^0 (w/w) transformed 57% of the initial RDX (3600 mg kg^{-1}) following a 12 month incubation.

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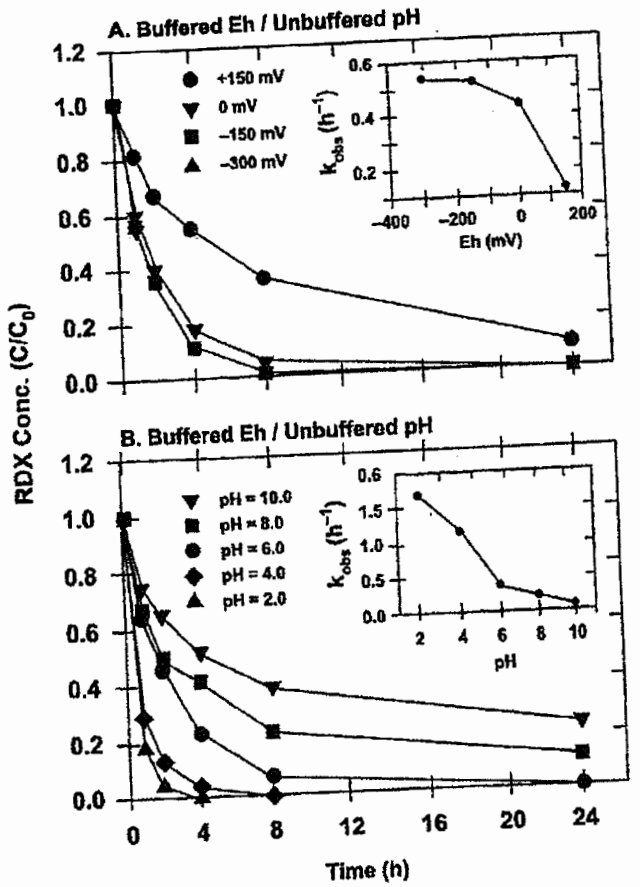

Figure 7. Changes in RDX concentration following Fe^0 treatment under buffered (A) Eh (+150, 0, -150, and -300 mV vs. Ag/AgCl reference electrode) and (B) pH (10, 8, 6, 4, 2). Originally printed in *Environmental Science and Technology* 33:1488-1494.

The effectiveness of Fe^0 to transform RDX in unsaturated soil opened the door for field-scale applications. But using zerovalent iron at the field scale requires the machinery that can thoroughly mix iron throughout the soil matrix. The importance of good mixing cannot be understated because unlike slurries were continual agitation would allow constant movement and contact with Fe^0, the radius of influence for Fe^0 in a static windrow is relatively stationary. The Microenfractionator® (H&H Eco Systems, North

Bonneville, WA) is the trade name of a high-speed mixer that has been specifically augmented to mix windrows of soil (Fig. 8). In 1999, we successfully utilized a pull-behind-tractor version of this mixer to remediate 1000 yd^3 of pesticide-contaminated soil with Fe^0 at the field scale (Comfort *et al.* 2001). In 2000, we attempted to evaluate the use of Fe^0 for treating HE-contaminated soil by conducting pilot-scale experiments (70 kg soil) with a bench-top replica of the field-scale unit (Fig. 8). Contaminated soil containing RDX, TNT, and HMX from an outwash pond that had previously been used for munitions wastewater disposal (Los Alamos National Laboratory, NM) was treated with Fe^0 and some acidifying amendments. Zerovalent iron effectively removed 98% of the RDX and TNT within 120 d under static unsaturated conditions (Comfort *et al.* 2003). Because HMX is considered less toxic than RDX (Bentley *et al.* 1977a, b, McLellan *et al.* 1988a, b), Los Alamos personnel did not initially considered it a contaminant of concern. Further soil analysis, however, revealed that HMX was present at very high concentrations (>30 000 mg kg^{-1}) and that this energetic compound was not effectively destroyed by the Fe^0 treatment.

To determine if low solubility was responsible for the inability Fe^0 to transform HMX, Park *et al.* (2004) attempted to increase HMX solubility with higher temperatures and surfactants. While higher temperatures increased the aqueous solubility of HMX (2 mg L^{-1} at 20°C; 8 mg L^{-1} at 45°C, 22 mg L^{-1} at 55°C), increasing temperature did not increase HMX destruction by Fe^0 when RDX and TNT were also present in the soil slurry

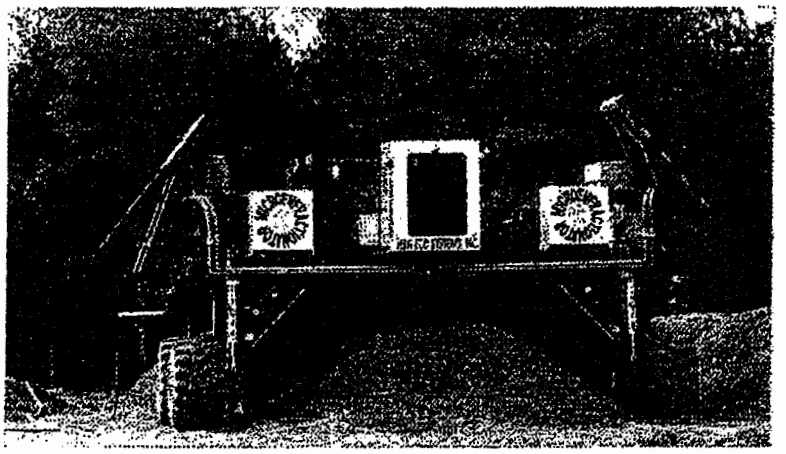

Figure 8. Photograph of field-scale soil mixer. Photo courtesy of H&H Eco Systems, Inc. (North Bonneville, WA).

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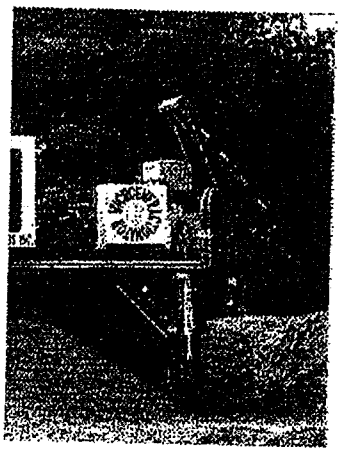

er. Photo courtesy of H&H Eco

matrix. Furthermore, by conducting batch experiments with single and binary mixtures of RDX and HMX, Park *et al.* (2004) showed that when RDX and HMX were present at equal molar concentrations, RDX was a preferential electron acceptor over HMX; consequently, iron-based remedial treatments of RDX/HMX-contaminated soils may need to focus on removing RDX first. The rationale for using surfactants is typically to get more of the contaminant in solution so that it can be degraded. Park *et al.* (2004) found that the cationic surfactants didecyl (didecyldimethyl ammonium bromide) and HDTMA (hexadecyltrimethyl ammonium bromide) could increase HMX solubility (~200 mg L^{-1}) and that both RDX and HMX were effectively transformed by Fe^0 in the surfactant matrix (Fig. 9). Preliminary laboratory studies also showed that didecyl plus Fe^0 could be used to treat HMX-contaminated soil under unsaturated conditions (unpublished data).

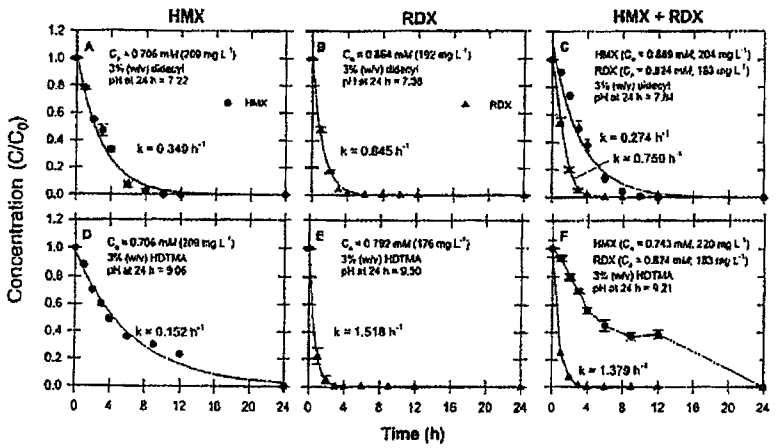

Figure 9. Destruction of HMX and RDX alone or in combination by unannealed Fe^0 in a 3% didecyl or HDTMA matrix. Originally printed in *Journal of Environmental Quality* 33:1305-1313.

Fe^0 Treatment of RDX/HMX-Contaminated Ground Water. Although more than 100 permeable reactive barriers have been installed worldwide (EnviroMetal, Inc. 2004) the majority of PRBs have been targeted for chlorinated compounds and only recently has research been aimed at using PRB for environmental contaminants with multiple nitro groups (e.g., TNT and RDX). Widman and Alvarez (2001) evaluated the potential benefits of an integrated microbial-Fe^0 system to intercept and treat RDX-contaminated ground water. They found that a combined Fe^0-based

bioremediation system may offer significant advantages over either Fe^0 or biodegradation when used alone. Specifically, anaerobic Fe^0 corrosion by water produces cathodic hydrogen, which can then serve as an electron donor for the biotransformation of RDX. Oh and Alvarez (2002) used flow-through columns to evaluate the efficacy of permeable reactive barriers to treat RDX-contaminated ground water. They found that extensive RDX removal (>99%) occurred by Fe^0 columns for more than one year. Through a variety of treatments, they also showed that the Fe^0 could interact with indigenous aquifer microcosms and produce hydrogen gas and acetate, which subsequently facilitated RDX degradation. Column experiments with TNT have shown that permeable iron barriers can reduce TNT to triaminotoluene (Miehr *et al.* 2003), which would be more prone to biotic oxidations (i.e., more biodegradable) in aerobic environments.

Chemical Reduction Using *In Situ* Redox Barriers

In situ redox manipulation (ISRM) is a technology that injects a chemical reductant (sodium dithionite buffered at high pH) into an aquifer. Because dithionite is a strong reductant, particularly in alkaline solutions (reduction potential of -1.12 V), it chemically dissolves and abiotically reduces amorphous and some crystalline Fe(III) oxides (Rueda *et al.* 1992, Chilakapati *et al.* 2000, Szecsody *et al.* 2001, Szecsody *et al.* 2004, US Patent 5,783,088), leaving behind several possible Fe(II) species such as structural Fe(II), adsorbed Fe(II), $FeCO_3$ precipitates, and FeS. The simple reaction describing the reduction of iron by dithionite is:

$$S_2O_4^{2-} + 2Fe^{3+} + 2\,H_2O \rightarrow 2Fe^{2+} + 2SO_3^{2-} + 4H^+ \qquad [1]$$

Because sulfate is eventually produced, extracting treated aquifers after dithionite injection is sometimes used if secondary drinking water limits are a concern (site dependent). 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 additionally by contaminants that can serve as electron acceptors (i.e., RDX, Cr(VI), TCE). The longevity of the reduced sediment barrier is dependent on the flux of electron acceptors. In relatively uncontaminated aquifers, dissolved oxygen in water is the dominant oxidant. Although oxidation of Fe(II) occurs relatively quickly at alkaline pH, slower rates of oxidation are likely for surface Fe(II) phases (Szecsody *et al.* 2004).

Considerable research on ISRM has been conducted with chlorinated solvents and Cr(VI) but only recently has this technology been investigated for high explosives. ISRM is currently being considered at the Pantex Plant

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for treatment of the RDX-contaminated perched aquifer. Initial testing by Pacific Northwest National Laboratory (PNNL) showed that RDX was quickly degraded (i.e., minutes) in batch and column studies by dithionite-treated Pantex sediments. As observed with Fe^0 treatment of RDX (Singh *et al.* 1998b), dithionite-reduced sediments also produced nitroso derivatives of RDX but these degradates were further reduced into ring fragments that were not strongly adsorbed (based on ^{14}C data, Szecsody *et al.* 2001). Subsequent biodegradation studies of the transformed products showed that the RDX degradates produced from the reduced sediments were readily biodegradable under aerobic conditions, with approximately 50% of the initial ^{14}C recovered as $^{14}CO_2$ after 100 d (Adams *et al.* 2005). Consequently, abiotic reduction of RDX by a redox barrier followed by biodegradation of the transformed products may result in a viable treatment scenario for ground water contaminated with RDX.

Field applicability of ISRM however, is also dependent on geochemical (redox capacity) and hydro geological considerations as well as injection design. Dithionite treatment of the perched aquifer material at Pantex yielded a high redox capacity (0.4% Fe(II)/g), which is equal or greater than other sites in which field-scale remediation is in progress or being considered (Szecsody *et al.* 2001). While 100% reduction of aquifer solids may never be achieved in the field (greater reduction near injection well and less reduction further away), it is plausible that partially reduced Pantex sediments (<0.4%Fe(II)/g) will also be able to reduce RDX, as can dithionite itself. Column studies conducted at PNNL indicate that reduced Pantex sediments are capable of treating several hundred pore volumes of ground water. Considering the hydrological characteristics of the Pantex site, this could relate to lifetime of 30 years or more for the redox barrier (Aquifer Solutions, Inc. 2002).

Electrochemical Reduction of RDX in Aqueous Solutions

Electrolysis, the use of electrical energy to drive an otherwise unfavorable chemical reaction, is a developing technology that has been used to remediate industrial wastes and recently applied to explosives for wastewater treatment (Meenakshisundaram *et al.* 1999, Rodgers and Bunce 2001a, Doppalapudi *et al.* 2002, Bonin *et al.* 2004). Some potential advantages of an electrochemical treatment include the low cost of electricity compared with the cost of chemical treatments, relatively low capital costs, modular design, operations under ambient conditions, and the possibility of higher energy efficiency than thermal or photolysis treatments (Rodgers and Bunce 2001a). Rodgers and Bunce (2001a) demonstrated electrochemical reduction of 2,4,6-trinitrotoluene (TNT) at a

reticulated vitreous carbon cathode while Bonin *et al.* (2004) utilized a cascade of divided flow through reactors and showed that an aqueous solution of RDX (48 mg L^{-1}) was completely degraded by a current of 10 mA after flowing through three reactors. The major degradation pathway involved reduction of RDX to MNX followed by ring cleavage to yield formaldehyde and methylenedinitramine, which underwent further reduction and/or hydrolysis (Bonin *et al.* 2004). Doppalapudi *et al.* (2002) also demonstrated that RDX (10 mg L^{-1}) could be degraded under anoxic and oxic conditions by electrolysis while Meenakshisundaram *et al.* (1999) found that RDX degradation increased with increasing current (~20 - 50 mA) and stir rate (630 -2040 rpm).

Chemical Oxidation for In Situ Remediation of Soils and Ground Water

In situ chemical oxidation (ISCO) is class of remediation technologies that delivers oxidants on-site and in-place to ground water or the vadose zone. While municipal and industrial companies have routinely used chemicals to oxidize organic contaminants in drinking and wastewater, it is the ability to treat contaminated field sites that has fueled ISCO popularity, especially when bioremediation is inadequate or where treatment time is considered a factor (Environmental Protection Agency 1998). Increased interest and research in ISCO has caused significant developments and application changes over the last five years with numerous site demonstrations (Vance 2002).

Much of the groundwork for ISCO applications can be traced back to the 20 years or more of research conducted on advanced oxidative processes (AOPs), which employ reactive oxidizing agents such as H_2O_2 or ozone, with or without additional catalysts or photolysis, to generate short-lived chemical species of high oxidation power. Past studies specific to the treatment of explosives include oxidative systems such as H_2O_2/ozone, H_2O_2/ultraviolet light (UV), ozone/UV, or Fenton's reagent for rapid destruction of nitroaromatic and nitramine compounds (see review by Rodgers and Bunce 2001b). Examples of this research include Ho (1986) who demonstrated that photooxidation of 2,4-dinitrotoluene by an H_2O_2/UV system resulted in a side-chain oxidation converting 2,4-DNT to 1,3-dinitrobenzene followed by hydroxylation and cleavage of the benzene ring to produce carboxylic acids and aldehydes. Fleming *et al.* (1997) used a 1:1 mixture of ozone and H_2O_2 at pH>7 (peroxone) to generate hydroxyl radicals and reported that RDX, HMX, and several nitroaromatics in ground water from the Cornhusker Army Ammunitions Plant were degraded by ≥64%, with a destruction efficiency of 90% for RDX. Bose *et al.*

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(1998a, b) also conducted a detailed evaluation of oxidative treatments for RDX using a combination of ozone, UV and hydrogen peroxide and showed that that side-chain oxidation and elimination of nitro radicals or nitrous oxide equivalents occurred, followed by cleavage of the heterocyclic ring that resulted in the formation of urea and formamide. A pilot-scale assessment of UV/photolysis is currently on-going at the Nebraska Ordnance plant for treatment of the RDX plume. In this test, a ground water circulation well (a combination of traditional pump and treat with an *in situ* treatment) is being used to extract and treat the water below surface grade. Results from this trial have shown RDX concentrations (5-78 ug L^{-1}) were typically reduced below 5 ug L^{-1} (Elmore and Graff 2001).

Successfully implementing ISCO requires that the oxidant react with the contaminants of concern and that an effective means of dispersing the oxidant to the subsurface is achieved. Technology advances in this regard include delivery processes such as deep soil mixing, hydraulic fracturing, mulit-point vertical lancing, horizontal well recirculation, and vertical well recirculation (U.S. Department of Energy 1999). Because of their high oxidation potential, the three oxidants commonly employed include hydrogen peroxide (H_2O_2, 1.78 V) either alone or in the form of the Fenton's reagent ($H_2O_2 + Fe^{2+}$), ozone (O_3, 2.07 V), and permanganate (MnO_4^-, 1.68 V). Specific examples illustrating the use of these oxidants for treating RDX/HMX-contaminated soil and water follow.

Permanganate. Chemical oxidation using permanganate has been widely used for treatment of pollutants in drinking water and wastewater for more than 50 years (U.S. Department of Energy 1999). In 2001, more than 100 field applications involving permanganate had been completed or planned (Siegrist *et al.* 2001). Like most of the abiotic treatments discussed thus far, these applications have focused on chlorinated solvents and only recently has permanganate treatments been directed toward treating explosives. Site specific issues are always a concern and the Office of Environmental Management concluded that ISCO using $KMnO_4$ is applicable for the destruction of dissolved organic compounds in saturated permeable zones with hydraulic conductivities > 10^{-4} cm/s, low organic carbon contents (<0.5%) and a pH range between 3 and 10 (optimum, 7-8) (U.S. Department of Energy 1999).

Commonly manufactured and sold as a solid ($KMnO_4$) or liquid ($NaMnO_4$), permanganate is an oxidizing agent with a strong affinity for organic compounds containing carbon-carbon double bonds, aldehyde groups, or hydroxyl groups. Research with chlorinated solvents has shown that permanganate is attracted to the negative charge associated with the π electrons of chlorinated alkenes such as tetrachlroethene, trichloroethene, dichloroethene, and vinyl chloride (Oberle and Schroder 2000). Although

the chemical structure of RDX and HMX does not readily lend itself to reaction with permanganate, IT and Stroller Corporation (2000) initially demonstrated effective RDX destruction by $KMnO_4$ treatment. Based on favorable laboratory results, a single-well push-pull test was also conducted at the Pantex site. In this test, permanganate was injected (push) into a single well, allowed to react, and then extracted (pull). Significant degradation of all HE compounds was observed with RDX half-life estimated at ~7d at a $KMnO_4$ concentration of 7000 mg L-1 (Siegrist *et al.* 2001).

In a follow up to the observations of IT and Stroller (2000), Adam *et al.* (2004) subsequently used ^{14}C-RDX with $KMnO_4$ and found that a 2.8 mg L^{-1} solution of RDX solution treated with 20,000 mg L^{-1} $KMnO_4$ decreased to 0.1 mg L^{-1} within 11 d with cumulative mineralization continuing for 14 d until 87% of the labeled carbon was trapped as $^{14}CO_2$. Moreover, they showed lower $KMnO_4$ concentrations (1000-4000 mg L^{-1}) also produced slow (weeks) but sustainable RDX destruction (Fig. 10) (Adam *et al.* 2004). Treatment parameters such as initial RDX concentration (1.3-10.4 mg L^{-1}) or pH (4.1-11.3) had no significant effects on reaction rates. Microcosm studies also demonstrated that RDX products produced by permanganate were more biodegradable than parent RDX. While Adam *et al.* (2004) hypothesized that permanganate may be facilitating hydrolysis of RDX and that 4-nitro-2,4-diaza-butanal (4-NDAB) may be an intermediate product of the reaction, more detailed studies are needed to determine destructive mechanisms. Nevertheless, the high destructive and mineralization rates observed combined with the ability of permanganate to remain active in the subsurface for weeks to months and allow wider injection well spacing (IT and Stoller 2000) lends supports for use of permanganate in treating RDX/HMX plumes.

Fenton Reaction. The Fenton reaction (Fenton 1894) is recognized as one of the oldest and most powerful oxidizing reactions available. This reaction has been used to decompose a wide range of refractory synthesized or natural organic compounds (Sedlak and Andren 1991, Watts *et al.* 1991). The Fenton reagent is a mixture of hydrogen peroxide (H_2O_2) and ferrous iron (Fe^{2+}), which produces OH radicals (Haber and Weiss, 1934).

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + \bullet OH + OH^- \qquad [2]$$

Although several propagating reactions can occur (Walling, 1975), Tomita *et al.* (1994) provided strong experimental evidence that the OH radical is the primary oxidizing species formed by Fe(II)-catalyzed decomposition of H_2O_2 in the absence of a iron chelator. The hydroxyl radical is second only to fluorine as an oxidizing agent and is capable of nonspecific oxidation of many organic compounds. If a sufficient

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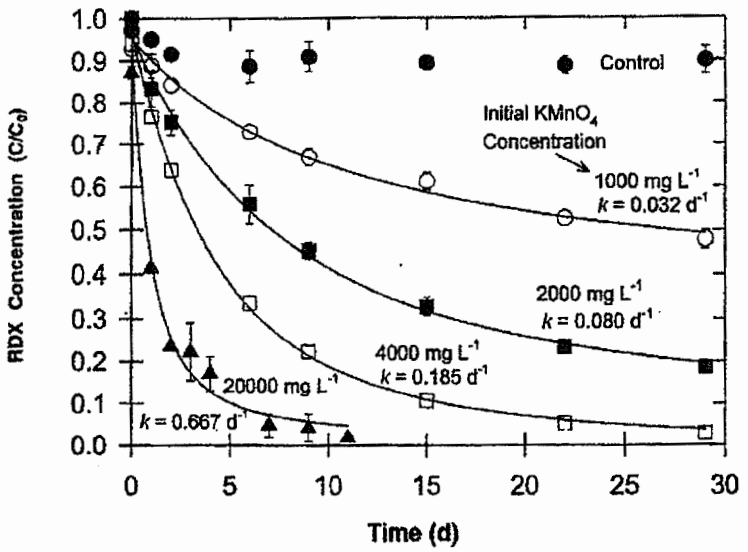

Figure 10. Loss of RDX from an aquifer slurry treated with varying $KMnO_4$ concentrations. Bars on symbols represent standard deviations of means (n=4); where absent, bars fall within symbols. Originally printed in *Journal of Environmental Quality* 33:in press.

concentrations of •OH are generated, the reaction can continue to completion, ultimately oxidizing organic compounds to CO_2, H_2O and low molecular weight mono- or di-carboxylic acids.

The Fenton reaction has been effective in treating volatile organic carbons (VOCs), light and dense non-aqueous phase liquids (LNAPL, DNAPL), petroleum hydrocarbons, PCBs, and high explosives. A significant advantage of using the Fenton reaction for treatment of RDX/HMX is that destruction is rapid. Zoh and Stenstrom (2002) investigated Fenton treatment of both RDX and HMX and reported 90% removal of RDX from a solution within 70 min, with HMX removal one-third as rapid. Most researchers have found that reaction works best between pH 3 and 5, but destruction has been observed across a wider pH range (3-7). High subsurface pH can limit the effectiveness of the reaction, especially when free-radical scavengers are present, such as carbonate (Siegrist *et al.* 2001).

Bier *et al.* (1999) found that Fenton's reagent readily oxidized RDX under a wide range of conditions. They performed experiments with baseline RDX concentrations ranging from 4.4 to 28 mg L^{-1} and controlled

reaction variables such as pH (2.0-7.5), ferrous iron concentrations (0-320 mg L^{-1}) and hydrogen peroxide (0-4%). Results showed a 100% transformation of all baseline RDX concentrations was achieved at pH 3 with hydrogen peroxide concentrations ≥0.5% and ferrous iron ≥8.2 mg L^{-1}. More relevant to aquifer treatments, Bier *et al.* (1999) also showed 80% transformation of RDX at pH 7.5. Bier *et al.* (1999) found formic acid, nitrate, ammonium were formed as intermediate or final oxidation products and presented evidence that methylenedinitramine might also be a product of Fenton oxidation of RDX. A nitrogen mass balance indicated that 80% of the nitrogen from RDX was accounted for by nitrate and ammonium. Recently, Liou *et al.* (2003) investigated Fenton and photo-Fenton processes for treatment of a wide variety of explosives in wastewater. Their results showed that RDX and HMX were more difficult to destroy than TNT but oxidation rates significantly increased with increasing Fe(II) concentrations and illumination with UV.

Although the majority of research with the Fenton reaction has been directed at treating wastewaters, examples of soil treatments are available (Gauger *et al.* 1991, Li *et al.* 1997a, b, c, Pignatello and Day 1996, Ravikumar and Gurol 1992, Tyre *et al.* 1991, Watts *et al.* 1990, 1991, 1993). Many soils contain enough iron to initiate the Fenton's reactions, but those with insufficient iron require the additional step of adding a source of Fe^{2+} (Gates-Anderson *et al.* 2001). Bier *et al.* (1999) also conducted oxidation tests with soil slurries, using soils from the Nebraska Ordnance Plant that had RDX concentrations >900 mg kg^{-1}. In one set of experiments, contaminated soil was washed with water and the wash solutions treated with Fenton's reagent. RDX in the wash solution was oxidized but not as rapidly as pure aqueous solutions due to the scavenging effects of soil organic matter, carbonates, or other oxidizable materials.

Soil washing combined with Fenton oxidation was also considered at the Massachusetts Military Reservation (MMR). Under this scenario, full scale soil washing equipment, like that used by Brice Environmental (Fairbanks, AK) (Fig. 11), would be used to remove lead-based bullets (also an environmental concern at training ranges) and reduce the volume of contaminated soil by concentrating the fine soil fraction, which contains the highest percentage of contaminants. This technology was adapted from the mining industry and essentially offers a physical approach to treating contaminated soils but when in combination with a Fenton oxidation treatment offers an innovative physical-chemical approach. Under this scenario, the Fenton's reagent would be added during the washing procedure or as post treatment for the wash water. Laboratory studies conducted by the University of Nebraska showed that a 15 min treatment of a MMR soil slurry (7% by weight) with 1% H_2O_2 and 80 mg Fe^{2+} L^{-1}

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Figure 11. Photograph of soil washing equipment used for physical and chemical treatment of contaminated soils. Photo courtesy of Brice Environmental Services Corporation (Fairbanks, AK).

significantly reduced RDX and HMX concentrations as well as other explosives and degradation products in the aqueous phase (Table 2) but solvent extractable soil concentrations did not meet the stringent soil remediation goals for the MMR site (RDX: 0.12 mg kg^{-1}; HMX: 0.25 mg kg^{-1}) unless other treatments were used (i.e., Fe^0).

Commercial applications of the Fenton reaction to treat soils include pilot and field-scale studies sponsored by the Gas Research Institute (Chicago, IL), where Fenton oxidation of contaminated soil slurries (primarily associated with manufactured gas plants) has been combined with biodegradation. Another unique example is the commercial remediation services provided by H&H Eco Systems (North Bonneville, WA) where their patented soil mixer (Microenfractionator®; Fig. 8) has been successfully used to spray and coat well-mixed soil with 50% H_2O_2 while self propelling itself through windrows, thus providing an ex situ treatment for unsaturated soils (Horn and Funk 1998).

A few commercial firms also specialize in using the Fenton reaction as well as other chemical oxidants to treat contaminated ground water (e.g., Geo-Cleansen International, Kenilworth, NJ; ORIN Remediation Techno-

Table 2. Aqueous solution concentrations of explosives and degradation products following Fenton oxidation of MMR soil slurry.

	Treatment							
	HMX	RDX	MNX	DNX	TNX	TNT	2ADNT	TNB
	ug L^{-1}							
Control	6.47	3.13	1.05	0.31	1.38	0.39	0.69	<0.30
Fenton	1.41	1.00	<0.30	<0.30	<0.30	0.34	<0.30	<0.30

[1]Slurry agitated for 15 min followed by 30 min settling time before decanting water. Fenton treatment was 1% H_2O_2 + 80 mg Fe^{2}+ L^{-1}.

[2]Abbreviations not previously defined: 2ADNT, 2-aminodinitrotoluene, TNB, trinitrobenzene.

[3]Values <0.3 ug L^{-1} indicate concentrations below reporting limits (Cassada *et al.* 1999).

[4]Source: Final report prepared for AMEC Earth and Environmental, Inc. entitled: Massachusetts Military Reservation, Innovative Technology Evaluation, Physical Treatment and Chemical Oxidation/Reduction Laboratory Results, March 30, 2001, by Brice Environmental Services Corporation and University of Nebraska-Lincoln.

logies, McFarland, WI). While specific applications are site dependent, ISCO treatments using Fenton's reagent typically include H_2O_2 concentrations between 5 to 50% (v/v) and where native iron is lacking or unavailable, ferrous sulfate is commonly added in mM concentrations (Siegrist *et al.* 2001). In some cases, acetic or mineral acids are added to reduce the pH. Potassium phosphate (KH_2PO_4) is sometimes added to prevent premature decomposition of hydrogen peroxide in soil systems (Tarr 2003a). Delivery systems have included common ground water wells or specialized injectors with compressed air or deep soil mixing equipment (Siegrist *et al.* 2001). Not all sites are appropriate for ISCO treatment with the Fenton's reagent. Suitable ground water characteristics for ISCO treatment using Fenton reagent typically include: pH <7.8; alkalinity ≥400 mg L^{-1} (as $CaCO_3$), depth to ground water >5ft below grade; and hydraulic conductivity >10-6 cm sec^{-1}.

Examples of Fenton treatment of RDX/HMX plumes in the field are limited but Geo-Cleanse International conducted a test program at a former munitions production facility that had contaminated ground water (Pueblo Chemical Depot, Pueblo, CO). In this field test program, 1,100 gallons of 50% H_2O_2 was injected with catalysts into a test plot (40 x 40 x 13 ft) over two days. After 26 d, HMX was completely removed and RDX

ves and degradation products

TNT	2ADNT	TNB
0.39	0.69	<0.30
0.34	<0.30	<0.30

ettling time before decanting
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2-aminodinitrotoluene, TNB,

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concentrations had decreased by 60%. Decreases in the nitroaromatic compounds also present decreased by 72 to 100 % (http://www.geocleanse.com).

Ozone. Ozone (O_3) was first discovered in 1840 and used as a disinfectant at the end of the 19th century (Beltrán 2003). Commonly used in treating drinking water, ozone has been more recently applied to treat organic contaminants in ground water and the vadose zone. Chemically, ozone can be represented as a hybrid of four resonance structures that present negative and positively charged oxygen atoms. This allows ozone to react through two different mechanisms, namely direct and indirect ozonation. Direct ozonation can be through electrophillic substitution while indirect results in the formation of hydroxide radicals. Ozone is also similar to permanganate in that it has a strong affinity for organic compounds containing carbon-carbon double bonds by forming unstable ozonide intermediates.

Slightly soluble in water, ozone is a very reactive reagent in both air and water. Ozone is a gas that is highly reactive and must be produced on-site. It can be vented into a soil profile for remediation purposes and has been studied as an alternative for unsaturated soils contaminated with compounds resistant to soil vapor extraction (Masten and Davies 1997, Hsu and Masten 1997, Choi *et al.* 2001, Kim and Choi 2002). Although the fate and reaction mechanisms of ozone in porous geologic media is not completely understood, it is probable that hydroxyl radical production will occur in the vadose zone through catalytic reactions of O_3 with iron oxides and organic material. The OH radicals produced should in turn be able to transform RDX present in the soil. While much is known regarding the destructive mechanisms of ozone on chlorinated solvents and HE in groundwater, far less is known regarding how ozone attacks and breaks down RDX in unsaturated soils (vadose zone).

Ozonation is being considered for the treatment of RDX in vadose zone at the Pantex site. In a preliminary feasibility study, we obtained vadose zone soil from the Pantex site (~20-30 ft deep) for treatment of soil columns with ozone under varing soil water contents. Soils initially had background concentrations of RDX (~1-2 mg kg^{-1}) but were augmented with ^{14}C-RDX to quantify mineralization. Ozone generated from O_2 was then passed through the soil columns (26-30 mg L^{-1}) at ~125 mL min^{-1} and subsequently through two midget bubblers containing 0.5 M NaOH to trap emitted $^{14}CO_2$. Initial experiments showed that ozonation was highly effective in mineralizing RDX with >80% of the initial ^{14}C recovered as $^{14}CO_2$; small differences were observed between columns that had different initial soil water contents (Fig. 12).

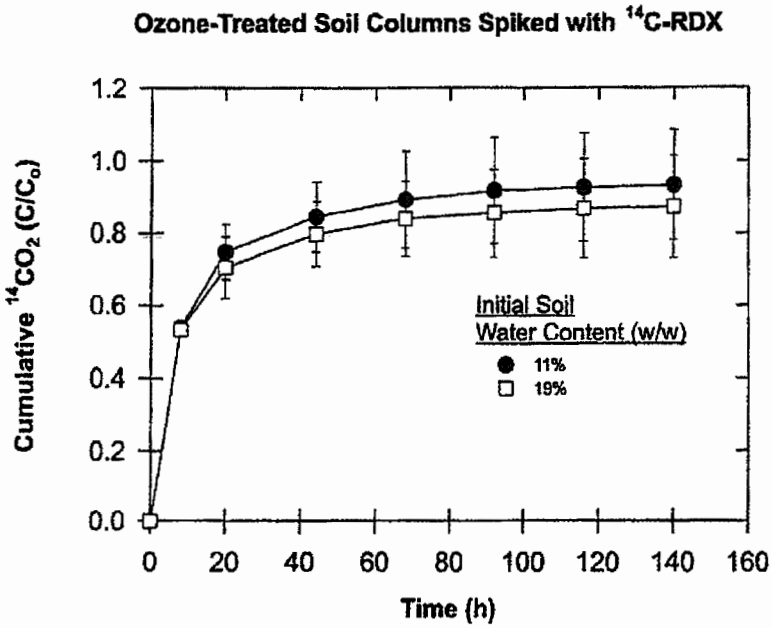
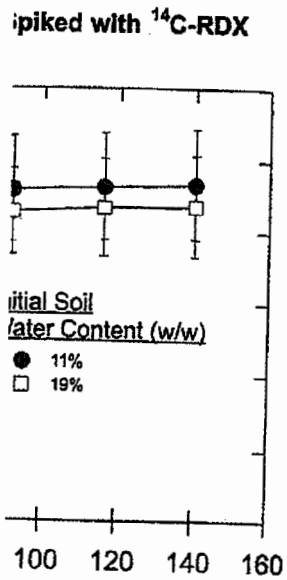


Figure 12. Cumulative $^{14}CO_2$ recovered following ozonation of columns packed with vadose zone soils from Pantex Plant (Amarillo, TX). C_o represents initial ^{14}C spiked into soil columns as RDX.

SUMMARY

Considerable progress has been made in developing and refining new and innovative abiotic approaches for remediating RDX/HMX contaminated soil and water. Although this chapter summarized some of these approaches, those reported should not be considered an inclusive list of treatments. Rather, other effective methods could have been mentioned (such as, supercritical water oxidation (Hawthorne *et al.* 2000), alkaline hydrolysis, (Bakakrishnan *et al.* 2003), solvated electron reduction, and thermal treatments (Tarr 2003b). Given the numerous treatments developed for remediating RDX/HMX contamination, it is perhaps noteworthy that when the EPA compiled all government-sponsored new and innovative field-scale technologies for treating contaminated soil, sediments and ground water (Environmental Protection Agency 2000), only 17 of the 601 reported projects dealt with explosives and more than two-thirds of those were biological approaches. Consequently, despite the considerable re-



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spite the considerable re-

search put forth on developing techniques for remediating munitions contamination, this work has not yet progressed into multiple field-scale demonstrations. While a number of government-based programs are in place for implementing field-scale technologies to meet DoD's most urgent environmental needs (e.g., Environmental Security Technology Certification Program, ESTCP), more aggressive efforts will be needed in the future to field test and document the performance of these abiotic approaches.

Acknowledgement

Sincere appreciation is expressed to my former and current graduate students for generating and synthesizing much of the data presented in this chapter. A contribution of Agric. Res. Div. Project NEB-40-002.

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