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Remediating RDX-Contaminated Ground Water with Permanganate: Laboratory Investigations for the Pantex Perched Aquifer

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ABSTRACT

Ground water beneath the U.S. Department of Energy Pantex Plant is contaminated with the high explosive RDX (hexahydro-1,3,5-trinitro-1,3,5 triazine). The USDOE Innovative Treatment and Remediation Demonstration (ITRD) program identified in situ oxidation by permanganate as a technology fit for further investigation. We evaluated the efficacy of $KMnO_4$ to transform and mineralize RDX by determining degradation kinetics and carbon mass balances using ^{14}C-RDX. Aqueous RDX solutions (2–5 mg L^{-1}) and RDX-contaminated slurries (50% solids, w/v) were treated with $KMnO_4$ at 1000, 2000, 4000, and 20 000 mg L^{-1}. Treating an aqueous RDX solution of 2.8 mg L^{-1} with 20 000 mg $KMnO_4$ L^{-1} decreased RDX to 0.1 mg L^{-1} within 11 d while cumulative mineralization proceeded for 14 d until 87% of the labeled carbon was trapped as $^{14}CO_2$. Similar cumulative mineralization was obtained when Pantex aquifer material was included in the solution matrix. Other experiments using 4000 mg $KMnO_4$ L^{-1} showed that initial RDX concentrations (1.3–10.4 mg L^{-1}) or initial pH (4–11) had little effect on reaction rates. Attempts to identify RDX degrades and reaction products showed that N_2O was a product of permanganate oxidation and constituted 20 to 30% of the N balance. Time-course measurements of a ^{14}C-RDX solution treated with $KMnO_4$ revealed few ^{14}C-labeled degrades but through liquid chromatography–mass spectrometry (LC–MS) analysis, we present evidence that 4-nitro-2,4-diaza-butanol is formed. Aquifer microcosm studies confirmed that the transformation products not mineralized by $KMnO_4$ were much more biodegradable than parent RDX. These results indicate permanganate can effectively transform and mineralize RDX in the presence of aquifer material and support its use as an in situ chemical oxidation treatment for the Pantex perched aquifer.

T HE U.S. DEPARTMENT OF ENERGY's Pantex Plant near Amarillo, Texas, has produced or dismantled conventional and nuclear weapons for the last 50 yr. Pre-1980 industrial operations included on-site disposal of high explosives (HE) and wastewater into unlined ditches. Surface runoff from these ditches into an aquifer-recharging playa has contaminated the perched aquifer beneath the Pantex Plant. The perched aquifer is contaminated with RDX, HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine), TNT (2,4,6-trinitrotoluene), 2,4-DNT (2,4-dinitrotoluene), 1,2-DCA (1,2-dichloroethane), TCE (trichloroethene), PCE (tetrachloroethene), and chromium. Of these, considerable attention has focused on the high explosive RDX because it is the most widespread. Hydrogeological characteristics of the site make implementing remediation technologies formidable. Foremost is that the perched aquifer is approximately 90 m (300 ft) below the surface and 30 m (100 ft) above the Ogallala (High Plains) aquifer, a major source of pristine drinking water. Second, the saturated thickness of the 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 bounds 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. The ITRD process for the Pantex Plant recommended three candidate technologies for further testing: (i) oxidation by $KMnO_4$, (ii) anaerobic biodegradation, and (iii) chemical reduction by dithionite-treated (reduced) aquifer material. This research discusses in situ chemical oxidation of RDX by permanganate.

In situ chemical oxidation involves the addition of a chemical oxidant to destroy contaminants in-place. Potassium permanganate ($KMnO_4$) is an oxidizing agent with a strong affinity for organic compounds containing carbon–carbon double bonds, aldehyde groups, or hydroxyl groups. Considerable research with chlorinated solvents has shown that permanganate is attracted to the negative charge associated with the π electrons of chlorinated alkenes such as tetrachloroethene, trichloroethene, dichloroethene, and vinyl chloride (Oberle and Schroder, 2000). Although the chemical structure of RDX does not readily lend itself to reaction with permanganate, IT Corporation and SM Stoller Corporation (2000) initially demonstrated effective RDX loss by $KMnO_4$ treatment. By using ^{14}C-labeled RDX and samples of the Pantex perched aquifer sand, our objectives were to measure RDX transformation and mineralization using varying $KMnO_4$ concentrations and determine the effects of initial pH and RDX concentration on reaction rates. Because mineralization was incomplete (<90%) when lower $KMnO_4$ concentrations were used, we also attempted to identify transformation products and determined the ability of native biota to mineralize degrades produced by permanganate in aquifer microcosms.

MATERIALS AND METHODS

Carbon-14 RDX Mass Balance Experiment

A continuous flow-through gas trapping system was used to measure loss of parent RDX, ^{14}C, and production of $^{14}CO_2$.

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Experimental units consisted of 250-mL glass round-bottom flasks connected in series to a flow-through vacuum system with two midget gas bubbling traps (Bier et al., 1999). Inlet air to the reaction flasks was passed through 5-cm glass tubes packed with NaOH-covered pellets (Ascarite II) and glass wool. This continuous flow-through system produced gentle bubbling inside the reaction flasks during treatment and provided a slow but constant agitation. Trapping efficiency of the flow-through system using acid-treated $NaH^{14}CO_3$ averaged 93.4% ($STD_{n-1} = 5.8\%$).

Initial tests treated replicated experimental units ($n = 4$) containing 150 mL of aqueous ^{14}C-RDX (2.5 mg L^{-1}, 30 000 dpm mL^{-1}, uniformly ring-labeled) with 20 000 mg $KMnO_4$ L^{-1}. Because no ^{14}C-labeled volatile organics were detected in initial trapping tests, subsequent experiments concentrated on measuring loss of parent RDX and ^{14}C activity from solution and production of $^{14}CO_2$. Solution samples from the reaction flask and CO_2 traps were taken daily for the first 5 d and at 48-h intervals in the following weeks. Changes in solution RDX concentrations were determined by removing 1.2-mL aliquots, quenching the reaction with 120 μL of 0.5 mg $MnSO_4 \cdot H_2O$ mL^{-1}, centrifuging at 12 000 × g for 10 min, and transferring 1.0 mL of supernatant to a high performance liquid chromatography (HPLC) vial for analysis. RDX was quantified at 220 nm by HPLC using a Keystone NA column (Keystone Scientific, Bellefonte, PA) with an isocratic mixture of methanol and H_2O (30:70) at a flow rate of 1.5 mL min^{-1} (Bier et al., 1999). Standards were prepared with analytical RDX obtained from AccuStandard (New Haven, CT). Changes in solution ^{14}C activity were determined by removing 0.5 mL of sample, mixing with 18 mL of Ultima Gold scintillation cocktail (Packard, Meriden, CT), storing for 24 h, and then determining activity by liquid scintillation (LS) analysis. At the end of the experiment, we filtered the solution from the reaction flask through Whatman (Maidstone, UK) #1 filters, and allowed the precipitate to dry. We then mixed 0.5 g of precipitate with 400 mL of Combustaid (Packard), and determined precipitated ^{14}C by combusting the precipitate in a Packard biological oxidizer. The oxidizer gas stream was trapped in a 3:2 (v/v) mixture of Carbosorb/Permafluor (Packard) and counted by LS analysis. RDX destruction kinetics were fit to a pseudo first-order rate equation by nonlinear regression analysis using the computer software SigmaPlot 2000 (SPSS, 2000).

Batch Experiments

Additional batch experiments were performed in 250-mL Erlenmeyer flasks and agitated with an orbital shaker. Initially, we duplicated the 20 000 mg $KMnO_4$ L^{-1} treatment used in the flow-through system (with and without aquifer solids), but subsequent treatments used lower $KMnO_4$ concentrations to treat RDX-contaminated slurries. For slurry experiments, we used fresh aquifer sediment obtained during drilling of the perched aquifer (approximately 90 m). Aquifer material was sent to our laboratory in ice-packed coolers and immediately transferred to a cold room (4.5°C) for storage. Soil analyses (Midwest Labs, Omaha, NE) determined that the aquifer material was approximately 91% (w/w) sand, 3% silt, and 6% clay with 0.1% organic material and had an alkaline pH (2:1 solution to soil ratio, pH = 9). Although mostly sand, our observations during handling of the Pantex material revealed that small pebble-sized occlusions of clay were also present.

Aquifer slurries consisted of 75 g aquifer material (dry weight) mixed with 150 mL of ^{14}C-RDX (2.5 mg L^{-1}). Slurries were treated with 0, 1000, 2000, and 4000 mg $KMnO_4$ L^{-1}. In a second experiment, these same $KMnO_4$ treatments were repeated but after 21 and 50 d, additional $KMnO_4$ (dry solid)

was added to the reaction flasks at the original concentrations to simulate repeated injections of $KMnO_4$. Sampling for temporal changes in RDX and ^{14}C was conducted as described above.

To determine permanganate consumption by the Pantex perched aquifer, five concentrations of $KMnO_4$ (5–500 mg L^{-1}, 2:1 solution to soil ratio) were mixed with the Pantex sand and shaken on an orbital shaker for 48 h. Permanganate concentrations were measured with a UV/vis spectrophotometer (UV-2101PC; Shimadzu, Kyoto, Japan) at 525 nm.

Effects of Initial RDX Concentration and pH

To quantify the effects of initial RDX concentration and pH on destruction kinetics, we repeated the slurry experiments with 4000 mg $KMnO_4$ L^{-1} and varied the initial RDX concentrations (1.3, 2.6, 4.3, 7.2, and 10.4 mg L^{-1}) and pH. The pH effects on RDX transformation and mineralization rates were determined by treating 5.0 mg RDX L^{-1} with permanganate in the following buffers: 10 mM NaH_2PO_4 (initial pH = 4.1), 10 mM Na_2HPO_4 (pH = 8.3), 10 mM Na_3PO_4 (pH = 11.3), 5 mM NaH_2PO_4 + 5 mM Na_2HPO_4 (pH = 7.5), and an unbuffered control (pH = 9.6). Temporal changes in RDX, ^{14}C, and pH were monitored.

RDX Transformation Products

To identify RDX transformation products, we used permanganate concentrations between 500 and 4000 mg L^{-1} to treat ^{14}C-labeled RDX solutions (150 mL) without aquifer material under batch conditions. Solutions were analyzed with an HPLC equipped with a photodiode array (Shimadzu) and radioisotope detector (Packard). Several combinations of HPLC columns and mobile phases were employed in an attempt to separate and identify degrade peaks and included Keystone NA and Aquasil reverse phase (Keystone Scientific) and Supelcogel C-610H ion exclusion columns (Supelco). Typical mobile phases were varied and included 20:80 acetonitrile to water or 50:50 methanol to water. Nitrate was analyzed using cadmium reduction, following Lachat Method 12-107-01-1C (Lachat Instruments, Loveland, CO). Ammonium was analyzed colorimetrically with a Reflectoquant test kit (EM Science, Gibbstown, NJ).

Headspace above an aqueous RDX solution (150 mL, 12.5 mg L^{-1}, ^{14}C-labeled) and slurry (150 mL, 75 g) was monitored for N_2O and $^{14}CO_2$ evolution following treatment with 4000 $KMnO_4$ L^{-1}. Each reactor contained a 7-mL scintillation vial filled with 6 mL of 0.5 M NaOH to trap evolved $^{14}CO_2$. Headspace, solution (RDX and ^{14}C), and $^{14}CO_2$ traps were sampled weekly for four weeks. We obtained N_2O samples by removing 1000 μL from the headspace of the batch reactors with a gas tight syringe and transferring to a 12-mL N_2–flushed sample vial. Headspaces were subsequently exposed to the atmosphere for approximately 5 min while we sampled for solution RDX and exchanged $^{14}CO_2$ traps. Sample vials were transported to the University of Nebraska's Water Sciences Laboratory where 500 μL of the diluted gas was injected into a Hewlett-Packard (Palo Alto, CA) 5890 GC equipped with a Restek (Bellefonte, PA) 80/100 Porapak Q Column (2-m length × 2-mm diameter) and electron capture detector (ECD). Calibration standards were prepared by diluting N_2O standards (Scott Specialty Gases, Plumsteadville, PA) and used to quantify N_2O concentrations.

Two liquid chromatography–mass spectrometer (LC–MS) systems were used to identify RDX degradation products: an LCQ HPLC–MS system (Finnegan, Austin, TX), which employs an ion-trap mass analyzer, and a Quattro micro triple

quadrupole LC–MS–MS (Waters, Milford, MA). Samples injected into the LCQ ion trap were separated with a Beta-Basic C-18 column at 50°C using a mobile phase of 0.01 M NH_4OOCH (in H_2O) and isopropanol (80:20, pH = 8 with NH_4OH) at a flow rate of 0.2 mL min^{-1} (Cassada et al., 1999). Data were collected in full scan mode (negative ion) from 50 to 600 amu. Samples injected into the triple quadrupole used the same column and flow rate, but the mobile phase consisted of 2% (v/v) formic acid–acetonitrile–methanol (60:24:16).

Biodegradation of Permanganate-Treated RDX

To determine the biodegradation potential of the RDX transformation products generated during $KMnO_4$ treatment, 12 flasks containing 75 g aquifer material and 150 mL of aqueous RDX (5 mg L^{-1}) were prepared. Eight of the flasks received 4000 mg $KMnO_4$ L^{-1}, while control flasks received none. We allowed $KMnO_4$ to react with RDX until RDX was undetected by HPLC (<50 µg L^{-1}). We then transferred 25 mL of solution from each of the flasks into 50-mL Teflon tubes, and quenched half (n = 4) with 400 µL $MnSO_4$ (0.5 mg $MnSO_4 \cdot H_2O$ per mL of H_2O); all of the tubes were centrifuged at 5500 × g for 10 min. The supernatant containing ^{14}C-RDX transformation products was then used as the stock solution (hereinafter referred to as ^{14}C stock) for the aquifer micro-cosm experiments.

Aquifer microcosms were prepared in 250-mL glass jars with septa-containing screw-top lids. Each experimental unit contained 75 g (dry weight) of fresh aquifer sand, 15 mL of a ^{14}C stock, and a $^{14}CO_2$ trap consisting of a 7-mL glass vial with 6 mL of 0.5 M NaOH. The 15 mL of added ^{14}C stock solution saturated the Pantex sand and provide a thin film of overlying solution. Radioactivity (dpm) of the unquenched and control treatments was diluted with H_2O to provide the same initial radioactivity concentration as the quenched treatment. Carbon dioxide traps were sampled once per week to determine cumulative $^{14}CO_2$ produced.

RESULTS AND DISCUSSION
Carbon-14 RDX Mass Balance Experiment

Treating aqueous RDX (pH 8–9) with 20 000 mg $KMnO_4$ L^{-1} reduced the RDX concentration from 2.8 to 0.1 mg L^{-1} in 11 d (i.e., 96% loss; Fig. 1). Loss of ^{14}C activity paralleled transformation of RDX and mirrored the cumulative $^{14}CO_2$ recovered. Approximately 87% of the ^{14}C activity was recovered as $^{14}CO_2$ after 18 d (Fig. 1). Combusting the precipitate (i.e., MnO_2) formed in the reaction flask during the experiment revealed insignificant activity (<0.1%) in the solid phase. The simultaneous decreases in solution RDX and ^{14}C, combined with the cumulative production of $^{14}CO_2$, provided proof that $KMnO_4$ could effectively mineralize RDX.

Effects of Permanganate Concentration

Repeating the 20 000 mg $KMnO_4$ L^{-1} treatment in batch mode produced a faster rate of RDX destruction (k = 0.76 d^{-1}, data not shown) than that observed with the gas-trapping system, which we in part attribute to a greater rate of agitation caused by the orbital shaker versus the low-flow bubbling of the flow-through system. When 50% solids from the perched aquifer were included in the batch reactor (i.e., aquifer slurry), destruction kinetics decreased (0.67 d^{-1}; Fig. 2), but the

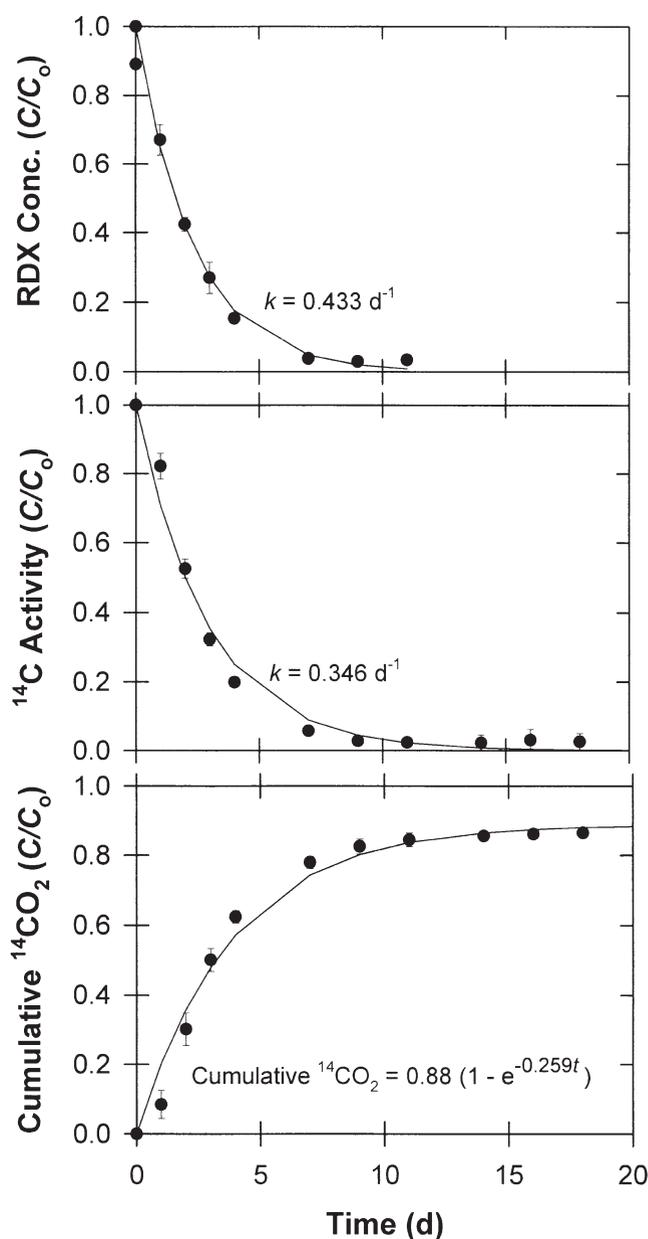Fig. 1. Loss of RDX and ^{14}C and production of $^{14}CO_2$ following treatment of RDX solution (without aquifer solids) with 20 000 mg $KMnO_4$ L^{-1} using a continuous flow-through trapping system. The term C_o represents initial RDX or ^{14}C in reaction flasks at t = 0 h. Bars on symbols represent standard deviations of means (n = 4); where absent, bars fall within symbols.

RDX concentration still dropped to <50 µg L^{-1} and cumulative mineralization remained high (84% in 37 d). This indicates that the aquifer material had little effect on overall RDX destruction or mineralization, and is likely explained by the limited capacity of the aquifer sand to consume or adsorb $KMnO_4$. Very little organic matter was present in the Pantex sand (0.1%, w/w) and our adsorption isotherm of $KMnO_4$ on the Pantex sand indicated an adsorption maximum of approximately 100 mg kg^{-1} at equilibrium concentrations of >200 mg L^{-1}.

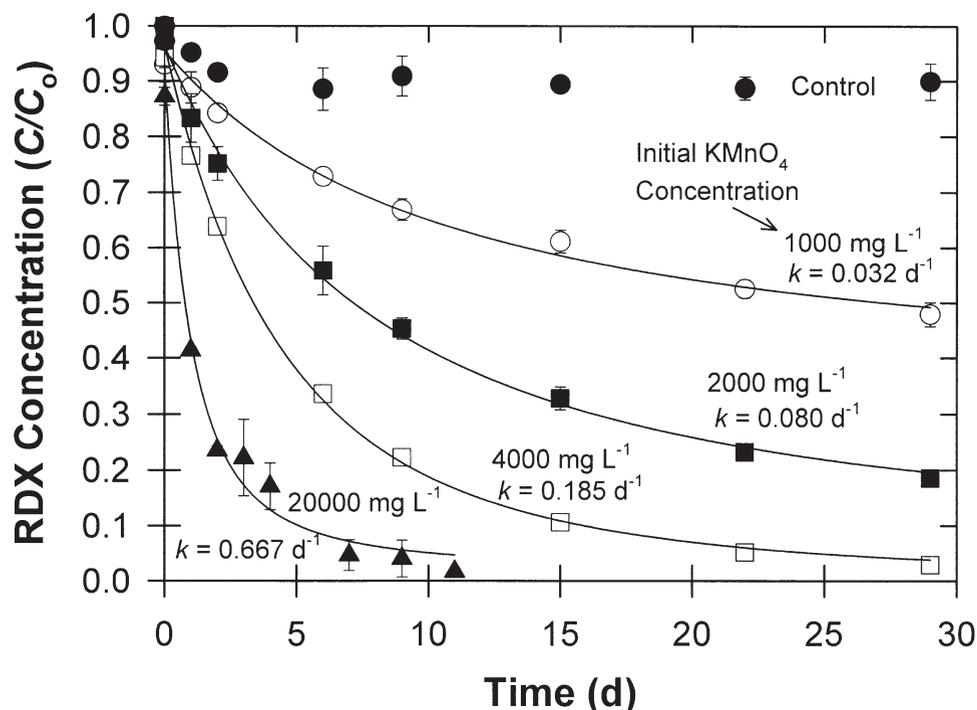Because 20 000 mg $KMnO_4$ L^{-1} may not be economical for application at the Pantex site, we also evaluated

Fig. 2. Loss of RDX from an aquifer slurry treated with varying KMnO₄ concentrations. Bars on symbols represent standard deviations of means ($n = 4$); where absent, bars fall within symbols.

lower KMnO₄ concentrations. Permanganate concentrations between 1000 and 4000 mg L⁻¹ resulted in lower destruction rates, but the reaction continued beyond 20 d in all treatments (Fig. 2). While many researchers have used second-order expressions to describe contaminant destruction rates by permanganate (first order with respect to MnO_4^- and contaminant), it is known that if MnO_4^- is maintained in excess (i.e., three to five times the stoichiometric requirement), the reaction can be adequately described by pseudo first-order kinetics (Siegrist et al., 2002). Using an initial permanganate concentration of 4000 mg L⁻¹ resulted in a pseudo first-order RDX destruction rate of 0.185 d⁻¹ (0.0055 h⁻¹), which compares favorably to earlier published work ($k = 0.005$ h⁻¹; IT Corporation and SM Stoller Corporation, 2000). When KMnO₄ was reseeded back into the reaction flasks, we found that multiple additions of 1000, 2000, and 4000 mg KMnO₄ L⁻¹ (at 0, 21, and 50 d) were highly effective in removing RDX from solution in the presence of the aquifer solids (Fig. 3). Specifically, RDX concentrations decreased from 2.8 mg L⁻¹ to less than 0.2 mg L⁻¹ in 71 d with as little as 1000 mg KMnO₄ L⁻¹ (Fig. 3). These lower KMnO₄ application rates were also effective in removing ¹⁴C from solution, but mineralization was less than 90% at permanganate concentrations of <4000 mg L⁻¹ (Fig. 3). Slight decreases in RDX and ¹⁴C by the control indicate some biodegradation of RDX occurred in the aquifer slurry.

Fitting first-order expressions to changes in RDX or ¹⁴C concentrations at $t = 0$ to 21, 21 to 50, and 50 to 71 d (intervals beginning with fresh KMnO₄ additions) revealed little change from the initial rate observed (0–21 d) (Fig. 3). A consistent observation from all KMnO₄

treatments was the slow (i.e., weeks) but sustained rate of RDX transformation and mineralization observed. This contrasts previous work where KMnO₄ destruction of chlorinated solvents has been reported to occur within minutes to hours (Yan and Schwartz, 1999) or other oxidative treatments of RDX where much faster destruction kinetics of RDX have been observed (e.g., Fenton reaction, Bier et al., 1999). The stability and longevity of permanganate in degrading RDX in the presence of the Pantex aquifer material should allow a larger volume of the contaminated plume to be treated from a single injection and permit a wider well spacing.

One potential problem with permanganate is the production of insoluble manganese dioxide. Li (2000) warned that MnO₂ can potentially cause plugging and flow diversion, and Lee et al. (2003) showed that low permeability zones can form along chlorinated solvent plumes, which decrease efficiency and lead to permanganate migrating away from the contaminant zone. Siegrist et al. (2002) showed that MnO₂ can commingle with clay and silt particles in water and increase the amount of filterable solids generated in situ. Our batch experiments with the Pantex aquifer solids support this, as we noticed that the slurry became progressively more viscous the longer the reaction took place, and sampling with a pipette became more tedious. This problem occurred even with the 1000 mg KMnO₄ L⁻¹ treatment but may have been exacerbated by the fact that the batch reactors were agitated during treatment, which suspended the clay in solution, rather than keeping the clay in lenses as in the undisturbed material. Although our laboratory batch experiments differ from the miscible displacement that would occur in the field, the potential for plugging
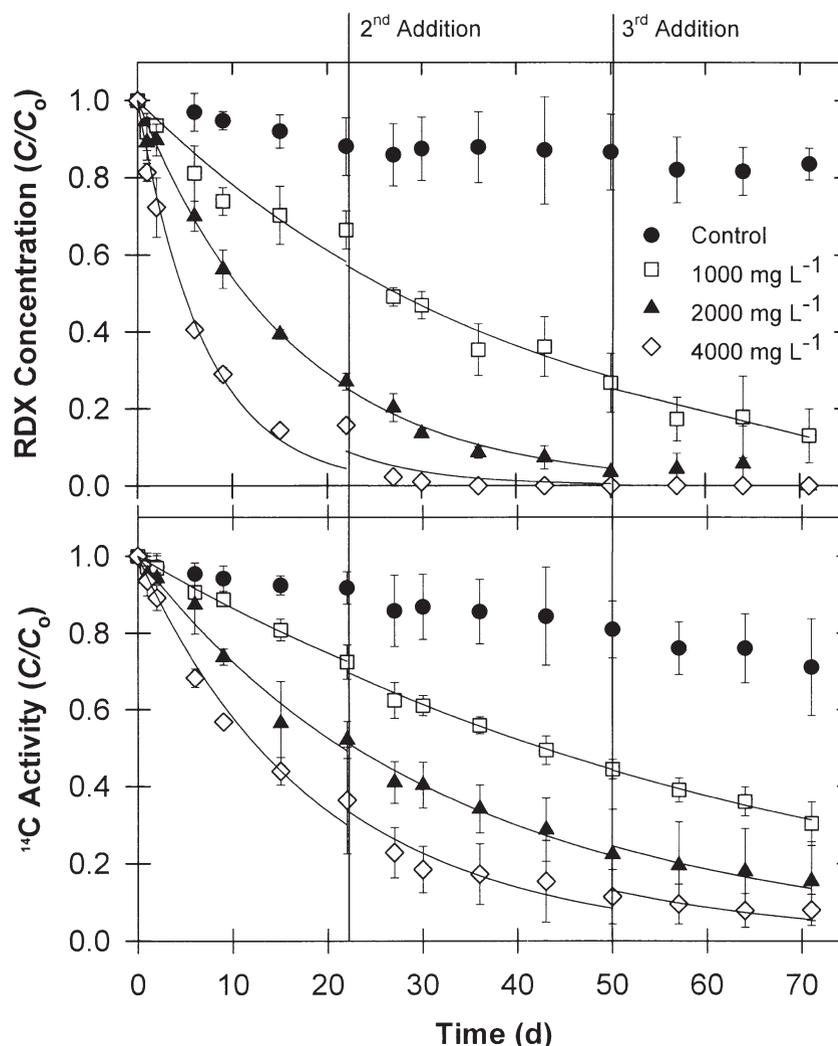
Fig. 3. Loss of RDX and ^{14}C from an aquifer slurry treated with repeated applications of varying $KMnO_4$ concentrations. Bars on symbols represent standard deviations of means ($n = 4$); where absent, bars fall within symbols.

within the perched aquifer still needs to be taken into consideration.

Effects of Initial RDX Concentration and pH

Initial RDX concentrations between 1.3 and 10.4 mg L^{-1} did not greatly affect reaction rates when treated with 4000 mg $KMnO_4$ L^{-1} (Fig. 4). RDX transformation rates (i.e., $k = 0.08$–0.108 d^{-1}) and the extent of mineralization that occurred were similar among all RDX concentrations (Fig. 4). This indicates that slight differences in initial concentrations had negligible effects on destruction kinetics. The RDX concentrations observed in the Pantex perched aquifer (IT Corporation and SM Stoller Corporation, 2000) are similar to those used in our experiments. Monitoring solution ^{14}C activity in the various RDX treatments revealed that roughly 40 to 50% of the activity was still present after 35 d (Fig. 4B). Because this was more than what we had observed in the previous experiment (10–30% ^{14}C remaining after 70 d; Fig. 3), we acidified the slurry (pH < 3) at the end of the experiment and observed that an additional

release of 35 to 40% of ^{14}C activity (Fig. 4B). The retention of ^{14}C activity by the permanganate-treated RDX solution (as dissolved CO_2 or HCO_3^-) is problematic and related to the alkaline conditions that occur during treatment (see initial pH results below). Consequently, acidification is needed for an accurate assessment of mineralization kinetics.

Regardless of the initial pH (4.1–11.3), we found that all treatments converged to between pH 8 and 9 after 35 d (Fig. 4E). The unbuffered control dropped from pH 9.6 to 7.8. Even though the initial pH differed considerably, RDX loss was similar among all treatments ($k = 0.134$–0.147 d^{-1}; Fig. 4C). Other researchers have also reported little pH effect on destruction rates. Yan and Schwartz (1999) investigated the oxidative treatment of chlorinated ethenes and found that trichloroethene destruction by permanganate was independent of pH (pH 4–8).

The only pH treatment effect noted was the greater loss of solution ^{14}C activity in the most acidic treatment (NaH_2PO_4) during the first few days (Fig. 4D). Because
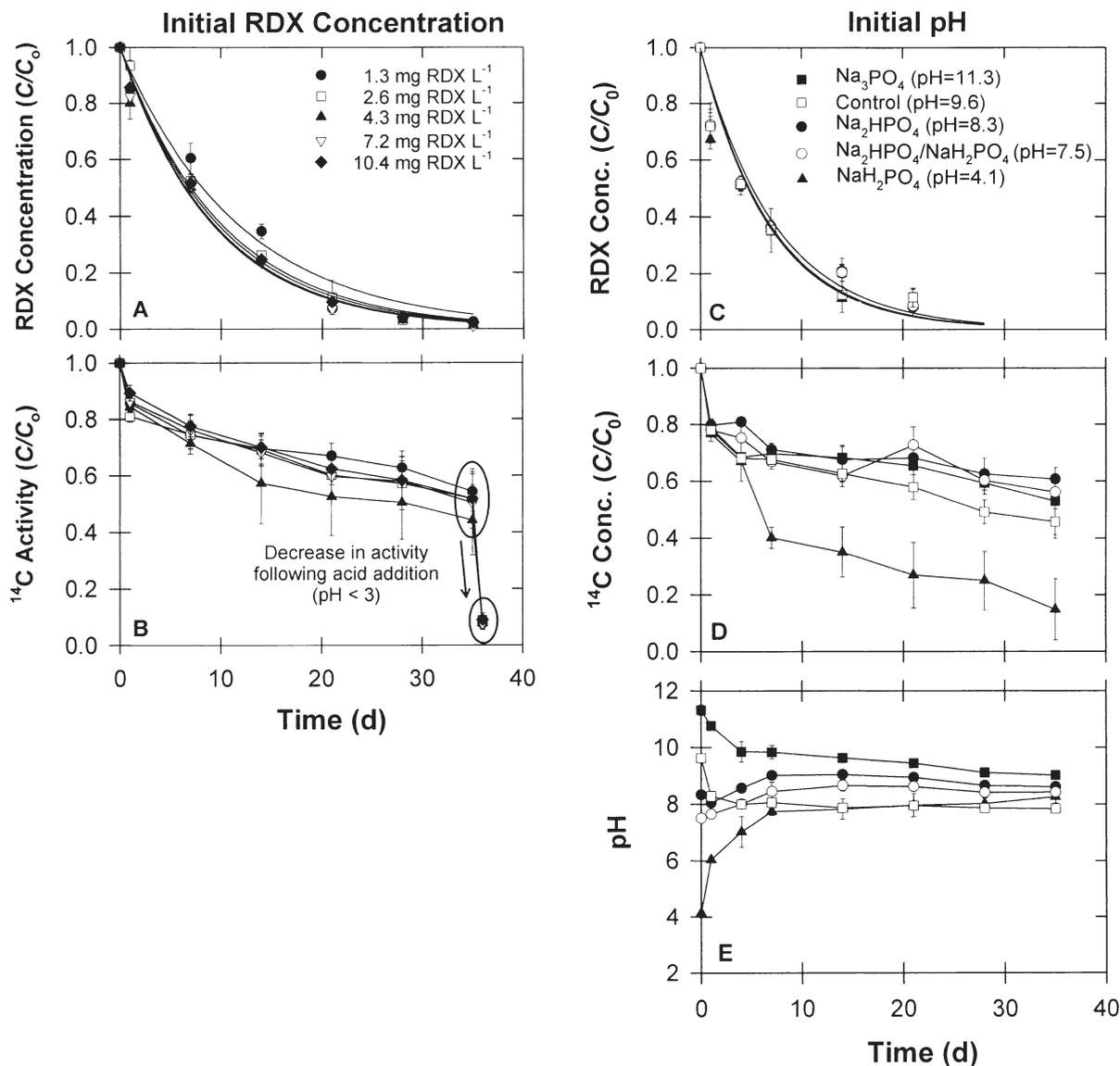
Fig. 4. (A) Effects of initial RDX concentration on RDX destruction and (B) loss of ^{14}C following treatment of aquifer slurry with 4000 mg KMnO$_4$ L^{-1}. Effects of initial pH on RDX destruction kinetics in an aquifer slurry following treatment with 4000 mg KMnO$_4$ L^{-1}. Changes in (C) RDX concentration, (D) ^{14}C activity, and (E) pH. Bars on symbols represent standard deviations of means ($n = 4$); where absent, bars fall within symbols.

the NaH$_2$PO$_4$ treatment was significantly more acidic than the other treatments (pH 4–6), we again attributed this observation to the release of dissolved CO$_2$ at the lower pH.

RDX Transformation Products

Past research has shown that permanganate is effective in attacking compounds with carbon–carbon double bonds, aldehyde groups, or hydroxyl groups and is especially attracted to the negative charge associated with the π electrons of chlorinated alkenes (e.g., tetrachloroethene, trichloroethene, dichloroethene, and vinyl chloride) (Oberle and Schroder, 2000). RDX has none of the above characteristics, and its complete oxidation (mineralization) can take several days to weeks (e.g., Fig. 2 and 3). By comparison, Yan and Schwartz (1999)

observed half-lives ranged from less than a minute to 4 h for chlorinated ethylenes treated with permanganate (1 mM MnO$_4^-$). By comparison, when we treated 1,3,5-trinitrobenzene (TNB; 2 mg L^{-1}) with permanganate (4000 mg L^{-1}), it was undetectable within 30 min. The large difference in destruction kinetics between a nitroaromatic (TNB) and a nitramine (RDX) indicates that different destructive mechanisms by permanganate are likely operative.

Considering that most of the reaction between KMnO$_4$ and RDX occurred under alkaline conditions, one hypothesis is that permanganate is reacting with hydroxyl ions to form hydroxyl radicals ($\cdot$OH) (Ladbury and Cullis, 1958; Wronska and Baranowska, 1964) and that the attack on RDX is indirect. Such an attack can occur at pH > 9 (Gates-Anderson et al., 2001). The limiting step
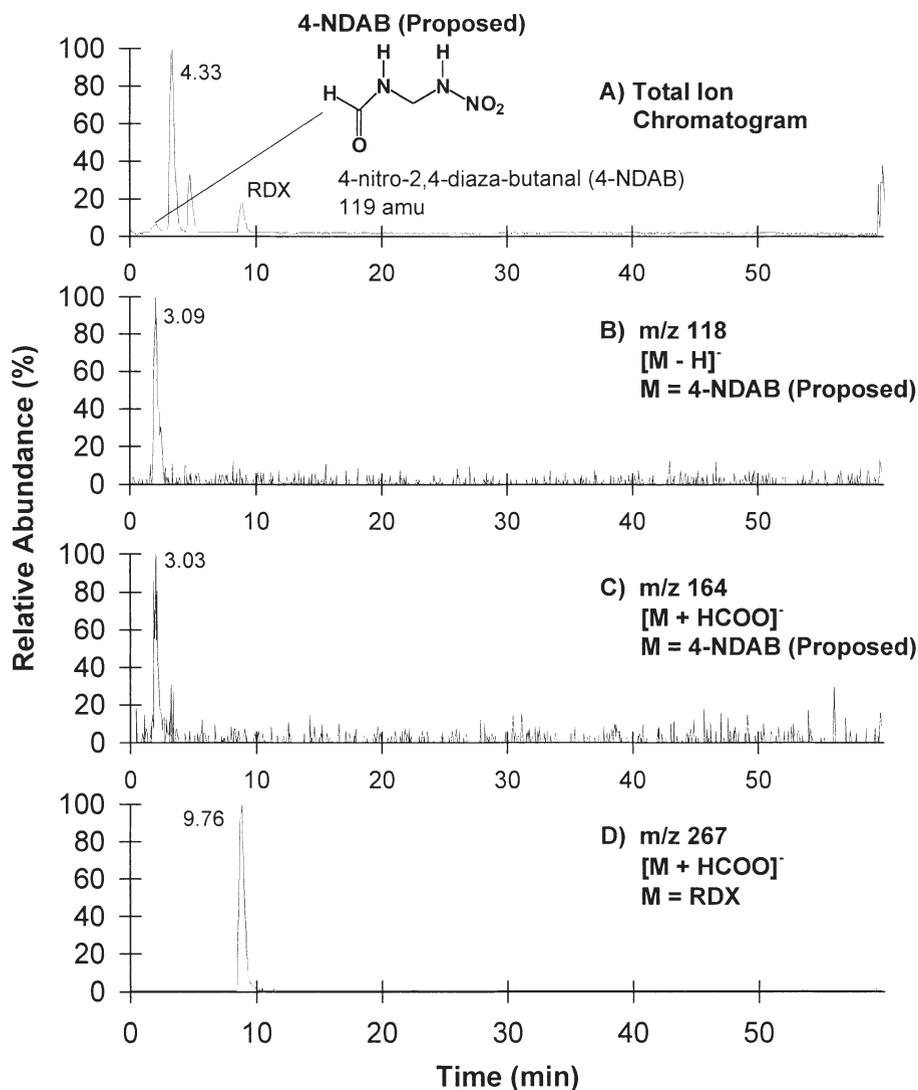
Fig. 5. Ion chromatographs for permanganate-treated RDX and quenched with H₂O₂. (A–D) Total ion chromatograph and selected ions (*m/z*) using ion trap detection.

would be the production of ·OH, which is responsible for the initial attack on the ring, and once that occurs, the permanganate concentration is high enough to quickly oxidize the RDX ring fragments. Although previous research supports ·OH formation under alkaline conditions, our pH experiments showed that pH had little influence on destruction kinetics (Fig. 4C). Moreover, earlier work by Bier et al. (1999) demonstrated that when ·OH attack on ^{14}C-labeled RDX was the dominant mechanism (via the Fenton reaction), at least six radioisotope peaks were detected within 2 h during temporal sampling with HPLC-radioisotope detection. Using a similar analytical system, no major ^{14}C-labeled degradates were detected during permanganate treatment of RDX (data not shown). The absence of detectable ^{14}C-labeled peaks indicates that the initial attack of RDX by permanganate is likely the rate-limiting step and further degradation of the intermediates is relatively fast.

An alternative explanation is that permanganate is facilitating RDX hydrolysis, either directly or in concert with MnO₂ production. The slow reaction kinetics observed (e.g., several weeks; Fig. 2) are more indicative of a hydrolysis reaction and as previously reported (Hoffsommer et al., 1977), once proton abstraction from the β carbon occurs and a nitro group is released (E2 reaction), the double bond formed on the triazine ring would favor attack by MnO_4^-. Although ·OH attack could also cause a double bond to form, Balakrishnan et al. (2003) studied alkaline hydrolysis of RDX and identified 4-nitro-2,4-diaza-butanal (4-NDAB) and N₂O as reaction products. We believe 4-NDAB is also a product of permanganate treatment of RDX. Liquid chromatographic analysis using both ion trap (Fig. 5) and triple quadrupole detection (data not shown) revealed the KMnO₄–treated RDX contained ion peaks at *m/z* 118 (M-H). Ion trap also revealed a *m/z* 164 peak (Fig. 5). 4-NDAB has a mass of 119 and based on the mobile phase used, we believe the *m/z* 164 detection peak is a negative formate adduct of 4-NDAB ([M + HCOO]⁻). Adduct ion formation and detection is en-

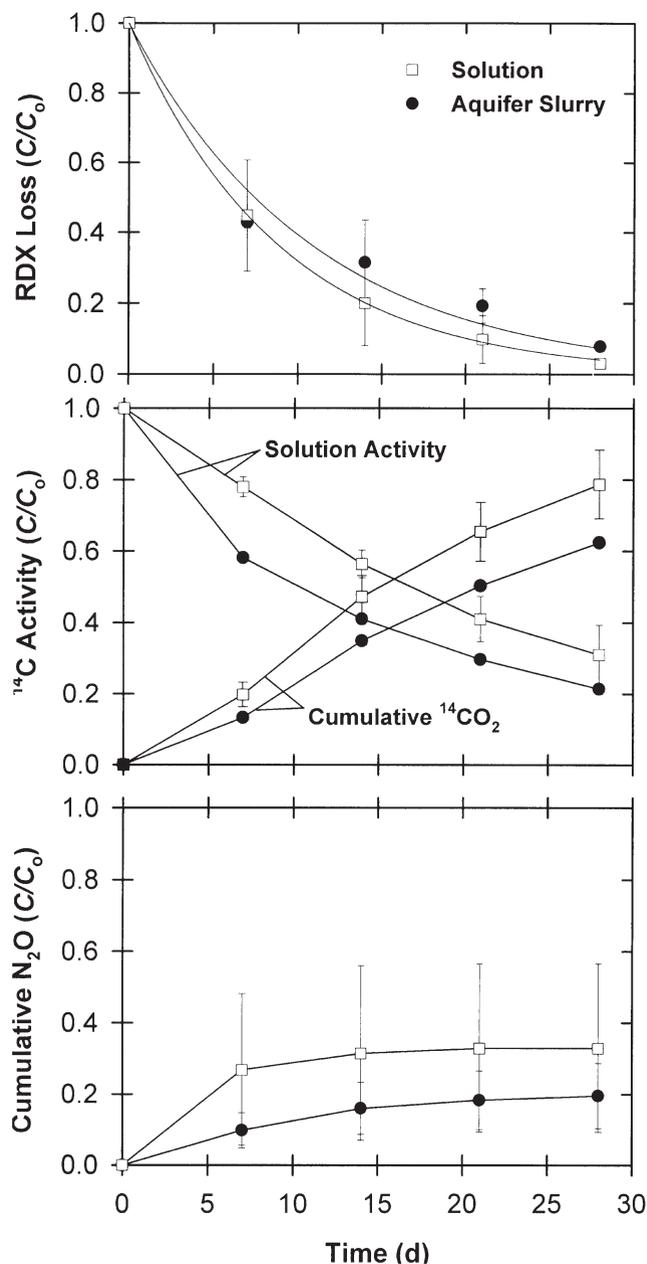Fig. 7. Cumulative $^{14}CO_2$ produced (% of initial ^{14}C) from aquifer microcosms incubated with KMnO$_4$-treated RDX (quenched and unquenched) and parent RDX. All microcosms received the same initial radioisotope activity (i.e., dpm). Bars on symbols represent standard deviations of means ($n = 4$); where absent, bars fall within symbols.

saturated triazine ring could produce formic acid, CO_2, NO_3^-, and NH_4^+ (Bose et al., 1998; Bier et al., 1999; Zoh and Stenstrom, 2002). Specific investigations using the Fenton's reagent (Bier et al., 1999; Zoh and Stenstrom, 2002) and ozone and H_2O_2 (Bose et al., 1998) showed a high percentage of the nitrogen was recovered as nitrate. In our tests, however, we did not observe an increase in NO_3^-. Analysis for ammonium also did not reveal any significant increases. Because no major ^{14}C degradates were observed with the radioisotope detector, it is unlikely that a significant quantity of C–N degradation products formed. Therefore, production of gaseous oxidized forms of nitrogen (such as N_2O) may explain the lack of nitrogen mass balance. Nitrous oxide has been predicted to be a product of RDX degradation through theoretical methods (M. Qasim, Waterways Experiment Station, Vicksburg, MS, personal communication, 2004) and verified experimentally (Balakrishnan et al., 2003; Hawari, 2000). It has also been suggested that once the heterogeneous ring is broken by a remedial treatment (i.e., abiotic, biotic), degradation pathways can lead to similar products (Hawari, 2000).

Measurement of nitrous oxide release showed that N_2O was a product of permanganate oxidation of RDX (solution and contaminated slurry) and constituted 20 to 30% of the N balance (Fig. 6). Comparisons between the treated RDX solution and slurry showed that loss of parent RDX was similar in both medias but N_2O production was greater from the pure solution (Fig. 6). This indicates that other reactions (i.e., biotic) may be occurring when the aquifer solids are present and altering the distribution of reaction products.

Biodegradation of Permanganate-Treated RDX

Although few degrades were detected following permanganate treatment of RDX, some ^{14}C activity remained in solution once the parent RDX was trans-

Fig. 6. Loss of RDX and ^{14}C and production of $^{14}CO_2$ and N_2O from permanganate-treated RDX. For N_2O production, C_o = maximum amount of N_2O that could be obtained based on moles of RDX nitrogen added. Bars on symbols represent standard deviations of means ($n = 4$); where absent, bars fall within symbols.

hanced in electrospray using a buffer such as ammonium formate or formic acid (Cassada et al., 1999). Because 4-NDAB is not commercially available, we could not confirm it in our sample. However, Fournier et al. (2002) similarly observed a degrade peak of identical mass (m/z 118) during RDX biodegradation by *Rhodococcus* sp. Strain DN22 and matched their chromatograph to one produced by alkaline hydrolysis of RDX. Methylene dinitramine and other nitroso-RDX degradation products were not detected in the permanganate-treated RDX solutions analyzed by LC–MS.

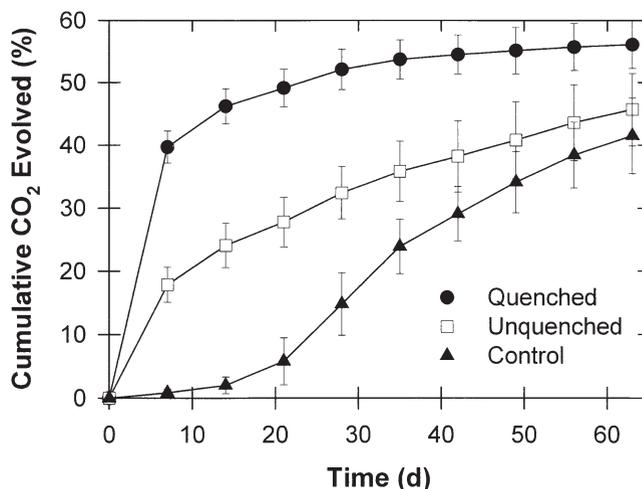Past research has indicated that oxidation of the RDX-

formed (^{14}C degrades and possibly dissolved ^{14}CO$_2$). To determine if the transformation products were biodegradable, we added residual ^{14}C into fresh aquifer microcosms. Mineralization of permanganate-oxidized RDX products ranged between 40 and 60%, with quenched products (permanganate removed from solution) mineralizing 50 to 60% and unquenched products 40 to 55% (Fig. 7). The control treatment (parent RDX) demonstrated a 21-d lag before significant mineralization was observed. Redox measurements taken in the microcosms indicated that the increase in RDX mineralization by the control treatment at Day 21 corresponded with the time the microcosms became anoxic. These results indicate that products produced during permanganate treatment are initially much more biodegradable than RDX. While the presence of residual permanganate initially decreased the amount of cumulative ^{14}CO$_2$ produced (0–7 d; Fig. 7), the relative rates of increase between the quenched and unquenched treatments were similar between Days 7 and 28; afterward, cumulative mineralization slowed down in the quenched treatment while mineralization in the unquenched treatment continued at a constant rate (Fig. 7).

In summary, we found that permanganate is an effective treatment for remediating RDX-contaminated water. Compared to other oxidative treatments, the KMnO$_4$ concentrations investigated here (especially $\leq$4000 mg L^{-1}) produce slow but sustained rates of RDX destruction and mineralization in the presence of aquifer material from the Pantex Plant. These results support permanganate as an in situ chemical treatment for remediating the RDX-contaminated aquifer at the Pantex site.

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