

Reduction of TNT and RDX by Core Material from an Iron Permeable Reactive Barrier

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ABSTRACT: We recently completed a pilot-scale permeable reactive barrier (PRB) with zero-valent iron (ZVI) to treat groundwater contaminated with explosives (TNT and RDX) at the Cornhusker Army Ammunition Plant (CAAP) near Grand Island, Nebraska. While the PRB at CAAP continues to be effective at removing explosives from the groundwater, the hydraulic performance is significantly reduced. This may be due to the accumulation of authigenic precipitates slightly up-gradient from the iron-containing zone. It is likely that the accumulation of new solid phases on the matrix materials in and around the treatment zone would also cause the system to be less effective at reducing contaminants. This, however, does not seem to be the case at CAAP. We report here that iron removed from the PRB is still quite reactive—with TNT and with RDX—when re-suspended and tested in laboratory batch experiments. Surprisingly, the up-gradient impacted samples showed reduction of TNT and RDX even though they did not contain ZVI. Also of note is that the core samples gave slower reduction of TNT than the dry ZVI/sand mixture, but the reverse was true for RDX. In all cases, however, the rates of TNT/RDX reduction by materials containing ZVI were within the range given by the design guidelines.

INTRODUCTION

Permeable reactive barriers (PRBs) made with zero-valent iron (ZVI) are a well established technology for remediation of groundwater contaminated with chlorinated solvents, and applications to other types of contaminants are becoming increasingly common (Tratnyek et al., 2003). One such group includes nitro-containing compounds, like the explosives 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-trihydroxytriazine (RDX). However, in spite of the abundance of laboratory work on reduction of explosives by ZVI (recent examples include Bandstra et al., 2005; Monteil-Rivera et al., 2005; Oh et al., 2002), there have been few well-documented field trials of this approach to remediating explosives contaminated sites (one exception being Comfort et al., 2003). Recently, we have reported results from a field demonstration of a full-scale ZVI PRB for removal of explosives from groundwater at the Cornhusker Army Ammunition Plant (CAAP) near Grand Island, Nebraska (Johnson et al., 2005; Johnson et al., 2008a; Johnson et al., 2008b).

The PRB at CAAP was effective at removing explosives from the groundwater, but permeability decreased over time, apparently because of the accumulation of authigenic precipitates in and slightly up-gradient from the iron-containing treatment zone. Such precipitates have been found to inhibit the reduction of contaminants by ZVI in many laboratory studies (Agrawal et al., 2002; Kohn et al., 2005; Zhang and Gillham Robert, 2005), but there is little direct evidence for decreased rates of contaminant degra-

ation due to precipitate formation on ZVI under field conditions. This could be because the new phases that form under in situ conditions are not as effective at passivating the iron and/or because the field measurements of contaminant degradation by ZVI PRBs are not sufficiently precise to detect the expected changes.

Here we describe results obtained with an intermediate experimental approach. We took cores through the PRB at CAAP and used subsamples of this material—resuspended in batch reactors—to measure the kinetics of TNT and RDX degradation under controlled laboratory conditions. The core material used was from three zones: the iron-containing zone, an impacted region immediately up-gradient from the PRB (determined by visible signs of precipitates), and an up-gradient region that did not appear to have been impacted by the PRB. The results provide a novel perspective on how biogeochemically-driven, medium-term changes in and around a PRB influence the removal of contaminants.

EXPERIMENTAL METHOD

Details of the design and installation of the ZVI PRB at CAAP have been reported in (Johnson et al., 2005). Briefly, the PRB was 15 m long by 4.5 m deep by 0.9 m thick and was composed of 30% (by weight) Peerless iron mixed with local sand. The water table at the site was 5–6 m below ground surface, and the top of the PRB was approximately at the water table.

Details of the core sampling and analysis are given in (Johnson et al., 2008a; Johnson et al., 2008b). Prior to core sample collection the overlying soils were removed down to near the water table. Angled core samples (ca 30° from vertical) were collected through the PRB, sampling in a down-gradient to up-gradient direction using a Geoprobe direct-push system with 3 m long, 5 cm diameter aluminum core barrels. Once the cores were retrieved from the subsurface, the intact cores were frozen with dry ice and transported to our laboratory.

At the lab, the aluminum core barrels were opened by splitting them along their lengths. Zones were labeled: (A) up-gradient un-impacted, (B) up-gradient impacted, (C) ZVI containing zone, (D) down-gradient impacted, (E) down-gradient un-impacted. Subsamples of these materials were transferred to a glove box, where they were used to assemble batch experiments.

The batch experiments were performed using protocols similar to those used in our previous work on reduction of TNT and RDX by ZVI (Bandstra et al., 2005; Tratnyek et al., 2002). We added 1.0 g/L core material to an initial concentration of 20 mg/L TNT/RDX in deoxygenated site water in 60 mL amber vials. TNT, RDX, and triaminotoluene (TAT) were analyzed using HPLC at pH = 7.0 in 20 mM phosphate buffer and methanol at a rotation of 40:60. The flowrate was 1.2 mL/min and the UV-vis was set at 230 nm. The HPLC column used was a Capcell C18 (Shiseido, Japan).

RESULTS

The impacted portions of the core were easily identified by a distinctly darker color. The coloration could be due to a variety of authigenic precipitates, including iron oxides, carbonates, and sulfides. In this case, we know that sulfate concentrations in the groundwater decrease significantly along the flow path and analysis of the solids (e.g., by X-ray photoelectron spectroscopy, XPS) showed that sulfur concentration on the surface of the

particles was high for the up-gradient impacted and PRB particles, whereas it was below detection limits in the original Peerless iron/sand mixture and in the up-gradient un-impacted samples (Johnson et al., 2008b). In the most impacted zone, XPS gave a strong signal for pyrite (FeS_2). None of the samples, however, were so strongly cemented by authigenic precipitates that they didn't disperse into a uniform mixture during mixing in the batch reactor.

Figure 1 summarizes the kinetic data obtained from batch experiments done with core materials from the CAAP PRB. Cores 1, 2, and 3 showed roughly the same zonation and they gave roughly the same patterns in reactivity with TNT. For each core, the samples from the up-gradient un-impacted zone (A) showed no reactivity toward TNT or RDX. However, the up-gradient impacted samples (B) showed reduction of TNT and RDX even though they should not have contained any ZVI. All of the samples from inside the PRB (C) gave reduction of TNT and RDX. Both types of down-gradient samples, impacted and un-impacted, were indistinguishable from the up-gradient controls; i.e., suggesting no significant reduction of TNT.

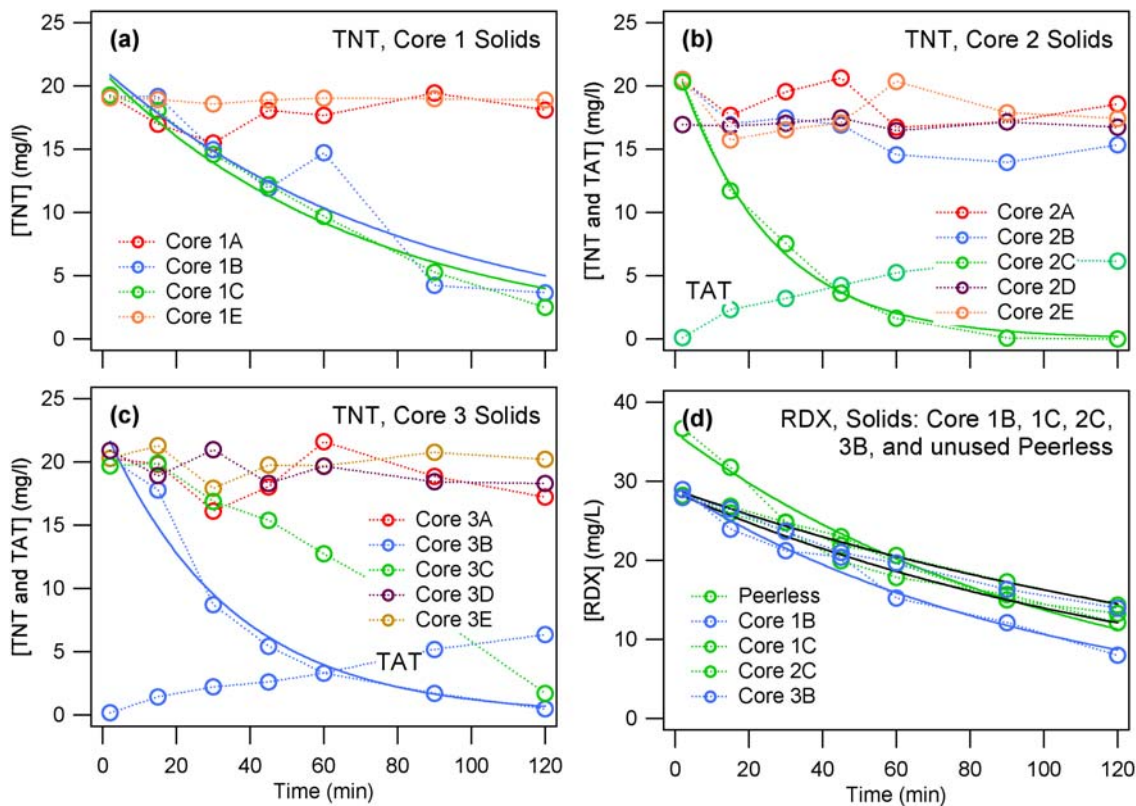


FIGURE 1. Disappearance of TNT and formation of the major product TAT (a, b, c) and disappearance of RDX (d) in batch experiments done with slurries of solids taken from cores taken through the PRB at Cornhusker AAP.

For the cases where we measured a significant decrease in TNT or RDX concentration, the time course data were fit to a first-order model for disappearance kinetics. The resulting pseudo first-order rate constants (k_{obs}) are summarized in Table 1. Data obtained with

the “control” material (a subsample taken from the dry Peerless iron/sand mixture before it was used in the PRB) are also included for comparison.

TABLE 1. Rate constants TNT/RDX disappearance.

k_{obs} (min ⁻¹) for TNT/RDX	Upgradient Unimpacted (A)	Upgradient impacted (B)	ZVI-containing zone (C)
Dry mix	--	--	0.1240 / 0.0032
1	NR	0.0121 / 0.0061	0.0139 / 0.0058
2	NR	NR	0.0140 / 0.0094
3	NR	0.0230 / 0.0100	*

* k_{obs} could not be determined because the data were not first-order, however TNT was degraded to below detection limits in less than 2 hours. All data are from the fits shown in Fig. 1. NR indicates no reaction was detected.

DISCUSSION AND CONCLUSIONS

To facilitate comparisons among the results given in Table 1, we have summarized the data for k_{obs} in Fig. 2, with the core zones represented on the abscissa. First, note that the TNT rate constants (left axis) and RDX results (right axis) are scaled independently and that all values of k_{obs} are larger for TNT than RDX. This trend has been noted previously (Tratnyek et al., 2003), but never fully investigated.

Another comparison that is facilitated by Figure. 2 is between the dry ZVI/sand mixture and the subsamples from the core. All values of k_{obs} obtained with the core materials (Zones B and C) were slower than the dry ZVI/sand mixture, which is consistent passivation of ZVI corrosion by less reactive precipitates. However, the relationship is reversed for RDX (k_{obs} for cores samples is greater than for the dry mix). This can be rationalized if, for example, iron sulfides that precipitate onto the ZVI are better at transferring reducing equivalents to RDX. This is plausible, but there is no evidence to explain why this effect should be observed for RDX and the opposite for TNT. Despite the apparent changes affected by the precipitates formed in and immediately up-gradient from the PRB, the observed rates of degradation, for both TNT and RDX, are still within the range given by the guidelines use in the original design of the PRB.

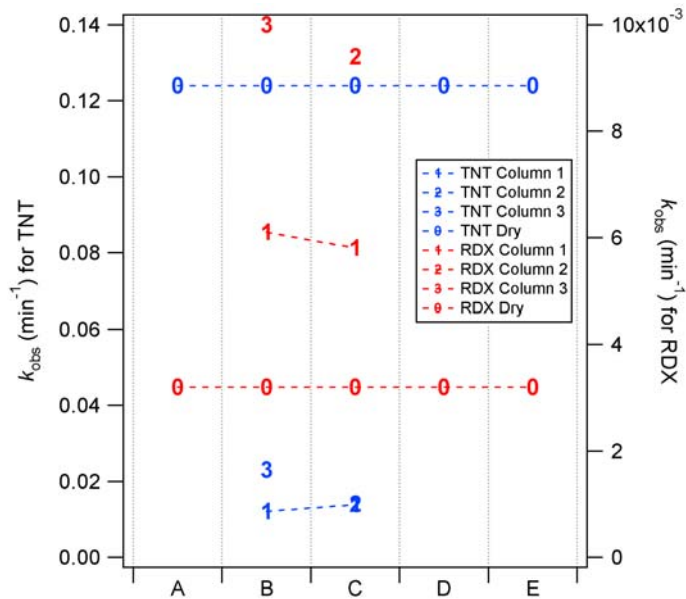


FIGURE 2. Summary of TNT and RDX disappearance rate constants along the five zones of distinct core material in cores taken from the CAAP PRB.

Overall, the most significant result here is probably that the up-gradient impacted zone consistently gives rates of reduction of TNT and RDX that are comparable to the material from the ZVI-containing zone. This is undoubtedly due to reduced iron/sulfur phases that precipitated on the up-gradient aquifer material (due to aspects of the installation process that are somewhat peculiar to this site (Johnson et al., 2008a; Johnson et al., 2008b)). There is little evidence that reduced sulfur species (e.g., mackinawite) will reduce nitro compounds like TNT and RDX, but there is abundant evidence that various forms of Fe(II) will rapidly reduce nitro-containing organics (e.g., Haderlein et al., 2000). These reduced iron/sulfur species are not expected to be as strong reductants as ZVI, however, so it is interesting that the rates of TNT/RDX removal in the two zones are comparable. Of course, the significance of this comparison will be unclear until the rates can be normalized to the concentration of relevant surface area in the materials from the two zones. Another interesting question that arises from this result concerns the capacity to reduce TNT, RDX, or any other oxidant. Presumably Zone B has much less capacity for reduction than Zone C (the ZVI-containing zone), but whether the capacity of the up-gradient impact zone is readily depleted under realistic operating conditions is unclear.

Finally, we note that Figure 2 shows that k_{obs} for the reactive zone (B and C) solids agree well for all three columns for TNT and for 2 out of the 3 columns for RDX. This is a somewhat surprising degree of reproducibility given the nature of the procedures involved.

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