

# **Report for 2005OH16B: Transport and Fate of Iron Nanoparticles in Groundwater**

## Publications

- There are no reported publications resulting from this project.

## Report Follows

# TRANSPORT AND FATE OF IRON NANOPARTICLES IN GROUNDWATER

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## Problem and Research Statement

Groundwater resources provide substantial quantities of drinking water statewide to both municipalities and personal land owners. In Ohio, many streams rely on groundwater baseflow to maintain yearlong sustained flows. Yet, many groundwaters have become contaminated from improper disposal of chemicals, most notably by petroleum products and chlorinated solvents. Extensive research efforts have focused on the remediation of contaminated groundwater, however success has been limited. Some chemicals particularly those resistant to biodegradation and that can be found in pure phase in the subsurface, are difficult to treat in any cost-effective manner. One efficient technology that has been utilized at numerous sites is the installation of permeable barriers constructed with iron filings. As contaminants are transported through the permeable barrier, the metallic iron serves as a strong reductant, reducing the targeted chemicals to less toxic or non-toxic products. This technology is extremely attractive because of its ability to detoxify a broad range of pollutants for an extended period of time. Also iron is inexpensive, non-toxic, and already common in the environment. Unfortunately, use of this technology is limited to sites with relatively shallow, confined contamination where construction costs for installing the barrier are minimized.

A promising new technology involves injecting nanoscale iron particles (i.e. 100 nm to 500 nm) directly into a contaminated aquifer. This technique has many of the advantages of macroscale iron, with the added flexibility of being able to inject iron to the subsurface at multiple locations and at great depth. Nanoscale iron particles increase reaction rates from 500 to 1000 times that of conventional granular iron filing remediation systems (Wang and Zhang, 1997). Current costs of nanoscale iron particles are \$50 per kilogram as opposed to a cost of about \$200 per kilogram for iron filings (Glazier et al., 2003). In addition, once injected into the groundwater, nanoscale particles can move with the contaminant plume to treat pollutants away from the injection source. This technology has been documented in the literature at two trichloroethene contaminated sites. Glazier et al. (2003) provided the results of a study performed at an industrial/research facility located in Research Triangle Park, NC. In this study, 1,600 gallons of 1.9 g/L iron nanoparticles were injected into a TCE plume (average concentration of about 14 mg/L) over a period of two days. TCE was completely removed within 20 days near the injection well and within 50 days 7.5 m downgradient. Similarly, Elliott and Zhang (2001) reported a field demonstration performed at a manufacturing site in Trenton, NJ. For this study, nanoscale palladium-coated iron particles were gravity-fed into groundwater contaminated by TCE and other chlorinated aliphatic hydrocarbons. Approximately 1.7 kg of nanoparticles were introduced

into the test area over a 2-day period. TCE reduction efficiencies of up to 96 percent were observed over a 4- week monitoring period.

This technology holds great promise for cleaning up contaminated groundwater throughout Ohio. Iron targets a broad range of chemicals and injection can occur over a wide range of site geologies, thus this technology is extremely versatile. Further, it is relatively inexpensive and utilizes non-toxic chemicals. Finally, creative application of this technology may allow for meeting varied site goals including: (1) treatment of dissolved chemicals away from the injection point as the iron nanoparticles transport with the groundwater, (2) targeted treatment of sources zones using direct push injection, (3) creation of stagnant treatment zones if the iron nanoparticles attach to the aquifer materials in significant quantities (Zhang, 2003). Clearly, an understanding of the transport and fate of the nanoparticles in the subsurface is critical information needed for successful implementation of this technology.

Many questions remain about the transport and fate of iron nanoparticles in groundwater. Little is currently known about the attachment rate of these particles to porous media under different chemical conditions and different delivery rates (Lecoanet and Wiesner, 2004). Further, the persistence and total catalytic capability of these particles under different chemical conditions has not been quantified (Lien and Zhang, 2001). Only through a greater understanding of these mechanisms can this technology be effectively utilized and optimized. Further, greater knowledge of the transport and fate of iron nanoparticles may allow for more creative remediation approaches.

In this research project we assessed the transport and fate of iron nanoparticles through aquifer sediment, by (1) fabrication and characterization of iron nanoparticles, (2) assaying the rate of 2,4,6-trinitrotoluene (TNT) transformation under various conditions, and (3) measurement of the transport of iron nanoparticles in sand columns.

## Methodology

### Production of Nano-size Zero Valent Iron

Two chemicals, sodium borohydride ( $\text{NaBH}_4$ ) and iron (III) chloride ( $\text{FeCl}_3$ ) were used to make nano-size zero valent iron (NZVI) in a process called reductive precipitation. Solid  $\text{FeCl}_3$  was stored in a dessicator to prevent oxidation. 10 mL of  $\text{NaBH}_4$  (1.6 M) were added dropwise to 10 mL of  $\text{FeCl}_3$  (1.0 M), and NZVI was formed immediately upon contact in a violent reaction (Li et al, 2003).



The mixture was stirred on a magnetic stir plate with a stir bar for 20 minutes to allow the reaction to come to completion, and to allow all gas formed to be released. The iron and supernatant were placed in 15-mL centrifuge vials and centrifuged for 10 minutes at 11,000 rcf. The supernatant was then decanted and discarded while the NZVI was rinsed with ultra pure water purged with  $\text{N}_2$  for 10 minutes and centrifuged again. The NZVI was rinsed and centrifuged a total of three times. It was then place in a beaker and dried in an oven at  $100^\circ\text{C}$

under nitrogen for several hours. The particles dried to the walls of the beaker and were scraped off. After the NZVI was removed from the sidewalls, it was stored in a microcosm bottle purged with N<sub>2</sub> and crimped shut with a Wheaton butyl septum cap (Millville, NJ).

### **Characterization of Nanoparticles**

Photos of the nanoparticles were taken with a transmission electron microscope (TEM) and with an S240 scanning electron microscope (SEM), shown in Figures 1 and 2. Photographs from the TEM show individual particles. The magnification on photos (1-2) is 22,800 and 34,390 on photos (3-8). These particles were used in an experiment before photographing them, so they are somewhat, if not entirely oxidized.

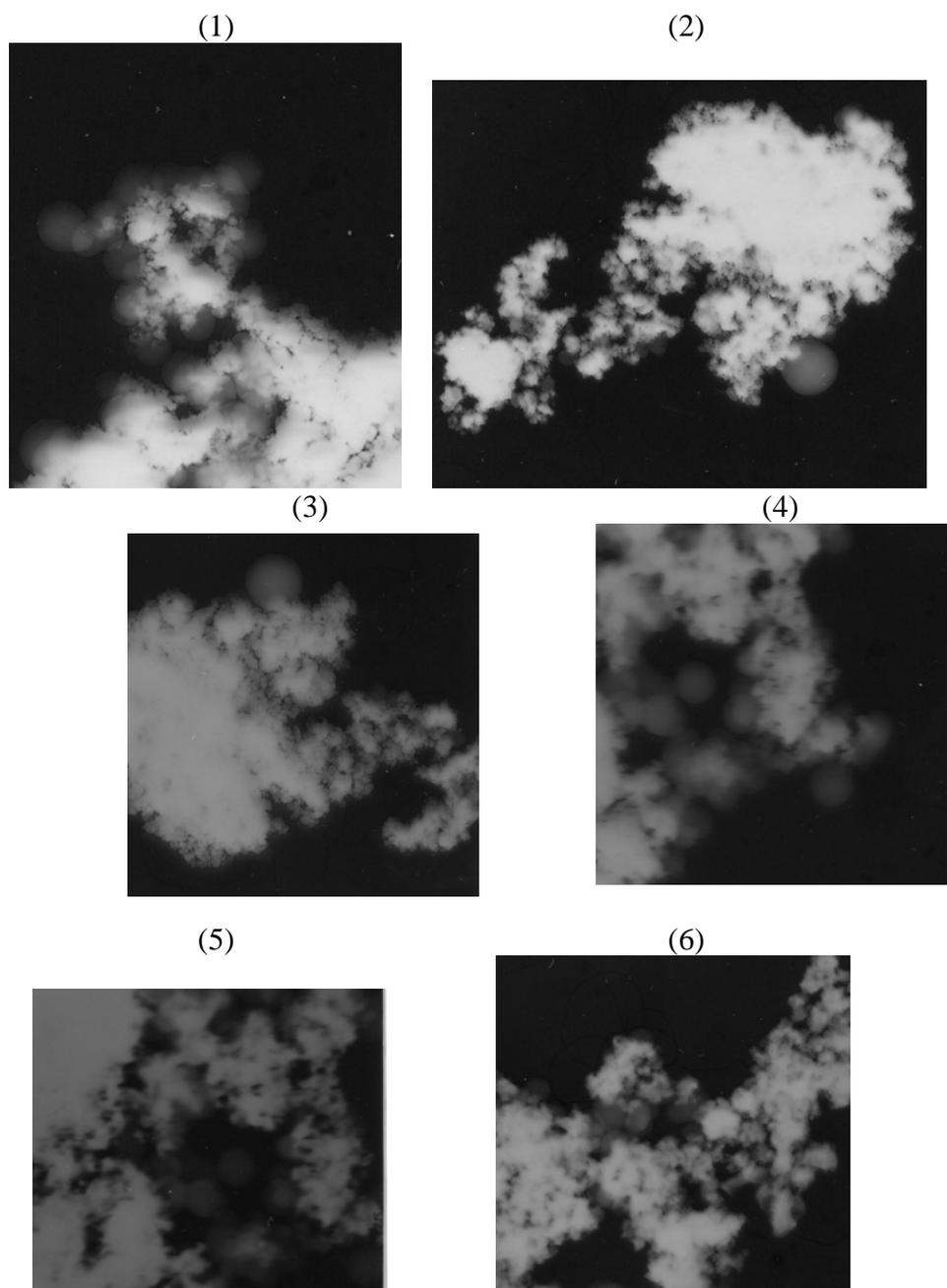
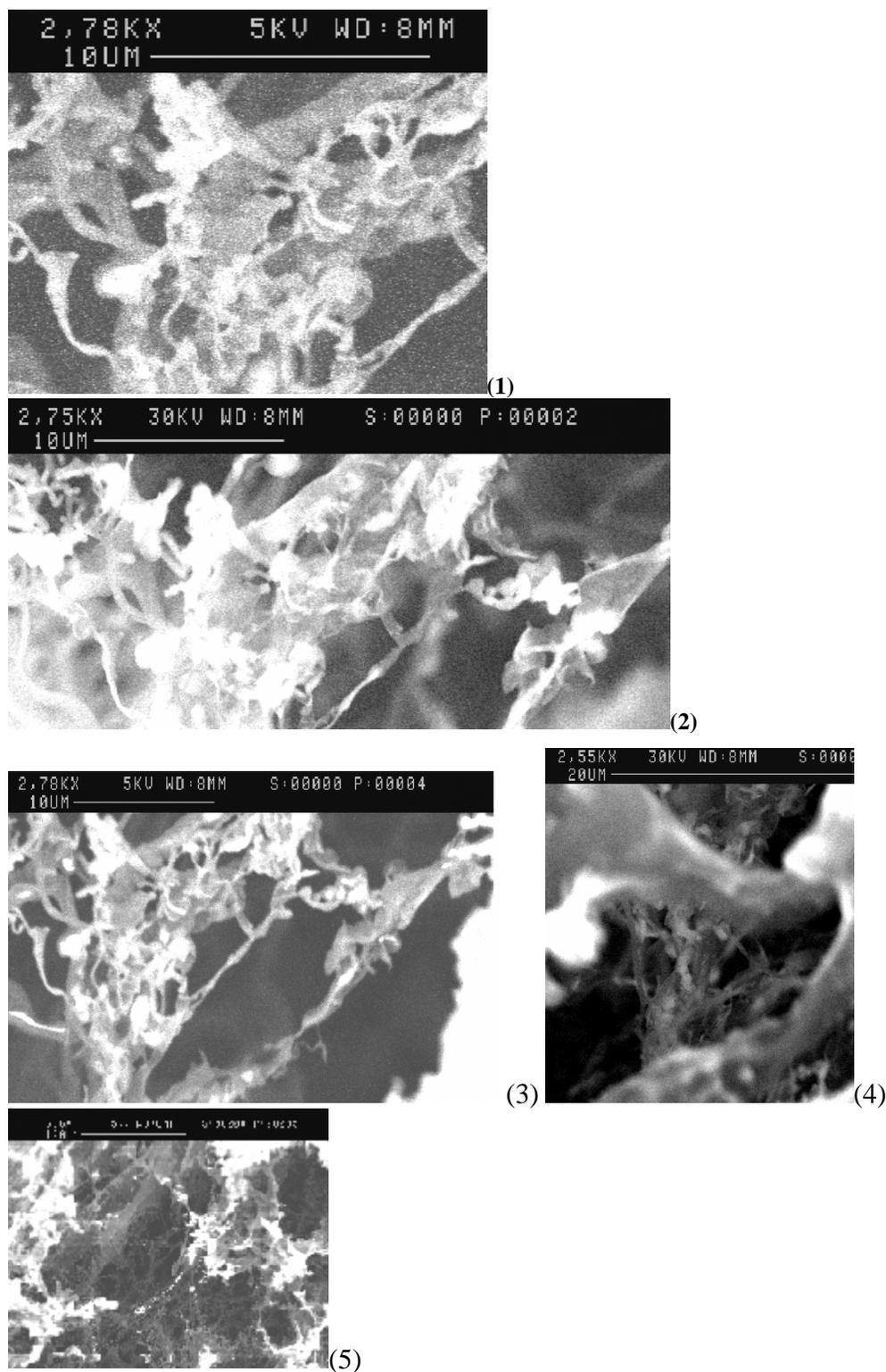


Figure 1: TEM Images of Regenerated NZVI. Photos: 1-2 10 nm = 2.28 mm; photos 3-6: 10 nm = 3.44 mm



**Figure 2: SEM Images of NZVI and 20 nm Silica Spheres**

Thus, even though a portion of surface area is probably lost through particle agglomeration, tremendous surface area is retained because of the web-like structure. 20 nm silica spheres

appear in white in the SEM photos for scale. These uniform microspheres were purchased from Bangs Laboratories (Fishers, IN).

### **HPLC Analysis**

TNT analysis was done on a Hitachi high performance liquid chromatographer (HPLC), which consists of a Hitachi AS4000 Intelligent Sampler, an L-6200 Intelligent Pump, a D-6000 Interfaces, and an L4500 Diode Array Detector (Tokyo, Japan). A 35% methanol eluent was used in the column (Thermo-Hypersil C-18 100mm × 4mm, 3µm particle size). The software used was Hitachi Model D7000 Chromatography Data Station. The monitoring wavelength was 254 nm and the chromatograms were integrated between wavelengths of 240-260 nm.

### **Preparation of HPLC Standards**

In order to identify TNT and its breakdown products by the HPLC, standards of known concentration were prepared. High concentrations of TNT, 2-ADNT, 4-ADNT, 2,4-DANT, and 2,6-DANT were purchased from AccuStandard (New Haven, CT). Standards were prepared in 2-mL HPLC vials in concentrations of 10, 20, and 50 mg/L, diluted with 35% methanol. Each standard was prepared in its own HPLC vial for ease in determining spectra properties and peak times. Standards were refrigerated between uses.

Standards were run on the HPLC for 30 minutes with an eluent of 35% MeOH. A spectra library was developed in order to quickly and easily identify TNT and its degradation products. Each compound has its own spectrum and peak time, which allowed for identification in samples.

Concentrations of samples were determined using calibration curves found with the standards. The standards were of known concentration, and HPLC absorbance units were matched in Excel to these concentrations by plotting the concentration of each standard against the corresponding absorbance unit value. The points were fit to a linear model that was forced through zero. These calibration curves allowed for the determination of TNT and by-product concentrations during experimentation.

### **Preparation of TNT Stock Solution**

A TNT stock solution of approximately 100 mg/L was prepared by combining 100 grams of TNT crystals with 1 L of ultra pure water. The TNT crystals purchased from Chem Service (West Chester, PA) were at most 30% water; pure TNT is not legally commercially available. Actual concentration of the stock solution was unknown until run on the HPLC. The solution was placed on a magnetic stirrer and allowed to mix continuously for several days at room temperature. TNT has a low solubility in water, so it was not used until completely dissolved. Once the TNT had fully dissolved, 100 mL was placed in a microcosm bottle and purged with N<sub>2</sub> for 10 minutes. The 100 mg/L deoxygenated stock solution was used for experiments with the NZVI. Due to its toxicity, the remaining volume of TNT stock solution was kept sealed and continuously stirred under a hood.

### **Kinetics Experiments**

In order to determine removal rates, TNT and iron were combined and samples were taken at regular intervals. As reaction rates became better understood through trial and error, optimal

time between sampling and total experiment time was determined. Reaction kinetics were easily monitored when 0.05 grams/L of NZVI was combined with 10 mL of TNT stock solution and tested every five minutes. The temperature for all experiments was 22°C and the water was at pH 6.

First, 0.05 grams of NZVI was weighed and placed in a microcosm bottle, sealed, and purged with N<sub>2</sub>. Then, 10 mL of TNT stock solution was added with a gas-tight syringe, and the bottle was placed on a shaker table at 150 rpm. The first sample was taken immediately after addition of the TNT and afterwards, every 5 minutes for 30 minutes. Sample volumes of 0.5 mL were extracted into a syringe filled with 0.5 mL of 35% methanol to stop the reaction between the NZVI and TNT. Samples were placed into 1.5 mL centrifuge vials and centrifuged for five minutes at 13,000 rpm to separate the nanoparticles from the liquid. Supernatant was then decanted into 2 mL HPLC vials and run on the HPLC. Controls consisting of 0.5 mL of TNT stock solution mixed with 0.5 mL of 35% methanol were run along with the samples.

Kinetics experiments were performed in triplicate. Once concentrations of all samples were determined, they were plotted in Excel. The resulting curve matched a first-order reaction type curve, and the kinetics were determined using a first-order reaction rate equation. The average of the three reaction rate constants was found and used as the final reaction rate constant.

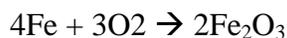
### **Re-spiked NZVI**

In order to determine the useful life of the iron, TNT stock solution was added repeatedly to the same mass of NZVI. Once again, 0.05 grams of NZVI was placed into a microcosm bottle and purged with N<sub>2</sub>. 10 mL of TNT stock solution was added and the bottle was placed on a rotary shaker at 150 rpm. Samples were taken at 1 minute and 30 minutes. After 30 minutes, when all TNT had been reduced, an additional 10 mL of stock solution was added. This was sampled immediately and every 10 minutes thereafter for 70 minutes. The samples were then centrifuged and run on the HPLC. After 24 hours, a third 10 mL of stock solution was added and sampled at the same intervals. This procedure was repeated until no further TNT removal was observed.

### **Efficacy of Oxidized Particles**

Groundwater is seldom completely anaerobic, so the efficacy of partially oxidized particles was determined in order to see how effectively partially oxidized particles remove TNT. Water samples with enough oxygen to cause 1%, 2%, 4%, 10%, 15%, and 20% oxidation of iron were added to NZVI. After samples were well mixed and oxidation reactions complete, TNT stock solution was added and samples were collected at 10-minute intervals for 1 hour. Samples were centrifuged and run on the HPLC.

Oxygen requirements for desired degrees of oxidation were determined based on the following equation.



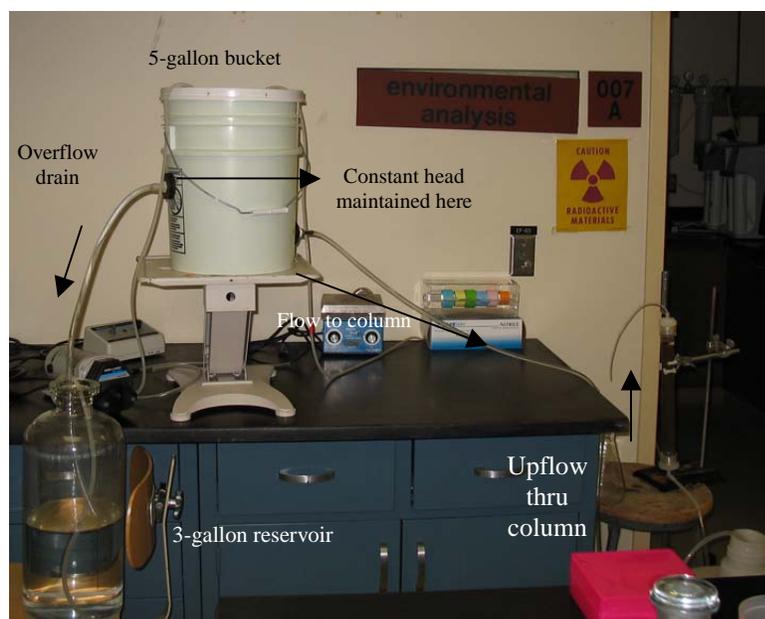
Oxygen was added to oxidize the selected percentage of total iron present as NZVI. The dissolved oxygen concentration of water in equilibrium with the atmosphere was measured and

the amount of air-saturated water required to deliver the desired mass of  $O_2$  determined. This water was then mixed with the anaerobic NZVI solution.

### Column Study

A column study was performed to understand how NZVI is transported through the soil and how it interacts with the soil. TNT fate and transport was also studied, as well as the interaction between NZVI and TNT in the soil.

Water from an elevated 5-gallon bucket flowed by gravity upward through a glass column, 300 mm long with a 26 mm internal diameter (see Figure 3). Water was continuously pumped from a 3-gallon reservoir into the bucket at a rate faster than the column flow rate to maintain constant head in the 5-gallon bucket at a drain port.



**Figure 3: Column Setup**

A conservative tracer analysis was performed first to determine the properties of the clean sand in the column. A chloride probe was used with a Denver Instruments Model 225 pH/ISE meter to determine the  $Cl^-$  concentration coming through the column. In order to introduce chloride into the column, a NaCl stock solution with 182 mg/L  $Cl^-$  was prepared and added to the bucket and the reservoir. The flow to the column was closed and the  $Cl^-$  solution circulated until the concentrations in the bucket and reservoir were equal. The flow to the column was then opened and column effluent samples were taken every two minutes for 90 minutes, or until the concentration stabilized. This was repeated three times and chloride tracer curves were obtained. Between each run, the column was flushed with ultra pure water for several hours to allow residual  $Cl^-$  to be removed.

To understand the properties of TNT in the column, a TNT solution was added and monitored. Flow to the column was closed and then 100 mg/L TNT was added to the reservoir and the

bucket and left to equilibrate for several hours. Once the concentrations in the bucket and reservoir were equivalent, flow was opened to the column and samples were collected every 2 minutes for 90 minutes. Effluent samples were collected in 0.5 mL volumes and combined with 0.5 mL of 70% MeOH and then run on the HPLC.

In order to study the behavior of NZVI in soil, a 5 g/L slurry was injected into the base of the column through a silicone tube. Changes in iron concentration were monitored using absorption spectrophotometry.

A Perkin-Elmer Analyst 300 atomic absorption spectrophotometer (Norwalk, CT) was used to determine the concentration of iron in the column effluent. 25 mL standards were made from a Fisher Scientific iron reference standard (Fair Lawn, NJ) in concentrations of 5, 10, and 20 mg/L. An air-acetylene flame was used for analysis with a Perkin-Elmer Intensitron Hollow Cathode Lamp (Norwalk, CT). Calibration of the three standards resulted in a correlation coefficient ( $R^2$ ) value of 0.999.

Samples were collected from the column effluent every two minutes for several hours. They were diluted 100× by taking 100  $\mu$ L of effluent and adding it to 9.9 mL of ultrapure water. The samples were then run on the AA until the iron concentration stabilized.

## Principal Findings

### Reaction between TNT and NZVI

Combination of 10 mL 75 mg/L TNT and 0.05 g of NZVI under anaerobic conditions results in the complete removal of TNT from water in less than 30 minutes. The TNT stock solution had a pH of about 7 and all experiments were performed at room temperature, 22°C. The curve formed from data collected shows a pseudo first-order reaction. Pseudo first-order kinetics were determined from this curve. Figures 4 and 5 show the TNT removal curves and corresponding pseudo first-order fits. The equation used in first-order kinetics was:

$$\frac{dC_{TNT}}{dt} = -k_1 C_{TNT} \quad (1)$$

where  $k_1$  = TNT degradation rate constant,  $t^{-1}$

The assumption with this model is that the concentration of the TNT is the only factor controlling the reaction and that the NZVI is in excess. For the five replicates,  $k_1$  values varied from -0.135 to -0.304  $\text{min}^{-1}$  with an average value of -0.216  $\pm$  0.074.

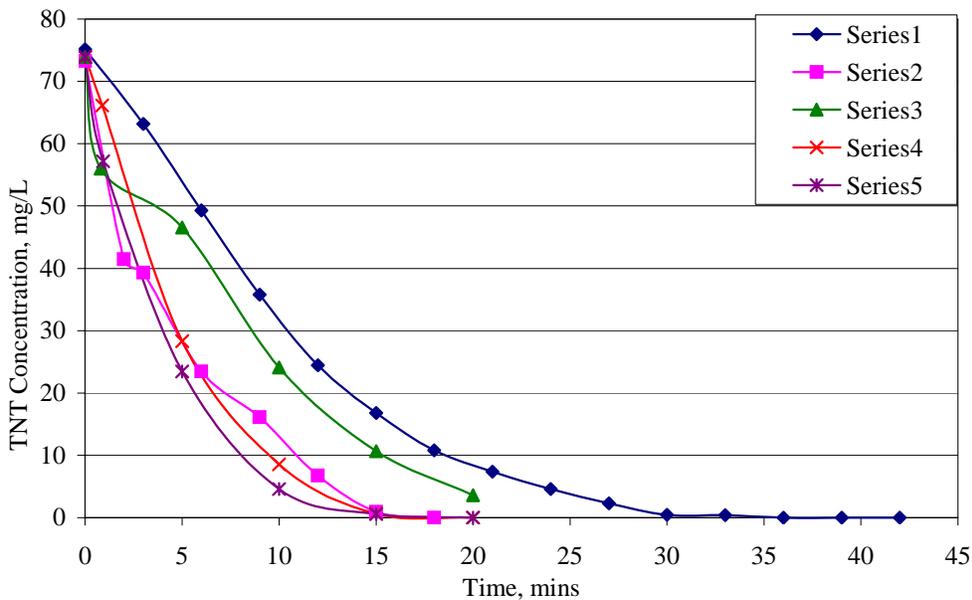


Figure 4: TNT Removal by NZVI

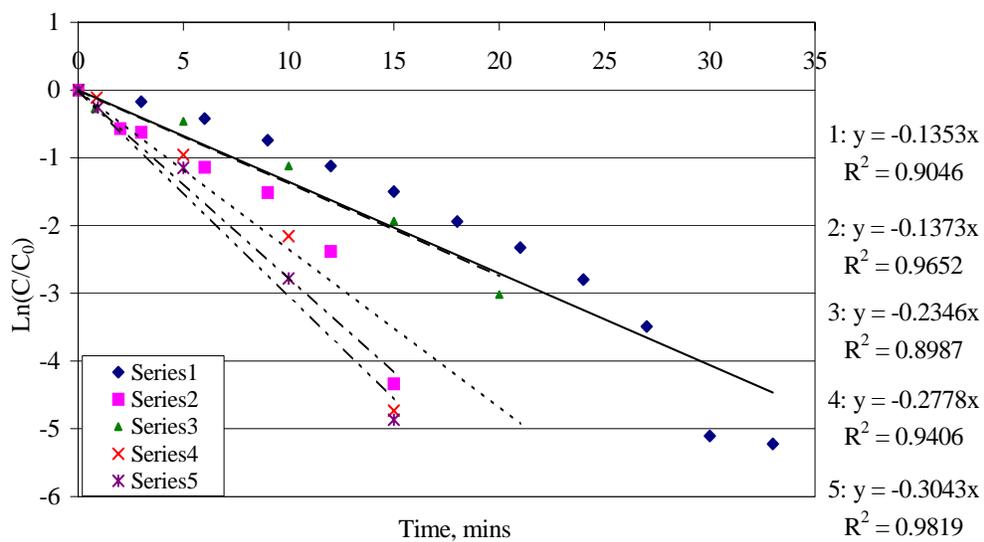


Figure 5: Pseudo First-order Kinetics of TNT Removal by NZVI

TNT degradation product formation was monitored along with TNT removal. Within 6 minutes of TNT exposure to NZVI, degradation is evident. Figure 6 shows the mass balance of TNT, 2-ADNT, 4-ADNT, 2,4-DANT, and 2,6-DANT for Series 1 on Figure 5. There is also a cumulative concentration curve shown. The mass balance is incomplete, and it is presumed that the missing mass is either in the form of TAT or azoxy dimers, both of which are highly unstable and therefore not monitored.

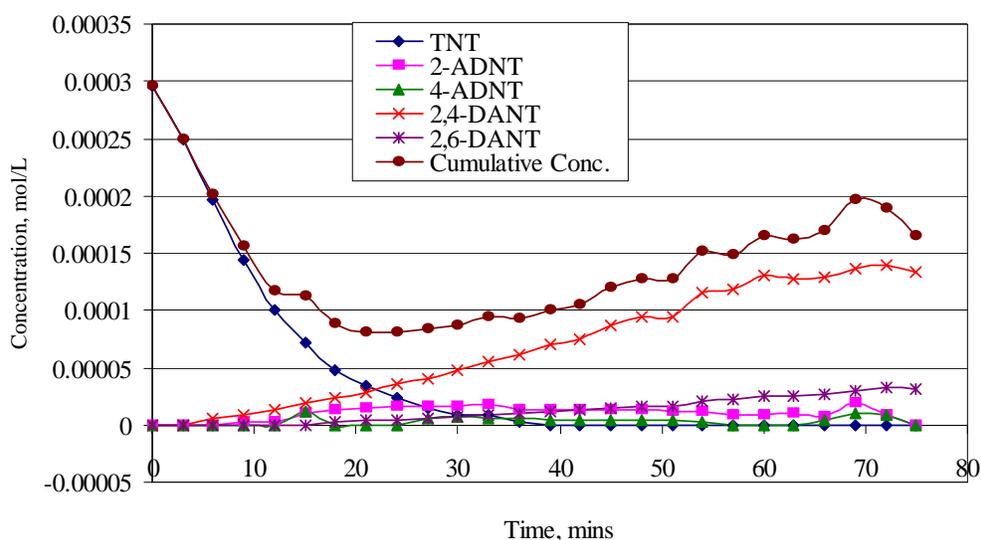


Figure 6: TNT and Degradation Products

### Re-spiked NZVI

In order to determine the useful lifetime of TNT in in situ applications, a mass of NZVI was spiked repeatedly with TNT until transformation ceased. The data were then fit to both pseudo first-order and second-order reaction rate equations. Figure 7 shows the decrease in TNT removal rates as the NZVI becomes increasingly oxidized. Seven spikings of 10 mL of 80 mg TNT/L each were required to render 0.050 g NZVI ineffective. These data were analyzed using a model that assumes second-order kinetics with linked TNT reduction and NZVI oxidation:

Figure 8 shows the second-order model and the data from the re-spiked NZVI experiment. The solid lines represent the model while the points represent the actual experimental removal. The model was designed with the following equations.

$$\frac{dC_{TNT}}{dt} = -k_2 C_{TNT} C_{NZVI} \quad (2)$$

$$\frac{dC_{NZVI}}{dt} = -k_3 \frac{dC_{TNT}}{dt} \quad (3)$$

where  $k_2$  = TNT degradation rate constant,  $t^{-1}$  and  $k_3$  = Fe oxidation rate constant,  $t^{-1}$ .

The model and the data match reasonably well. As the iron is oxidized, its available surface area for oxidation decreases, decreasing the rate of TNT transformation. For this model, the value used for  $k_2$  was determined independently from the pseudo first-order kinetics described earlier and was set equal to  $k_1$ . Only the value for  $k_3$  was varied to fit the data. All of the curves were simultaneously fit to a single parameter set. That the model fits well suggests that the reaction behaves pseudo first-order initially and then second-order afterwards. That is, the NZVI is in excess for a period of time, but then as the degree of oxidation increases, the concentration of the NZVI that is not oxidized limits the rate of transformation.

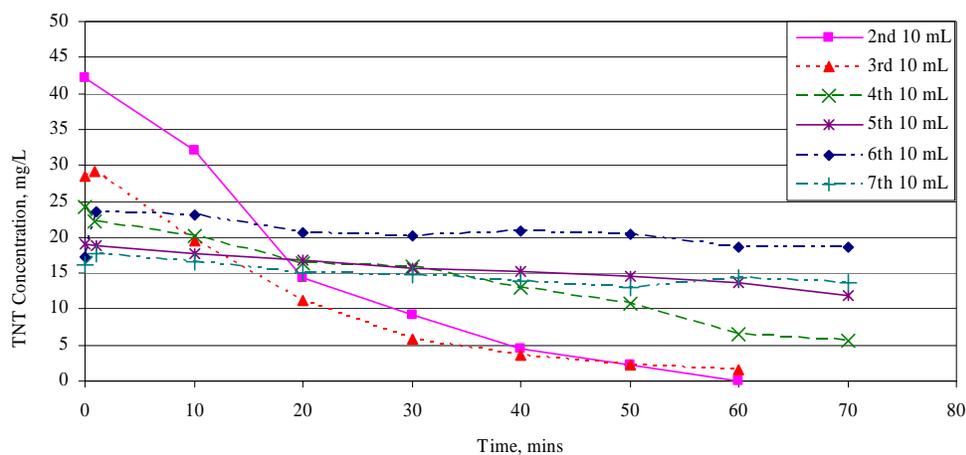


Figure 7: NZVI Spiked with TNT Multiple Times

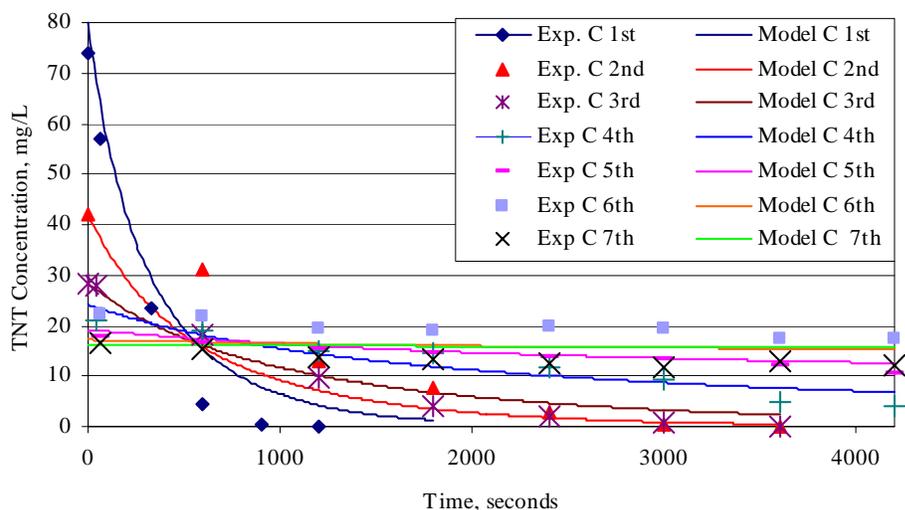


Figure 8: Second-order Kinetics Model

When both  $k_2$  and  $k_3$  are varied within the model, the sum square error (SSE) value changes only 7.4%, and the value for  $k_2$  changes from  $-0.216 \text{ min}^{-1}$  to  $-0.254 \text{ min}^{-1}$ . The values for  $k_3$  change only slightly also, from  $-0.348 \text{ min}^{-1}$  to  $-0.348 \text{ min}^{-1}$ .

### Efficacy of Oxidized Particles

Figure 9 shows the effect of NZVI oxidation on TNT removal. Degrees of oxidation as low as 4% appear to have a significant effect on TNT transformation. Pseudo first-order fits to the kinetic assays are shown in Figure 10 and results are reported in Table 1. These compare with a fully reduced  $k_1$  value of  $-0.216 \text{ min}^{-1}$ . Even with only 1-2% oxidation, dramatic decreases in activity are observed. 4% and above behave similarly with near complete inactivation of NZVI. These results indicate NZVI is highly sensitive to oxidation. The minimum amount of oxygen to effectively inactivate 1 gram of NZVI is 26.9 mg  $\text{O}_2$ .

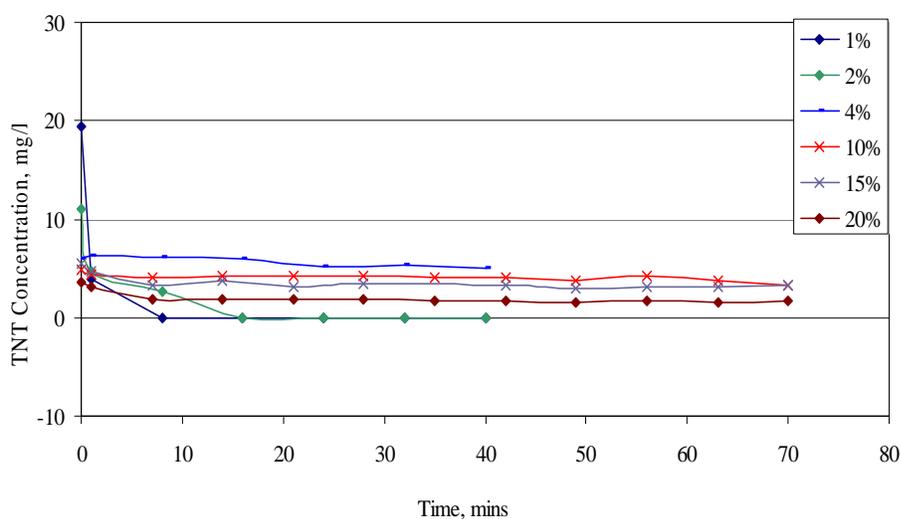
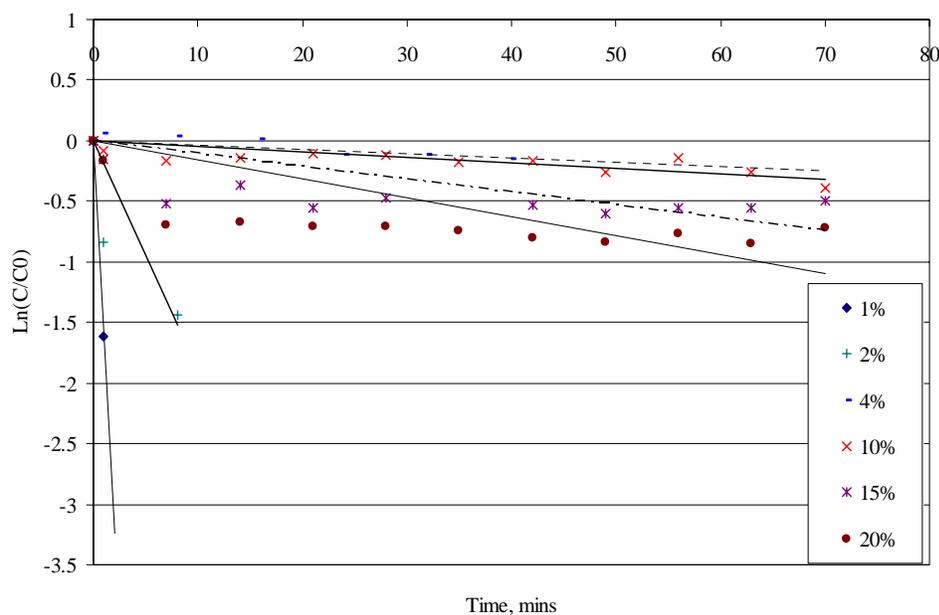


Figure 9: TNT Removal at Various ZNVI Oxidation Stages



**Figure 10: First-order Removal of Oxidized NZVI**

**Table 1: NZVI k Values**

% Oxidation	k, min <sup>-1</sup>	R <sup>2</sup>
1	-1.6195	1
2	-0.1905	0.5985
4	-0.0036	0.7011
10	-0.0046	0.5329
15	-0.0106	0.3628
20	-0.0157	0.2733

Activities after oxygen oxidation were compared to activities after TNT oxidation. TNT reduction assays from repeated spikings were fit with a pseudo first-order model (Equation 1) and results are reported in Table 4. Also reported are values of iron concentration remaining at the beginning of each spiking as determined from the second order model (Equations 2 and 3). This model accounts for iron oxidation due to TNT reduction and is analogous to the iron oxidation from oxygen exposure.

**Table 2: NZVI k Values**

Spiking #	% NZVI, Available	$k_L, \text{min}^{-1}$	$R^2$	% NZVI, Oxidized
1	100	-0.2203	1	0
2	54.09	-0.0556	0.9798	45.91
3	29.85	-0.0507	0.994	70.15
4	14.59	-0.0192	0.9436	85.41
5	4.560	-0.0061	0.9711	95.44
6	1.06	0.0028	-1.6692	98.94
7	0.223	-0.0029	0.7305	99.77

### Column Study

The behavior of NZVI, TNT, and their interaction within soil has importance for in situ applications. Figure 11 shows three chloride breakthrough curves used to understand behavior of flow through the column. In these experiments, inflow to the column initially had zero chloride and at  $t = 0$ , chloride was added continuously to the influent. Source concentrations of chloride were between 29 and 39 mg/L. This figure shows a consistent 95%  $\text{Cl}^-$  breakthrough between 15 and 19 minutes and an average of  $17 \pm 2$  minutes. This is important to understand because  $\text{Cl}^-$  is conservative, that is, it will not react with soil and is thus not expected to adsorb. Should TNT or NZVI adsorb to soil, it will be evident if the breakthrough is greater than 17 minutes.

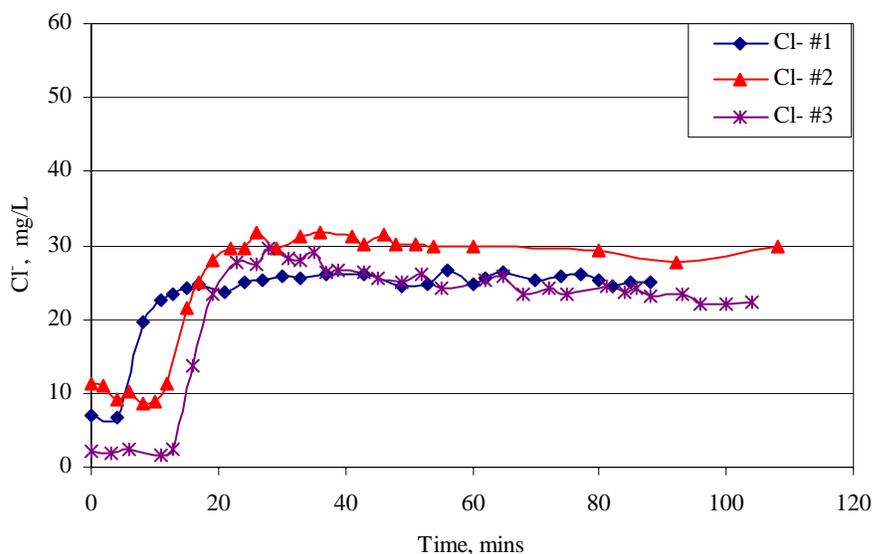
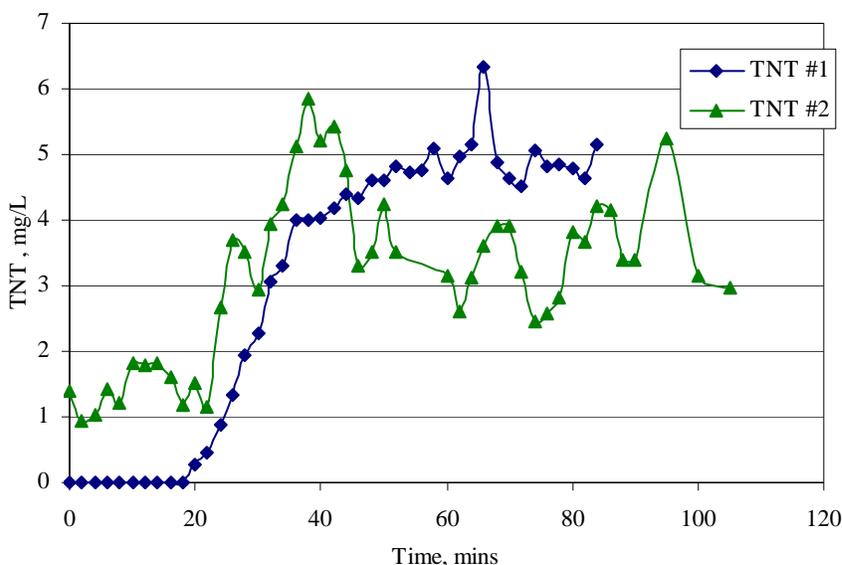
**Figure 11: Chloride in Column**

Figure 12 shows TNT breakthrough curves. In this experiment, inflow to the column initially had zero TNT and at  $t = 0$ , TNT was added continuously to the influent at concentrations between 7-9 mg/L. The time of TNT 95% breakthrough, 18 minutes, corresponds well to the time of  $\text{Cl}^-$  breakthrough, suggesting that adsorption on to the soil medium is not a factor. However, it is evident from the difference between the source and effluent concentrations that not all TNT

introduced actually flows through, since no metabolites were detected. This may indicate that the TNT does encounter some adsorption during its flow through the column.



**Figure 12: TNT in Column**

This experiment involved adding 50 mg of NZVI to the column by spiking it at  $t = 0$ . Initial NZVI slurry was 5 g/L; 10 mL were added. Figure 13 suggests the same fate for NZVI as for TNT: breakthrough is around 20 minutes, but the concentration injected was several magnitudes greater than that in the effluent. The concentration of NZVI introduced into the column was approximately 5 g/L, while the maximum effluent concentration from the column was just below 160 mg/L. The actual concentration introduced is never reflected in the effluent concentration. This suggests significant adsorption of NZVI to the clean sand and poor transport through the column. The NZVI injected appears to act as a continuous source of low concentration NZVI far beyond the expected breakthrough time. The NZVI concentration did not approach 0 mg/L until more than 12 hours after injection.

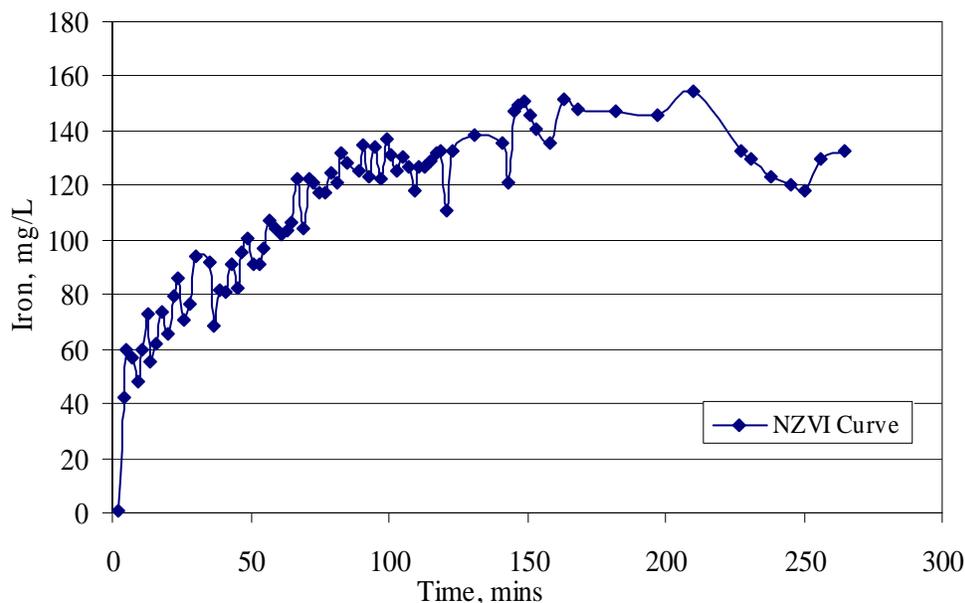


Figure 13: NZVI in Column

## Significance

Use of NZVI for TNT remediation is a very promising technology. NZVI is affordable, easily made, and is appropriate for *in situ* applications. TNT is quickly transformed to its degradation products, 2,4-DANT and 2,6-DANT, which are less toxic and biodegradable, unlike the parent compound. This technology can help make contaminated areas safe for development and increase the volumes of clean water available. Further, it does not require disposal of degradation products or spent NZVI, making the overall process more attractive. Only 5 g of NZVI are needed to transform 1 L of 100 mg/L TNT.

There are some drawbacks, however. Once produced, NZVI agglomerates and must be kept agitated to prevent settling. Dried particles must be crushed to a fine powder before use. The particles are highly sensitive to oxidation and can be completely inactivated at 4% oxidation. The mass of O<sub>2</sub> required to oxidize 1 gram of NZVI is only 26.86 mg. Oxygen present in groundwater will likely have a detrimental impact on remediation efforts. It is therefore advisable to verify anoxic groundwater conditions if at all feasible before introduction of NZVI.

NZVI and TNT combined follow second-order kinetics. Reaction rate constants  $k_2$  and  $k_3$  were  $-0.216 \text{ min}^{-1}$  and  $-0.348 \text{ min}^{-1}$ , respectively. The required mass of NZVI for *in situ* applications is likely much higher than the value reported above, due to both oxidation rates of NZVI and high degrees of adsorption in soil. The recommended minimum mass of NZVI to transform 1 L 100 mg/L of TNT *in situ* is therefore 100 mg.

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