

In Situ Chemical Oxidation of RDX-Contaminated Groundwater with Permanganate at the Nebraska Ordnance Plant

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Abstract

Groundwater beneath the former Nebraska Ordnance Plant (NOP) is contaminated with the explosive hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX). The current pump and treat facility is preventing offsite migration but does not offer a short-term solution. Our objective was to quantify the effectiveness of permanganate to degrade RDX in situ. This was accomplished by performing laboratory treatability experiments, aquifer characterization, and a pilot-scale in situ chemical oxidation (ISCO) demonstration. Treatability experiments confirmed that permanganate could mineralize RDX in the presence of NOP aquifer solids. The pilot-scale ISCO demonstration was performed using an extraction-injection well configuration to create a curtain of permanganate between two injection wells. RDX destruction was then quantified as the RDX-permanganate plume migrated downgradient through a monitoring well field. Electrical resistivity imaging (ERI) was used to identify the subsurface distribution of permanganate after injection. Results showed that RDX concentrations temporally decreased in wells closest to the injection wells by 70% to 80%. Observed degradation rates (0.12 and 0.087/d) were lower than those observed under laboratory batch conditions at 11.5 °C (0.20/d) and resulted from lower than projected permanganate concentrations. Both ERI and spatial electrical conductivity measurements verified that permanganate distribution was not uniform throughout the 6.1-m (20 feet) well screens and that groundwater sampling captured both treated and nontreated groundwater during pumping. Although heterogeneous flow paths precluded a uniform permanganate distribution, pilot-scale results provided proof-of-concept that permanganate can degrade RDX in situ and support permanganate as a possible remedial treatment for RDX-contaminated groundwater.

Introduction

The former Nebraska Ordnance Plant (NOP) located near Mead, Nebraska, was a military loading, assembling, and packing facility that produced bombs, boosters, rockets, and shells during World War II and the Korean conflict. Ordnances were routinely loaded with the high explosives (HE) 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX). To reduce chemical exposure to NOP workers during ordnance production, munition residues that collected on floors and manufacturing equipment were routinely rinsed with water, and this process waste water was then diverted outside into unlined ditches and sumps. These ditches became grossly contaminated with TNT and RDX with soil concentrations exceeding 5000 mg/kg near the soil surface (Hundal et al. 1997). When rainfall

exceeded infiltration rates, ponded water that formed in the drainage ditches literally became saturated with munition residues (i.e., reached HE solubility limits, ~130 mg/L TNT and ~40 mg/L RDX) before percolating through the profile. Considering this process occurred unabated for more than 50 years, groundwater beneath the NOP eventually became contaminated. Further compromising NOP groundwater was the extensive use of trichloroethene (TCE) to degrease and clean pipelines by the U.S. Air Force in the early 1960s. As a result, the RDX, TCE, and RDX/TCE contaminant plumes beneath the NOP currently cover several square miles.

To prevent contaminated groundwater from migrating offsite and in the direction of municipal well fields, an elaborate system of 11 extraction wells and pipeline networks were constructed to hydraulically contain the leading edge of the RDX/TCE plumes. Currently, this 33 million dollar facility treats approximately 15,142 cubic meters of groundwater per day (4 million gallons of groundwater per day) with granular activated carbon (GAC). Annual operating costs are approximately \$800,000 per year with an

estimated treatment time of 125 years. As stated in EPA's Record of Decision for treatment of NOP groundwater, additional cleanup efforts beyond the current GAC system will be required to remediate the groundwater.

Although treatability experiments by Adam et al. (2004) showed that permanganate could effectively mineralize RDX in the presence of aquifer solids, field-scale applications of using permanganate to treat explosives have been limited (Struse et al. 2002; Weeks et al. 2003). Our objective was to quantify RDX destruction via in situ chemical oxidation (ISCO) with permanganate at the NOP. This was accomplished by performing laboratory-based treatability experiments specific to NOP's geological and hydrogeological conditions, characterizing the aquifer at the test site, and conducting a pilot-scale ISCO demonstration with sodium permanganate (NaMnO_4) on a small section of RDX-contaminated groundwater at the NOP.

Materials and Methods

Treatability Experiments

Soil Oxidant Demand

Batch and column experiments were performed to quantify the soil oxidant demand (SOD) of the NOP aquifer material from the ISCO injection site. Soils from depths of 16.7 to 22.9 m (54.79 to 75.13 feet) were obtained via Direct Push Technologies (DPT) (Geoprobe® Model 6610DT) and allowed to air dry before determining the SOD. SOD determined via batch studies followed the American Society for Testing of Materials (ASTM) Standard Method D7262-07 (ASTM Standard 2007) and were conducted by mixing 50 g of air-dried aquifer material with 100 mL of NaMnO_4 in 250-mL Erlenmeyer flasks. Initial NaMnO_4 concentrations were performed in triplicate and included: 100, 250, 500, 1000, 5000, 10,000, 15,000, and 20,000 mg/L. Permanganate was quantified via a UV/V is spectrophotometer (UV-2101 PC; Shimadzu, Kyoto, Japan) at a wavelength of 525 nm. Standard calibrations showed a linear response by the UV/V is detector up to concentrations of 70 mg/L; therefore, all samples were diluted to within this concentration range before quantification. SOD was calculated by the methods described by Huang et al. (2000).

Batch studies are generally conducted in lieu of column studies because of their simplicity. However, quantifying oxidant demand during transport may be more representative of field conditions by mimicking contact times between oxidant and soil (i.e., match groundwater velocity) and allowing the use of much higher soil to solution ratios. Therefore, SOD was also assessed in column studies during miscible displacement experiments where initial NaMnO_4 concentrations ranged from 164 to 12,300 mg/L. All transport experiments were conducted in 20-cm long, 5-cm diameter Plexiglas columns (Soil Measurement Systems, Tucson, Arizona) using a similar system to that described by van Genuchten and Wierenga (1986, p. 1037). Soil columns were prepared by uniformly packing air-dried aquifer material into columns to yield bulk densities between 1.6 and 1.7 g/kg. Each soil column was saturated and conditioned

with 3 mM CaCl_2 for 24 h before receiving permanganate. Permanganate was delivered to the column as a slug (i.e., pulse) and was spiked with tritiated water ($^3\text{H}_2\text{O}$), which served as a conservative tracer. After steady flow was established in the soil columns, the effluent was switched from 3 mM CaCl_2 to NaMnO_4 - $^3\text{H}_2\text{O}$ for 8 h and then back to 3 mM CaCl_2 . Darcy flux was 19.44 cm/d with a pore water velocity of 57.6 cm/d; these values approximated the average groundwater velocity of the pilot-scale test site (61 cm/d) calculated by Wani et al. (2007). Once the permanganate was flushed through the column, column effluent was fractionated as a function of time and column pore volume. A 1-mL subsample of each effluent fraction was mixed with 6 mL of Ultima-Gold scintillation cocktail and ^3H activity determined on a Packard 1900TR liquid scintillation counter. Permanganate concentrations were determined as previously described.

Relative MnO_4^- and $^3\text{H}_2\text{O}$ concentrations (C/C_0) were calculated by dividing the concentrations of the permanganate and tritium by the initial concentrations of the NaMnO_4 - $^3\text{H}_2\text{O}$ pulse (C_0). Both NaMnO_4 and ^3H breakthrough curves (BTCs, C/C_0) were plotted with time and integrated. The mass of NaMnO_4 added to the columns was calculated from the total volume delivered to the column and the initial NaMnO_4 concentration of the pulse. This mass was equated with the integrated area of the $^3\text{H}_2\text{O}$ BTC. We then subtracted the integrated area of the NaMnO_4 BTC from the ^3H BTC to determine the mass of NaMnO_4 consumed. The mass of NaMnO_4 consumed was divided by the mass of aquifer media in the column to yield an SOD for the respective NaMnO_4 concentrations.

Aquifer Slurry Experiments

RDX degradation kinetics were quantified in the presence of NOP aquifer solids (Todd Valley aquifer sand) and compared with previous aqueous and soil slurry investigations (Adam et al. 2004). Todd Valley aquifer sands contained 90% sand, 4% silt, and 6% clay with an organic matter content of 0.4%. To quantify RDX transformation and mineralization in the presence of aquifer solids, 75 g (oven dry) of Todd Valley aquifer sand was combined with 150 mL of ^{14}C -labeled RDX ($C_0 = 3.3$ mg/L). Experimental units consisted of twelve 250-mL Erlenmeyer flasks (nine reaction flasks and three control flasks) filled with 84.975 g of aquifer media (gravimetric water content = 13.3%) and 140.025 mL of double deionized water. Crystalline potassium permanganate (KMnO_4) was weighed and added to nine reaction flasks to produce the desired initial concentrations (10,000, 15,000, and 20,000 mg/L). Once KMnO_4 was added, all 12 flasks were placed on a gyrotory shaker (G-10: New Brunswick Scientific Company, New Brunswick, New Jersey) and spiked with 1 mL of 500 mg/L RDX in acetone and ^{14}C -labeled RDX.

Temporal changes in RDX concentrations were quantified by withdrawing 1-mL aliquots at 6, 12, 24, 36, 48, 72, 120, 168, 240, and 336 h. Each aliquot was placed in a microcentrifuge vial and quenched with 150 μL of MnSO_4 (0.5 g/mL) to reduce MnO_4^- to MnO_2 and stop further RDX transformations by permanganate. The microcentrifuge vials were capped, shaken by hand, and centrifuged

for 10 min at 19,481g to settle out suspended silt, clay, and MnO₂ colloids. Once centrifuged, 1 mL of supernatant was transferred to a high-performance liquid chromatography (HPLC) glass vial for analysis.

RDX was quantified at 220 nm by HPLC using a Keystone NA column (Keystone Scientific, Bellefonte, Pennsylvania) with a 70:30 water:methanol mobile phase and a flow rate of 1 mL/min. ¹⁴C-activity was quantified by removing 0.5-mL aliquots from the permanganate-RDX mixtures at the same times RDX samples were obtained. ¹⁴C aliquots were mixed with 0.5 mL 0.2 M HNO₃ to acidify and release any dissolved ¹⁴CO₂. Six milliliters of Ultima-Gold scintillation fluid (Perkin Elmer, Shelton, Connecticut) was then added to each vial and stored in the dark for 48 h before analyzing on a liquid scintillation counter (Packard 1900TR, Meridian, Connecticut).

Treatment of NOP Groundwater and Effect of Temperature

Adam et al. (2004) previously showed that permanganate can effectively degrade and mineralize (i.e., completely oxidize to CO₂) RDX. RDX concentrations at the NOP site are much lower than those used by Adam et al. (2004) and range from approximately 300 µg/L to nondetect. RDX-contaminated groundwater from the NOP was collected from a monitoring well upgradient from the pilot-scale injection site and treated with 15,000 mg/L KMnO₄ at room temperature (23 °C) under aerobic conditions. To accomplish this, 100 mL of the NOP groundwater (C₀ = 210 µg/L) was added to 250-mL Erlenmeyer flasks and placed on a gyrotory shaker. Each flask received 1.5 g of crystalline KMnO₄ and was agitated. The crystalline KMnO₄ was observed to dissolve within 4 min at 23 °C. Temporal changes in RDX concentrations were determined by removing 1.5 mL aliquots at selected times (0, 0.166, 24, 48, 96, 192, and 288 h) and quenched as previously described. Because of the low RDX concentrations present in the NOP groundwater (µg/L vs. mg/L), RDX was quantified by liquid chromatography/mass spectrometry (LC/MS) on a Thermoquest LCQ ion trap mass spectrometer. Details of this LC/MS procedure are described in Cassada et al. (1999).

In situ temperatures measured in monitoring wells at the field site ranged from 11 °C to 13 °C. Temperature effects on MnO₄⁻/RDX reaction kinetics have not been previously reported. Thus, we compared destruction efficiencies at 11.5 °C and 23 °C by treating 150 mL of 3.3 mg/L RDX with 15,000 mg/L KMnO₄.

A cold water bath reciprocal shaker (BLUE M, New Columbia, Pennsylvania) was used to maintain the experimental units at 11.5 °C. Twelve 250-mL Erlenmeyer flasks were filled with 149 mL of double deionized water. Six flasks were used as treatment flasks and six as controls. Permanganate treatments received 2.235 g of KMnO₄. Once KMnO₄ dissolved, three treatment flasks and three control flasks were placed in a cold water bath shaker for 24 h and allowed to equilibrate at 11.5 °C. The remaining six flasks, three reaction vessels and three controls, were placed on a reciprocal shaker (Eberbach 6010, Ann Arbor, Michigan) at room temperature (23 °C). After 24 h of acclimation, all flasks were spiked with 1 mL of 500 mg/L RDX in acetone and agitated. Temporal changes in RDX concentrations

were quantified by withdrawing 1-mL aliquots at 0, 6, 12, 24, 36, 48, 72, 120, 192, and 264 h.

Aquifer Characterization

Permanganate transport in the subsurface is dictated by aquifer heterogeneities (Seol et al. 2003). Slug tests were conducted, including fully screened and multilevel, in order to identify aquifer heterogeneities within the injection site. Full-screen pneumatic slug tests (Zurbuchen et al. 2002) were conducted on 12 existing wells installed by Wani et al. (2007) during an earlier biodegradation demonstration as well as six additional monitoring wells that were added for this study (MW-12-17, Figure 1). All wells in the site were screened from 16.76 to 22.86 m (55 to 75 feet) in the upper fine sand layer of the Todd Valley aquifer. Multilevel pneumatic slug tests were conducted using both a single packer (Albano 2009) and a straddle packer with a 0.67-cm interval (Zlotnik and McGuire 1998; Zlotnik and Zurbuchen 2003) on 10.16-cm (4-inch) diameter monitoring wells at the study site (IW-1, IW-2, and MW-15) to quantify spatial differences in hydraulic conductivities across the well screen. Additional site characterization included monitoring well water-level gauging, quantifying RDX concentrations from 18 wells (procedures described in the following sections), and obtaining continuous soil cores from the test site for grain-size analysis, which were then compared with soil electrical conductivity (SEC) measurements performed at the site via DPT.

Pilot-Scale ISCO Demonstration with Sodium Permanganate

Permanganate Extraction-Injection Procedure

An extraction-injection procedure was used to deliver the permanganate to the groundwater in an attempt to create a “curtain” of permanganate between injection wells. Wani et al. (2007) had previously used these wells and injection procedure in a bioremediation study. The natural gradient of the site was sufficient to replenish the site with RDX prior to our study. The extraction-injection well configuration was composed of a center extraction well and two lateral injection wells (Figure 1). For modeling purposes, we assumed that the permanganate curtain would be complete as soon as the front of the permanganate injected into IW-1 and IW-2 arrived at EW-1 after traveling distance *l* with local velocity *v*(*x*). In the schematic diagram (Figure 2), the center circle represents the extraction well (EW-1) at coordinate *x* = 0, *y* = 0 and is flanked by injection wells IW-1 and IW-2 with coordinates *x* = -*l*, *y* = 0 and *x* = +*l*, *y* = 0, respectively (Figure 2).

The approximated volume (*V*) required for creating a continuous curtain of permanganate was estimated using Equation 1 with the following parameters: *b* is equal to well screen length of 6.1 m (20 feet), *n* is equal to effective porosity (approximately 0.3 for sand), and *l* is the distance between the extraction well and the injection well of 4.6 m (15 feet). Derivation of this equation can be found in Albano (2009):

$$\text{volume} = \frac{\pi b n l^2}{2} = \frac{\pi \times 6.096\text{m} \times 0.3 \times 4.6^2 \text{m}^2}{2} \quad (1)$$

$$= 60.9\text{m}^3 = 60,900\text{L}$$

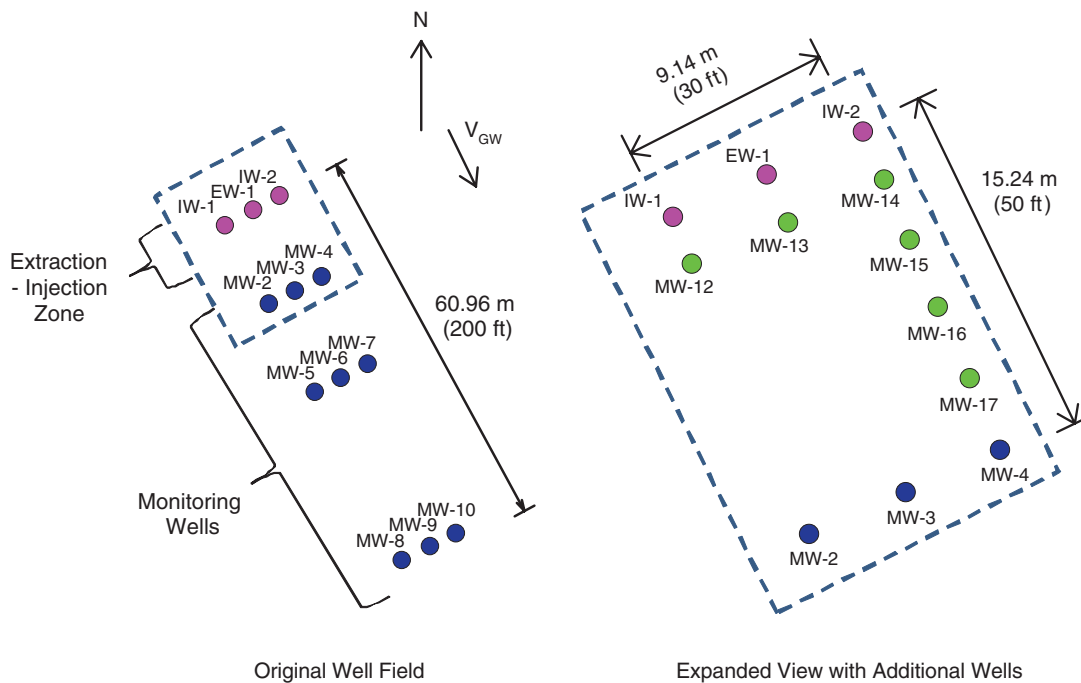


Figure 1. Extraction-injection wells and monitoring well network (left) with expanded view displaying additional wells added for this study (right).

Sodium permanganate was injected into the field via a proportional mixing-injection trailer system (Aquifer Solutions Inc., Evergreen, Colorado). Groundwater was extracted from the center extraction well (EW-1) (Figure 1) via a submersible pump (Aermotor A+ 75-500, Delavan, Wisconsin) at a rate of 151.6 L/min (40 gpm) and delivered to an intake manifold located onboard the trailer system. Approximately 1707.2 L (451 gallons) of 40% (w/w) NaMnO_4 was pumped at 3.79 L/min (1 gpm) from 1041 L (275 gallons) totes to an intake manifold where extracted groundwater and NaMnO_4 were mixed at a ratio of 40 : 1. The solution was then pumped into each of the two neighboring injection wells, IW-1 and IW-2 (Figure 1), at approximately 77.7 L/min (20.5 gpm) for 413 min. Following the NaMnO_4 injection, extracted groundwater from EW-1 was recirculated to wells IW-1 and IW-2 for 42 min.

Sodium permanganate concentrations were periodically measured on site with a portable spectrophotometer (Hach model DR 2800, Loveland, Colorado) to monitor both sodium permanganate concentration delivered to the injection wells and breakthrough at the extraction well. Specific

conductivity was measured using an YSI 3000 T-L-C meter (Yellow Springs, Ohio) during each NaMnO_4 measurement to establish a calibration curve, similar to that used by Cavé et al. (2007) to relate specific conductivity to NaMnO_4 concentration.

Electrical Resistivity Imaging of Permanganate Injection

To obtain electrical resistivity imaging (ERI) of the test site before permanganate injection, background images were obtained approximately 1 month prior to injection. ERI measurements were collected along 10 transects that criss-crossed the test area. ERI installation consisted of installing metal stakes (surface electrodes) approximately 15 cm into the ground every 3 m. The electrodes were attached to a cable and the ERI data were collected with a 56 electrode array using an Advanced Geosciences Inc. (Austin, Texas) *SuperSting R8* system that induced a current, measured the potential, and stored the data. Data were processed using the Halihan/Fenstermaker processing technique (Halihan and Fenstermaker 2004). The electrode array generated a 165 m (541 feet) long transect that imaged approximately 33 m (108 feet) deep. This arrangement was selected to cover the injected volumes within the injection site. This image depth also allowed the ERI to capture downward movement during injection. The ERI method measures apparent resistivity with a resolution equal to half the electrode spacing, in this case 1.5 m (4.9 feet) both horizontally and vertically.

During the permanganate injection, a 12-line ERI data set was collected. Two of these data sets maintained identical electrode locations during the data collection, and 10 lines had electrodes removed and replaced for the second measurement. ERI measurements were also taken at later dates (i.e., 30, 60, and 90 d), but these readings failed to

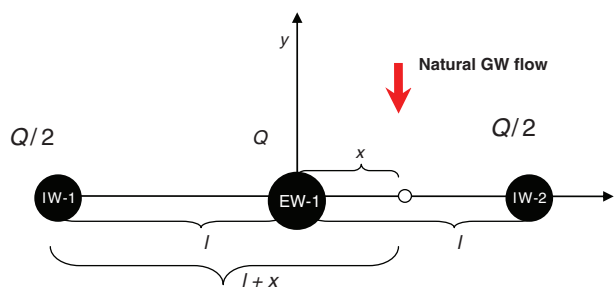


Figure 2. Schematic of injection curtain with variables used in volume calculations.

conclusively locate permanganate-treated groundwater. Additional ERI details and results from this study are provided in Halihan et al. (2009).

Groundwater Sampling

Groundwater was sampled from monitoring wells biweekly for 8 weeks after injection. Prior to sampling, electrical conductivity was measured at 0.6 m (2 feet) depth intervals in each well and converted to permanganate concentrations (via regression) to estimate vertical stratifications of NaMnO_4 entering the well screen. Groundwater samples were collected via a Grundfos Redi-flo2 submersible environmental pump (Olathe, Kansas) with a variable frequency drive converter. A minimum of three well volumes were purged prior to collecting a groundwater sample. Groundwater samples were placed in 250-mL amber bottles and quenched with MnSO_4 to precipitate sodium permanganate. All samples were placed in a cooler and transferred to a laboratory refrigerator until analysis. Permanganate concentrations were determined as previously described. RDX analyses were conducted on LC/MS by the University of Nebraska Water Science Laboratory (Cassada et al. 1999).

Results and Discussion

Treatability Experiments

Soil Oxidant Demand

Results from column and batch SOD experiments showed that permanganate consumption generally increased with increasing permanganate concentrations in the range studied (Table 1). A comparison of the two techniques showed that SODs observed in column studies were lower than SODs observed in batch studies. Xu (2006) similarly observed that SODs determined in columns were considerably less

than SODs calculated from batch studies. This difference is attributed to less mixing and shorter permanganate-soil contact times during miscible displacement compared with a well-mixed batch reactor. We were unable to quantify permanganate consumption above 5000 mg/L NaMnO_4 during batch experiments because dilution effects and variability offset the minimal changes in permanganate concentrations observed before and after exposure to the Todd Valley aquifer solids. Because column experiments used more soil mass than the batch experiments (50 vs. ~755 g), higher initial permanganate concentrations were used, and an exponential increase in permanganate consumption with increased influent concentrations was observed (Table 1). Regardless of the SOD technique used, both batch and column studies confirmed that the Todd Valley aquifer had a very low SOD (generally less than 1 g/kg). These results are consistent with Hønning et al. (2007) who observed SODs of 0.5 to 2.0 g MnO_4^-/kg soil for glacial melt water sands. Low SOD are also generally observed when aquifers have very low organic content (Mumford et al. 2005; Siegrist et al. 2001).

Aquifer Slurry Experiments

Including Todd Valley aquifer material in the permanganate-RDX batch reactor had no effect on RDX destruction kinetics using KMnO_4 . Greater than 99% RDX degradation was observed within 14 d (Figure 3) for each treatment. Moreover, approximately 90% of ^{14}C -labeled RDX was removed by 15,000 and 20,000 mg/L KMnO_4 treatments, indicating a high degree of mineralization (Figure 3). RDX degradation rates varied from 0.387 to 0.656/d for the three initial KMnO_4 concentrations. These data are similar to that published by Adam et al. (2004) who reported an RDX (initial concentration of 2.8 mg/L) degradation constant of $k = 0.667/\text{d}$ in the presence of aquifer media (91% sand, 3% silt, 6% clay, and an organic content of 0.1%) treated with 20,000 mg/L KMnO_4 .

Although high degrees of RDX mineralization were observed by treatment with permanganate (Figure 3), it is clear that kinetic transformation of RDX by permanganate is considerably slower than those observed with permanganate and chlorinated solvents where half-life is typically observed in hours (Yan and Schwartz 2000) vs. days for RDX. This difference can be attributed to the mechanism by which permanganate attacks RDX. Chocejaroenrat (2008) proposed that the first step in the RDX-MnO_4^- is rate limiting and proposed two possible RDX degradation pathways. The first mechanism is favored at neutral pH and involves removal of a hydride from the methylene carbon followed by hydrolysis and decarboxylation. The second mechanism is similar to the previously reported hydrolysis pathway (Hoffsommer et al. 1977; Balakrishnan et al. 2003) where proton abstraction from the methylene hydrogens occurs causing a nitro group to be released and a double bond formed on the triazine ring.

Treatment of NOP Groundwater and Temperature Effects

Complete RDX degradation was observed within 8 d following treatment of NOP groundwater ($C_0 = 210 \mu\text{g/L}$ RDX) with 15,000 mg/L KMnO_4 at a temperature of 23 °C

Method	Initial NaMnO_4 Concentration (mg/L)	SOD ¹ (g/kg)
Batch	100	0.121 (0.01)
	250	0.166 (0.01)
	500	0.345 (0.06)
	1000	0.205 (0.03)
	5000	0.711 (0.69)
Column	164	0.008
	820	0.009
	4100	0.043
	8200	0.273
	10,791	0.312
	12,300	1.270

¹Results from batch tests are average values ($n=3$) calculated after 216 h of contact time. Parenthetic values indicate sample standard deviations.

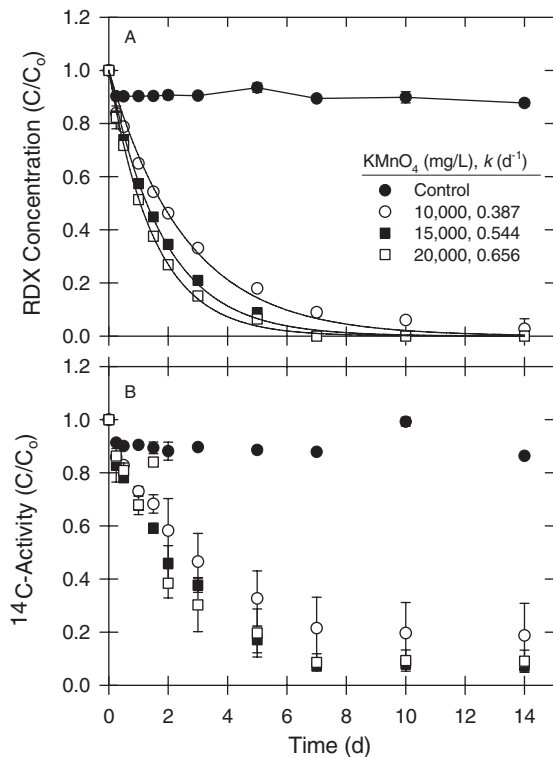


Figure 3. Temporal changes in RDX and ¹⁴C concentrations following treatment with three initial permanganate concentrations. Error bars represent standard deviation of means ($n = 3$); where absent, bars fall within symbols.

(Figure 4). RDX degradation kinetics were similar to our aquifer slurry batch experiment ($k = 0.598/\text{d}$ for NOP groundwater vs. $0.544/\text{d}$ in slurry experiment [Figures 3 and 4]). Adam et al. (2004) also observed no appreciable change in RDX degradation kinetics in batch experiments where RDX initial concentrations ranged from 1.3 to 10.4 mg/L.

Ambient groundwater temperatures observed at the NOP were found to strongly influence RDX destruction kinetics. A comparison of room temperature vs. subsurface groundwater temperature ($23\text{ }^{\circ}\text{C}$ vs. $11.5\text{ }^{\circ}\text{C}$) showed that destruction kinetics were nearly threefold slower at the lower temperature ($0.628/\text{d}$ at $23\text{ }^{\circ}\text{C}$ vs. $0.202/\text{d}$ at $11.5\text{ }^{\circ}\text{C}$; Figure 4). Complete RDX degradation was observed within 8 d at room temperature, while RDX-permanganate solutions at $11.5\text{ }^{\circ}\text{C}$ still maintained approximately 20% of initial RDX concentration. Although permanganate/RDX degradation kinetics at low temperatures have not previously been reported, batch studies involving permanganate and chlorinated ethenes have shown decreased kinetics with decreased temperatures (Dai and Reitsma 2004; Yan and Schwartz 2000). Weeks et al. (2003) conducted a treatment study for the Massachusetts Military Reservation using permanganate to treat RDX in batch reactors. Their study showed that 10,000 mg/L permanganate could effectively degrade RDX from 110 to 10 $\mu\text{g/L}$ at $11\text{ }^{\circ}\text{C}$ within 21 d.

Aquifer Characterization

Background RDX concentrations at the test site were found to vary from 34 to 76 $\mu\text{g/L}$ (Figure 5). To characterize aquifer heterogeneity within the study site, pneumatic slug

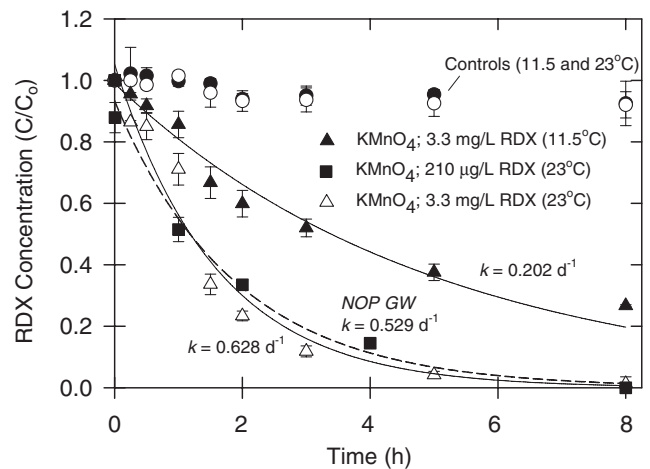


Figure 4. Treatment of NOP groundwater with 15,000 mg/L KMnO_4 ($C_0 = 210\text{ }\mu\text{g/L}$) and the effect of temperature ($11.5\text{ }^{\circ}\text{C}$ and room temperature, $23\text{ }^{\circ}\text{C}$) on temporal changes in RDX concentration ($C_0 = 3.3\text{ mg RDX/L}$) in an aqueous solution treated with 15,000 mg/L KMnO_4 . Error bars represent standard deviation of means ($n=3$); where absent, bars fall within symbols.

tests were conducted on 18 monitoring wells. These wells were screened in the upper fine sand layer of the Todd Valley aquifer (Figure 6). Test data results showed the average well horizontal hydraulic conductivity (K_h) values ranged from 4 to 20 m/d (Figure 5). These values are in agreement with average K_h of the upper fine sand layer previously reported at 15 m/d by the Army Corp of Engineers (Woodward-Clyde 1995). The calculated horizontal hydraulic gradient within the test site was 0.002, the same as that reported by Woodward-Clyde (1995).

Data from soil core collection and SEC data analyses near MW-15 indicate roughly 5.5 m (18 feet) of Peoria Loess above at least 16.2 m (53 feet) of medium-to-fine sand (maximum soil core depth was 22.3 m [75 feet] below ground surface). SEC analysis showed changes in conductivity at approximately 5.5 m (18 feet), 10.1 m (33 feet), and 18.3 m (60 feet). These data are in agreement with the grain-size analyses obtained from the collected cores and indicate that roughly 5.5 m (18 feet) of Peoria Loess is located above a coarsening downward sand sequence (Figure 6).

In addition to the pneumatic slug tests, multilevel slug tests (MLST) were performed on three 10.16 cm (4 inch) diameter wells, IW-1, IW-2, and MW-15, located within the study site in order to observe spatial differences in K_h along the well screen interval. The MLST data collected in MW-15 yielded K_h ranging from 3 to 27 m/d with highest conductive intervals between 18.9 and 19.8 m (62 to 65 feet) below ground surface (Figure 6). Groundwater velocities within the study site were approximated using Darcy's law ($V_{\text{gw}} = (K_h i)/n_e$), where K_h is the horizontal hydraulic conductivity, i is the horizontal hydraulic gradient, and n_e is effective porosity. Using K_h values calculated from MLST conducted on MW-15 (3 to 27 m/d), i of 0.002, and an estimated n_e of 0.3, we estimate groundwater velocities to range between 0.02 and 0.18 m/d.

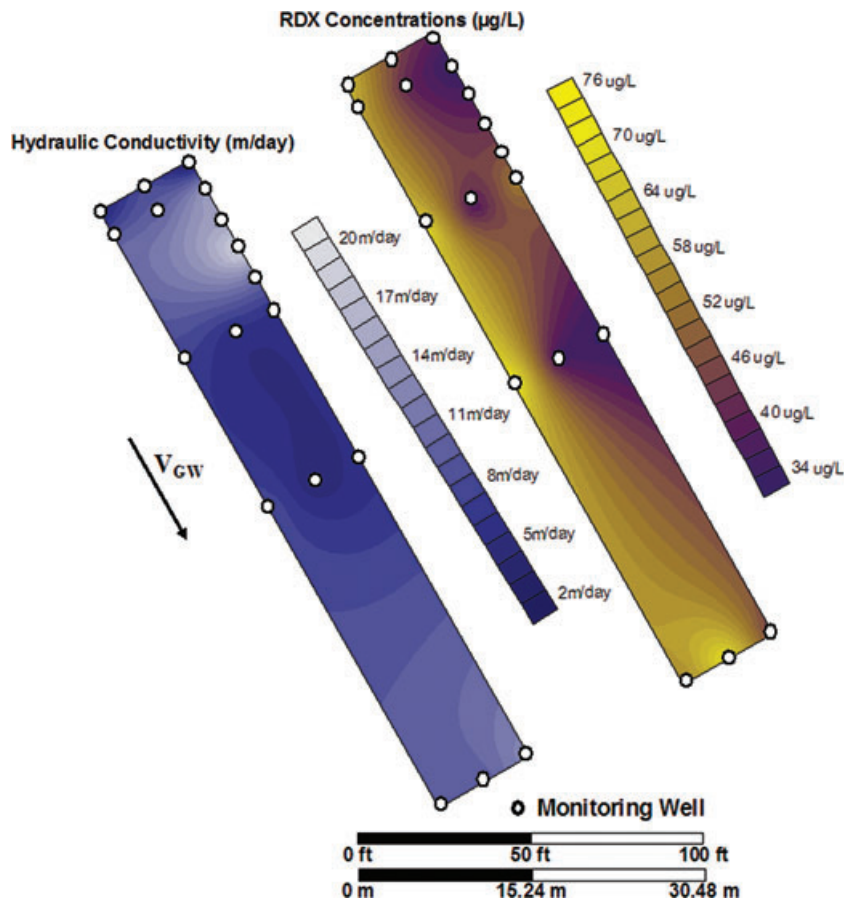


Figure 5. Hydraulic conductivities (m/d) and initial RDX concentrations ($\mu\text{g/L}$) prior to permanganate injection in pilot-scale test site.

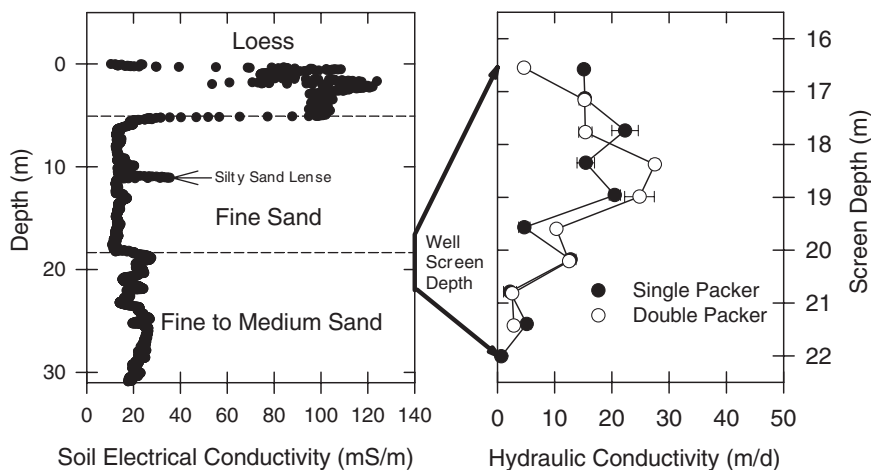


Figure 6. Soil electrical conductivity measurements via DPT and hydraulic conductivity within MW-15 screened interval.

Pilot-Scale ISCO Demonstration with Sodium Permanganate

Based on our modeling efforts of the extraction-injection well configuration (Equation 1; Figure 2), and assuming a homogeneous geologic media and piston-type flow (i.e., no dispersion), approximately 7 h of pumping (extraction-injection) would have been needed to complete the permanganate curtain. Initial permanganate

breakthrough at the extraction well, however, was observed within 77 min. Once all the permanganate had been injected into IW-1 and IW-2 ($t \sim 7.15$ h), the measured sodium permanganate concentration in EW-1 had only reached 2386 mg/L, compared with the 15,000 mg/L sodium permanganate concentration injected, indicating permanganate was not uniformly distributed across the injection wells.

ERI results indicated discernable differences between preinjection and immediately postinjection values of electrical resistivity. The majority of these changes were observed on transects placed over the injection wells (IW1 and IW2) (Figure 7) and downgradient of the injection plane (Figure 7). At these locations, both positive and negative changes occurred ranging from -13% to 13%. Spatial analysis indicates that significant changes occurred above the water table. The other change occurred upgradient of the injection wells and vertically below and to the southwest of the injection wells as shown by the composite ERI image (Figure 7). These results signify that the permanganate followed some preferential flow paths that were not congruent with the direction of the ambient groundwater flow and locations of the monitoring wells. ERI conducted during the injection process also indicated that the permanganate was not uniformly distributed within the injection well locations. Following injection, permanganate breakthrough was observed in all wells within 15.24 m of the injection zone except MW-2 and MW-3. Electrical conductivity measurements conducted throughout the well screens immediately prior to groundwater sampling indicated that the permanganate plume did not uniformly enter the wells (Figure 8).

Results obtained from monitoring wells running parallel to the direction of ambient groundwater flow (MW-14 to MW-16, Figure 9) showed that as the permanganate migrated away from the injection zone, the permanganate appeared to sink or move downward in MW-14, then into and upward into MW-15, and into MW-16 but at much lower concentrations (Figure 8). The permanganate distribution in MW-15 reasonably reflected the preferential flow paths found during multilevel slug testing of MW-15 prior to permanganate injection (Figure 6).

Further evidence of permanganate plume bifurcation, or plume fingering, within the site was obtained via DPT where groundwater sampling using a 1.2-m (4 feet) deployable screen uncovered distinct layers of permanganate sandwiched between layers with no detectable permanganate (Halihan et al. 2009). This bifurcation may be due to preferential pathways caused by the depositional nature of the Todd Valley sands, which were deposited in a braided stream system. The sedimentology of a braided stream is complex and encompasses several channels characterized by high width/depth ratios, steep slopes, and usually low sinuosity (Miall 1977). Because of this stratification, monitoring wells only captured fingers of permanganate, and

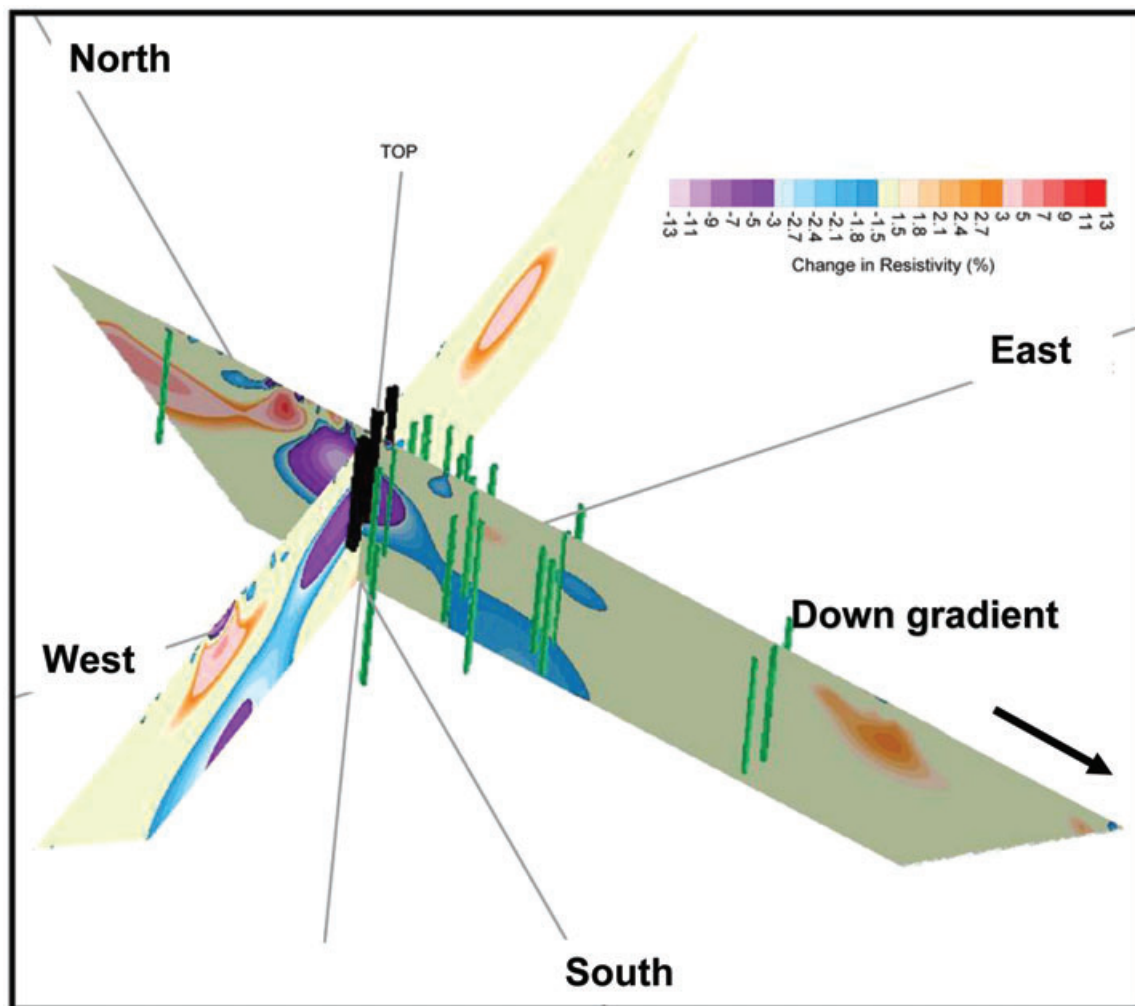


Figure 7. ERI composite of resistivity differences after injection with locations of wells used to develop permanganate curtain (black) and monitoring wells (green). Purple-blue regions signify permanganate location.

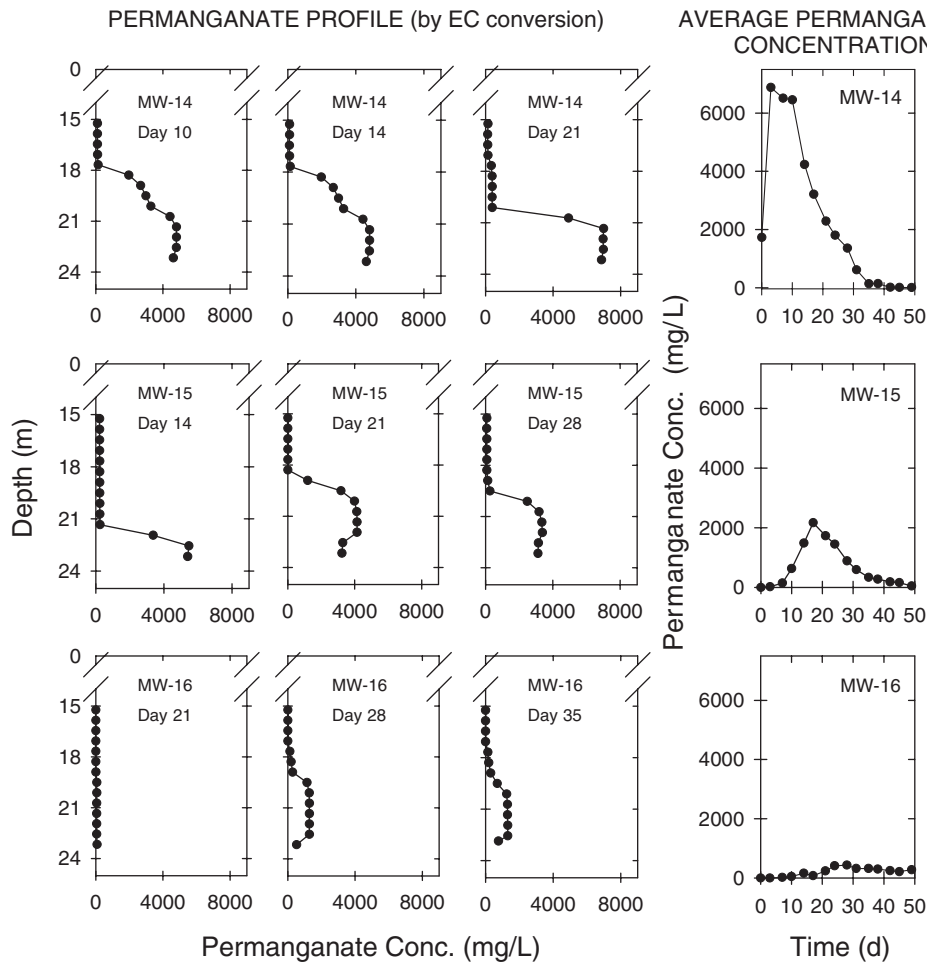


Figure 8. A comparison of permanganate profile concentrations determined by spatial conductivity measurements and average permanganate concentrations determined by well sampling.

this permanganate ended up being mixed with nontreated groundwater during pumping, thereby diluting permanganate within the well and artificially inflating RDX concentrations. This mixing of treated and untreated groundwater is evident when the spatial permanganate concentrations are compared with the average permanganate concentrations obtain via well sampling (Figure 8).

Multilevel samples taken via DPT verified that significant permanganate concentrations were present below the well screen depth more than 22.86 m (75 feet) up to 72 d after injection. Because permanganate is denser than ambient groundwater, the possibility of density-induced advection must be considered (e.g., Domenico and Schwartz 1990). Using a derivation of Holzbecher and Yusa (1995) equations, which calculated forced vs. free convection in porous media, Clayton (2008) derived an equation in the context of field hydrogeologic parameters to demonstrate the relationship between density-driven flow and advection. Using parameter inputs of amendment solution density, horizontal hydraulic gradient and K_z/K_h ratios, Clayton (2008) showed that under isotropic conditions ($K_z/K_h = 1$) both density-driven flow and advection were possible at varying groundwater velocities. However, when horizontal hydraulic conductivity is 10 times greater than the vertical hydraulic

conductivity ($K_z/K_h = 0.1$), as is the case at our pilot-scale demonstration site, density-driven flow was minor compared with advection, especially when amendment concentrations were below 10,000 mg/L. Although the initial permanganate concentration injected was 15,000 mg/L (calculated density 1.01 g/mL), permanganate concentrations observed in monitoring wells were less than 7000 mg/L (Figure 9). These calculations further support preferential flow as the reason for bifurcation of the permanganate plume.

Temporal sampling of the monitoring wells showed that average RDX concentrations temporarily decreased in wells closest to the injection wells (IW-1, IW-2, Figure 9) as the permanganate migrated downgradient. We observed RDX degradation rates of 0.12/d in MW-12 and 0.087/d in MW-14 (Figure 9). These rates were lower than what was observed under batch conditions at 11.5 °C (Figure 4, 0.20/d) and likely a result of a lower initial permanganate concentration (6000 vs. 15,000 mg/L) due to mixing of treated and untreated groundwater. RDX concentrations decreased nearly 80% (from 64.6 to 13.1 µg/L) in MW-12, 70% in MW-14 (from 54.3 to 16.2 µg/L), 73% in MW-15 (from 87.3 to 23.5 µg/L), and 75% (from 45 to 11 µg/L) in MW-16 before permanganate breakthrough was complete. We observed a slight decrease in RDX in MW-17

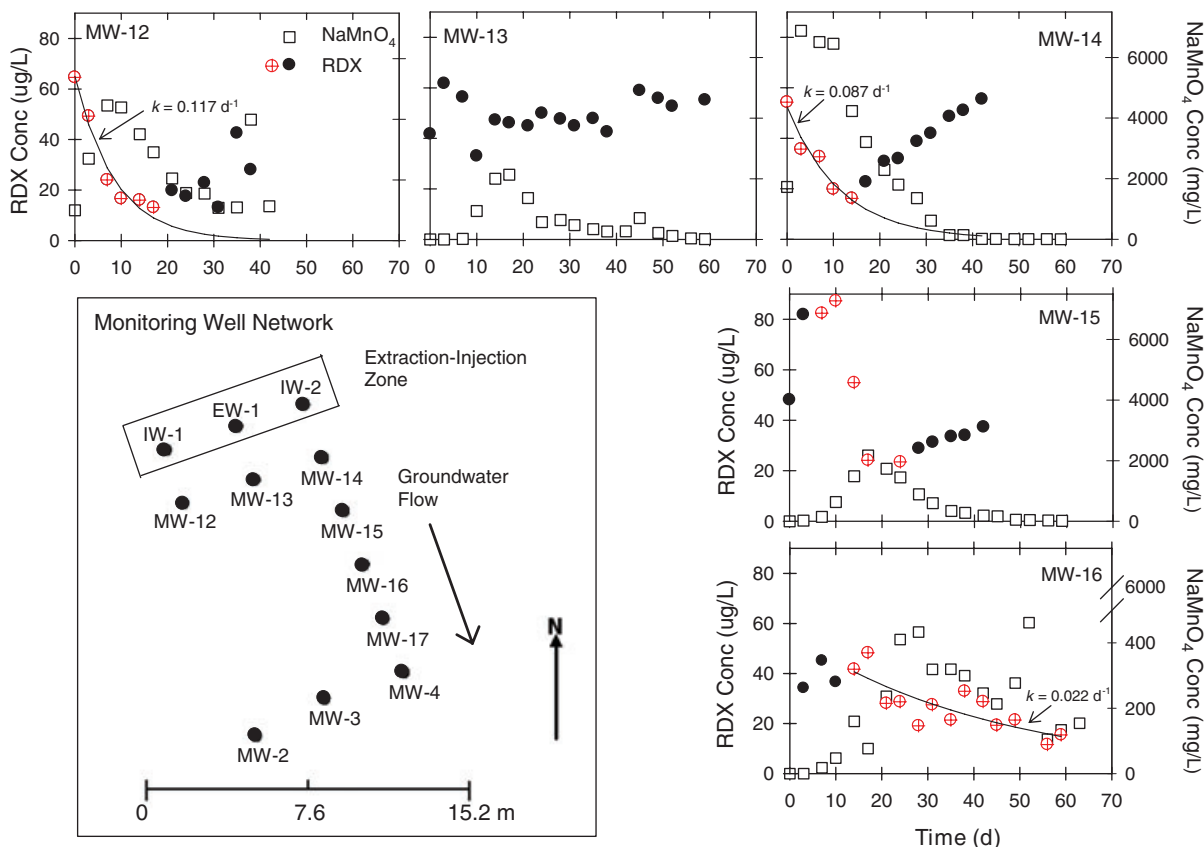


Figure 9. RDX and permanganate BTCs observed in field monitoring wells. Open red circle symbols with crosses were used in calculation of RDX degradation kinetics (i.e., fitted lines).

and MW-4 (data not shown). The permanganate concentrations sampled in MW-17 and MW-4 did not show a true breakthrough, which corresponds to the scattering RDX concentrations measured in both wells. As shown in Figure 9, RDX concentrations measured in MW-12 and MW-14 began to rebound as the sodium permanganate moved downgradient. This is attributed to upgradient mobile RDX ($K_{oc} \sim 100$ L/kg) and untreated groundwater moving into monitoring well screens. Although heterogeneous flow paths precluded a uniform permanganate distribution, the observed RDX destruction rates from this pilot-scale demonstration provide proof-of-concept that permanganate can degrade RDX in situ and support permanganate as a possible remedial treatment for the RDX-contaminated groundwater.

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