PROJECT COMPLETION REPORT

PILOT-TESTING AN INNOVATIVE REMEDIATION TECHNOLOGY FOR IN-SITU DESTRUCTION OF CHLORINATED ORGANIC CONTAMINANTS IN ALABAMA SOILS AND GROUNDWATER USING A NEW CLASS OF ZERO VALENT IRON NANOPARTICLES

Don Zhao*, Principal Investigator (PI), Associate Professor

Feng He, Graduate Research Assistant and Ph.D. Candidate

Department of Civil Engineering
238 Harbert Engineering Center, Auburn University, Auburn, AL 36849

*Telephone: 334-844 6277; Fax: 334-844 6290; E-mail: dzhao@eng.auburn.edu

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ABSTRACT

Currently, Alabama owns 12 EPA-designated NPL (National Priorities List) sites and 2 proposed NPL sites. Of all toxins detected at these sites, chlorinated hydrocarbons such as PCE, TCE and PCBs are among the most wide-spread and most harmful contaminants to our groundwater, which serves as over 60% of the State’s drinking water source.

Despite extensive research efforts, degradation of these chemicals in water and soils remains a costly and challenging environmental issue. Our prior AWRRI project resulted in a new class of carboxymethyl cellulose (CMC) stabilized zero-valent iron (ZVI) nanoparticles, and preliminarily tested the great promise of applying the nanoparticles for in situ rapid destruction of chlorinated contaminants. The objective of this current study was to pilot-test this cutting-edge technology at an Alabama site to confirm the soli mobility and degradation effectiveness of the nanoparticles.

The test was carried out in collaboration with an environmental company (Golder Associates) at a northern Alabama site which was heavily contaminated with chlorinated hydrocarbons such as PCE, TCE and PCBs. This well-characterized site was prepared with an injection well and three monitoring wells spaced 5 ft apart (two down-gradient wells and one up-gradient well). Approximately 150 gallon of 0.2 g/L Fe-Pd (CMC = 0.1 wt%, Pd/Fe = 0.1 wt%) nanoparticle suspension was synthesized on site, and then gravity-fed into the test area over a 4-h period. Based on transport of a tracer Br⁻, ~37.4% and ~9% of the injected iron were observed in the 5 ft and 10 ft down-gradient monitoring wells MW-1 and MW-1, respectively, indicating the mobility of the nanoparticles through the aquifer. The ORP of groundwater extracted from MW-1 was reduced from -40 mv to -254 mv following the injection, indicating a favorable environment for reductive dechlorination. In accord with our prior experimental data, the CMC-stabilized nanoparticles exhibited unprecedented soil mobility and reactivity for destroying the primary contaminants such as PCE, TCE and PCBs under field conditions. The concentrations of PCE, TCE and PCB1242 in MW1 were lowered by up to 77%, 85%, and 83%, respectively, after deducting dilution effect in the first 10 days and continuously reduced by 59%, 96%, and 10% at the end of 29 days. In MW2, the concentrations of PCE, TCE and PCB1242 were lowered by up to 98%, 82%, and 95% respectively in the first 10 days and continuously reduced by 99%, 100%, and 93% at the end of 29 days. Application of the nanoparticles greatly boosted sustained biodegradation of the primary contaminants. As the degradation data are still being monitored, steady degradation of all the three chlorinated compounds was continuously observed four months after the treatment. For example, at 29 days after injection, the concentrations of TCE in MW-1 and MW-2 were 72 ppb and < 10 ppb compared to the concentration of 1655 ppb and 3710 ppb before injection. It is proposed that the H₂ from the Fe corrosion acts as the electron donor and the CMC and its metabolites provide the ideal nutrients for enhanced biodegradation of the chlorinated organic contaminants.

The research has resulted in two conference presentations and one journal paper. In addition, the grant partially supported two graduate students and one summer undergraduate student from Rice University.
STATEMENT OF THE PROBLEM AND STATE OF THE TECHNOLOGY

Chlorinated hydrocarbons, such as polychlorinated biphenyls (PCBs), tetrachloroethylene (PCE) and trichloroethylene (TCE), are well-known potent toxins to human health and the environment (1, 2). Although the uses of chlorinated hydrocarbons have now been either banned or highly restricted, the past massive production and applications have left an environmental legacy that large areas of soils and groundwater in Alabama are contaminated with dangerously high concentrations of chlorinated hydrocarbons. In recent years, high concentrations of PCE and TCE have been detected in areas adjacent to dry cleaners, automobile manufacturers or shops, asphalt processing plants, and military bases. The nationally known PCE/TCE site in Alabama is the “Montgomery capital plume” site located right in downtown Montgomery. The contaminated groundwater plume is believed to exist throughout the downtown Montgomery area. Following a 17 months of investigation of PCE contamination in the capital city, the Alabama Department of Environmental Management (ADEM) concluded in 1995 that there are a minimum of 6 ground water plumes contaminated with PCE and benzene, toluene, ethylbenzene and xylene (BTEX) (3). On May 11, 2000, the site was proposed to be listed on the National Priorities List (NPL). Currently, the city of Montgomery has shut down the two contaminated wells, and initiated an $18.6 million clean up action.

Unfortunately, there have been no cost-effective and environmentally benign remediation technologies available for remediation of chlorinated soils and groundwater despite tremendous research efforts in the past three decades. To a great extent, current remediation practices rely on excavation and landfill of contaminated soils, which are extremely costly and environmentally disruptive (the associated cost is between 100-700 dollars/yard³ (4). For cases like the capital plume site, since the site is located in the heavily populated downtown area, engineered processes (e.g., excavation) are highly restricted. In recent years, the concept of in-situ dechlorination by directly injecting zero-valent iron (ZVI) nanoparticles into the contaminated subsurface has attracted increasing interest. Compared to the traditional passive processes such as the “funnel and gate’ or permeable reactive barrier (PRB) processes, the in-situ injection technology offers a number of key advantages. For example, it can proactively attack contaminant plumes in the source zone instead of passively ‘wait and intercept’, and it can be applied to source zones in deep aquifers or to areas where lands are occupied.

However, this promising technology has been held back by a key technical barrier that the nanoparticles tend to agglomerate and grow to micron-scale or larger in a few minutes, thereby losing their soil/sediment mobility and chemical reactivity rapidly (5-7). Typically, Fe(0)-based nanoparticles are prepared by reducing Fe(II) or Fe(III) in aqueous phase using sodium borohydride (8-9). Although other solvent-based methods such as micro-emulsion-based methods (10), sonication assisted methods (11, 12) and sol-gel methods (13) have been reported, the water-based approach appears most suitable for environmental applications for its minimal use of environmentally intensive solvents or chemicals. However, because of rapid agglomeration, the steady-state mean size of the ‘nanoparticles’ is actually ~17.7 μm (5). Since particles of 3 μm or larger are easily intercepted by soil matrix (6), the ‘nanoparticles’ are hardly mobile in soils, and thus, not suitable for injection uses.

To overcome the particle agglomeration, we have recently developed and patented a new class of ZVI nanoparticles that are stabilized using low-cost and “green” carbohydrates such as starch or cellulose (7, 14). Our preliminary research findings provide compelling evidence that low-cost starch, cellulose and their derivatives can serve as effective stabilizers to yield
highly dispersible and reactive Fe(0) nanoparticles suitable for injection into the subsurface and for in-situ destruction of chlorinated hydrocarbons. The nanoparticles have been judged the most suitable nanoparticles for in situ dechlorination uses by a group at University of Michigan (15), and the technology has attracted national interest. To ultimately apply this promising technology in the field, pilot-test is a critical and logical step, and will yield critical information on the technical and cost effectiveness and necessary design and operating parameters.

Therefore, this research aims to pilot-test this cutting edge in-situ remediation technology for rapid and complete destruction of chlorinated hydrocarbons such as PCE, TCE and PCBs in Alabama soils and groundwater. The specific research objectives are to:

1). Test the feasibility (dispersibility, reactivity, and reactive longevity) of the iron nanoparticles when applied under field conditions at a chlorinated solvent site in Northern Alabama;
2). Probe the effects of field environmental conditions (pH, dissolved oxygen (DO), oxidation and reduction potential (ORP), ionic strength, and dissolved organic matter (DOM)) on the effectiveness;

METHODS AND PROCEDURES

Site Selection and Test Area Description. The site selected for the pilot test is an abandoned metal processing plant site in northern Alabama. The test area is located within one of the relatively well-characterized source zones. The dimensions of the test area were approximately 15.0 ft by 9.0 ft, as shown in Figure 1. An injection well, denoted IW-1, was installed to inject the stabilized Fe suspension into the subsurface. The injection well was screened from 45 ft to 50 ft (right above the bed rock) below ground surface. The test area also contained three monitoring well with one (MW3) at 5-ft up-gradient and two others (MW1 and MW2) located 2ft at 5ft and 10ft, respectively, down-gradient of the injection well along the groundwater flow direction. MW-1 and MW-3 were screened from 45 ft to 50 ft, while MW-2 was screened from 40 ft to 45 ft due to the change of bed rock level (from 50 ft to 45 ft). The hydraulic conductivity (K) of the aquifer within the test zone was determined to be 20 ft/day (i.e. 0.42 cm/min).

Groundwater Quality in the Test Area. Groundwater quality within the test area has been monitored regularly for approximately a decade. Several chlorinated hydrocarbon contaminants including tetrachloroethene (PCE), trichloroethene (TCE), cis-dichloroethene (cis-DCE), trans-dichloroethene (trans-DCE), vinyl chloride (VC) and PCB1242 at levels ranging from ~ 1ppb to 220 ppm have been recorded. The concentration of the primary contaminants PCE, TCE and PCB1242 ranged from 1.2 ppm to 12.0ppm, 1.6ppm to 23.8ppm, and 6.9 ppb to 97.4 ppb, respectively, right before the field study.
Field Preparation of Stabilized Nanoparticles. The field preparation of the stabilized Fe suspension is briefed as follows. Approximately 28 gallons of tap water were placed in a 65 gallon polyethylene reactor and rapidly stirred with a 1/3 horsepower motorized impeller. The polysaccharide powder (sodium carboxymethyl cellulose, NaCMC) 564g was then added near the impeller while mixing, and the solution was mixed until no visible clumps were observed (~ 3 hours). During mixing, the nitrogen gas was also supplied to purge the oxygen out of the reactor and help mixing. After the completion of NaCMC dissolution, approximately 564g FeSO₄·7H₂O (Fisher, Fair Lawn, NJ) was dissolved in 1 gallon tap water and added into the reactor. As the stirring and N₂ purging continued, 146g NaBH₄ (98%, Acros Organics, Morris Plains, NJ) was dissolved in 1 gallon tap water. Then, the NaBH₄ solution was added into the reactor at a rate of 0.5L/min. The solution in the tank turned from a milky white to inky black as the nanoparticles were produced. Finally, about 0.5g Na₂PdCl₄·3H₂O (Strem, Newburyport, MA) was dissolved in 100ml tap water and slowly added into the reactor. In this way, Pd was coated on the surface of iron nanoparticles to form bimetallic ZVI nanoparticles. The expected NaCMC concentration was 0.5% by weight and Fe concentration was 1g/L with Pd/Fe = 0.1% (w/w). The 1g/L Fe solution was then pumped into a 200gallon reactor for dilution, in which 120gallon tap water had been purged with N₂ for 3 hours. The diluted Fe solution had a concentration of 0.2g/L with a volume of 150 gallons. Before the injection, 34g KBr (dissolved in 100ml water) was added into the 200 gallon reactor to be used as a tracer.

Iron Suspension Injection and Groundwater Monitoring. The 0.2g/L Fe suspension was injected into the screened interval of injection well IW-1 using a peristaltic pump. The

*: The plume schematic is adopted from Biochlor 2.2

Figure 1. A sectional view of the aquifer at the testing site and schematic of the in situ injection of CMC-stabilized Fe-Pd nanoparticles.
injection rate was adjusted to avoid the overflow of Fe suspension from the well. The final injection rate was fixed at 0.67 gallon/min. The nanoparticle suspension was driven into the aquifer through the static hydraulic head only (the pump did not exert additional pressure). Groundwater samples were collected from two monitoring wells MW-1 and MW-2 before and after injection. Samples were collected without purging using 12V dedicated submersible pumps installed in each of the three monitoring wells. Also, a multi-parameter probe with a flow-through cell was used to collect pH, specific conductance, oxidation-reduction potential (ORP), dissolved oxygen (DO), and temperature readings during sampling activities.

Laboratory Feasibility Studies. Prior to the field test, laboratory feasibility studies were conducted using groundwater from the site. During the tests, 20 mL stabilized Fe suspension (1g/L, 0.5% CMC, Pd/Fe = 0.1%) was mixed with 23 mL groundwater obtained from MW-3. The batch vials (43 mL) were then cap-sealed with Teflon-lined septa and placed on a rotary shaker at 50 rpm for degradation tests. Parallel experiments were also performed to degrade PCE and TCE in deionized water solution. To test the change in particle reactivity with the particle age (i.e. storage time in water), replicate samples of 0.1g/L lab-synthesized Fe-Pd nanoparticle suspension were stored in sealed glass vials (with zero headspace) and kept in a refrigerator at 4 °C for up to 9 days before being tested. The particle reactivity was then evaluated through the degradation of TCE following the procedure described elsewhere (14).

The soil mobility of the CMC-stabilized Fe-Pd nanoparticles was tested with 2.7 mL of a loamy sand soil (obtained from Auburn, AL) packed in a glass column (1 cm I.D.). For comparison, parallel tests were also carried out for a tracer (i.e. 0.6 g/L KBr) and non-stabilized Fe-Pd particles. The salient soil properties are as follows: porosity = 0.35; hydraulic conductivity = 0.25 cm/min; sand content = 84%; silt = 10%; clay = 6% clay. In the breakthrough tests, a solution containing the tracer, 1.0 g/L (as Fe) of non-stabilized or CMC-stabilized (1% w/w NaCMC) iron nanoparticles was passed through the soil bed under a constant static hydraulic head of 7.1 cm. The particle breakthrough history was then followed by analyzing the total iron in the effluent until the full breakthrough was achieved. Then, DI water was pumped into the column by the HPLC pump at a constant superficial liquid velocity of 0.23 cm/min. Iron elution history was then followed for ~10 pore volumes.

Laboratory Analysis. The analysis of primary contaminants PCE, TCE was carried out in the lab. In brief, 0.1 mL of the groundwater sample was withdrawn from the 43 mL vials using a 100 μL gas-tight syringe; then the sample was transferred into a 2 mL GC vial containing 1 mL of hexane for extraction of TCE; upon phase separation, the extract was analyzed for chlorinated solvents using a HP 6890 GC equipped with an RTX-624 capillary column (32 m long and 0.32 mm ID, Restek Co. Bellefonte, PA, USA) and an ECD. For PCBs analysis, 33 mL groundwater was extracted using 3 mL hexane in the 43 mL vials. PCBs in the hexane phase were then analyzed using an HP 6890 GC equipped with an HP5 capillary column (32 m long, 0.25 mm ID, Agilent, Santa Clara, CA, USA) and ECD.

For total iron tests, 1mL of the groundwater sample was withdrawn, dissolved in 4 mL HCl, diluted with DI water to 15 mL, and analyzed for total iron using a flame atomic-absorption spectrophotometer (AAS) (220FS, Varian, Palo Alto, CA). Bromide and sulfate were analyzed using a Dionex Ion Chromatography (DX-120, Dionex, Sunnyvale, CA) equipped with an AS14 column, an AG14 guard column and a 100 μL sample loop. Before analysis, groundwater sample was filtered through a 0.45 μm membrane filter to remove the colloids.
PRINCIPAL FINDINGS AND THEIR SIGNIFICANCE

In this one-year intensive research project, we tested the feasibility of using a new class of reactive bimetallic nanoparticles for in situ destruction of chlorinated organic compounds such as PCE, TCE and PCBs at a northern Alabama site. Using a low-cost and environmentally safe carboxymethyl cellulose as a stabilizer, we successfully prepared a new class of Fe-Pd nanomaterials on site that showed significant mobility and high reactivity in the northern Alabama soil.

Prior to the pilot test, lab feasibility studies were carried out and showed that the PCE and TCE in the groundwater collected from the site were readily degradable by the stabilized Fe-Pd nanoparticles and the particles were dispersible in a loamy sand soil bed that has a comparable hydraulic conductivity to that of the site aquifer. Approximately 150 gallon of bimetallic nanoparticle suspension (Fe = 0.2 g/L, CMC = 0.1 wt%, Pd/Fe = 0.1 wt%) was synthesized on site and gravity-fed into the test area over a 4-h period. Compared to the tracer Br\textsuperscript{-}, ~37.4% and ~9% of the injected Fe was observed in a 5 ft and 10 ft down-gradient monitoring wells MW-1 and MW-2, respectively, indicating the significant migration of the nanoparticles in the test area, which resulted in a highly reactive colloidal barrier. Consequently, rapid and significant degradation of primary contaminants PCE, TCE, and PCBs was observed in both MW-1 and MW-2 up to 4 days before exhibiting various degrees of recovery. After that, further enhanced biodegradation of PCE and TCE was also observed. This pilot test, for the first time, realized the concept of effective in situ soil remediation using our patented stabilized Fe-Pd nanoparticle technology. The fact of combining abiotic remediation and bioremediation with the injection of Fe particles further increases the attractiveness of this technology as a source zone remediation alternative.

The most important results are summarized as follows.

**Laboratory Testing Results.**

Figures 2 depicts the reduction of PCE and TCE in batch tests with the field groundwater extracted from monitoring well MW-3 and with PCE/TCE solutions prepared using DI water. Complete destruction of TCE (C\textsubscript{0} = 15.0 ppm) was achieved within 3 h for the groundwater sample containing 0.465g/L Fe-Pd (Pd/Fe = 0.1 wt%). More than 70% removal of PCE (C\textsubscript{0} = 9.6 ppm) in the groundwater sample was also achieved within the tested timeframe of 6 h. Although it appears that PCE is more persistent than TCE to Fe-Pd reduction in groundwater, both of them are readily degradable by the stabilized Fe-Pd nanoparticles. Much more rapid degradation of both PCE and TCE was observed in lab-prepared PCE/TCE solution. Complete destruction of both PCE and TCE was achieved in 1 h. According to our prior studies, the reactivity of the stabilized Fe-Pd nanoparticles is essentially a function of solution pH, ionic strength and dissolved organic matters (DOM) (16). Since the pH and the ionic strength of the two studied samples were set to be similar, the reduced reactivity of the nanoparticles in groundwater is attributed to competitive effects of other oxidizing agents such as DO and sulfide, and to inhibitive effect due to adsorption of the groundwater DOM on the particle surface, which competes the reactive sites and hinder the dechlorination of the target chlorinated compounds.
Figure 2. Reduction of PCE and TCE in a field groundwater and DI water with Fe-Pd nanoparticles synthesized in the lab. Iron dose was 0.465 g/L, Pd/Fe = 0.1 wt%, $C_{PCE,0} = 9.6$ ppm, $C_{TCE,0} = 15.0$ ppm.

Figure 3. Column breakthrough and elution histories of a tracer (Br⁻), CMC-stabilized and non-stabilized Fe-Pd nanoparticles with a loamy sand soil. Iron dose was 1.0 g/L, CMC = 1.0 wt%.
Figure 3 compares the breakthrough curves for the tracer (KBr), non-stabilized and CMC-stabilized Fe-Pd nanoparticles in a loamy sand soil that has a comparable hydraulic conductivity with the site aquifer. The fact that the breakthrough curves for the tracer and stabilized nanoparticles nearly coincided suggests that the soil retention of the nanoparticles was minimal. Subsequently, when DI water was pumped through the soil bed, the nanoparticles were almost completely (confirmed by iron mass balance) washed out in <5 pore volumes of DI water, indicating that no nanoparticles were retained irreversibly. Because of agglomeration, non-stabilized iron particles precipitate rapidly. Based on the data in Figure 3, only ~0.6% of the non-stabilized iron was detected in ~18 pore volumes of the effluent water.

**On Site Nanoparticle Preparation**

The on site scale-up synthesis of CMC-stabilized Fe-Pd nanoparticles was successfully implemented. Figure 4 presents the appearance of the field-prepared stabilized Pd-Fe nanoparticle suspension. The nanoparticle suspension appeared as black and inky liquid. Based on our prior lab tests, the resultant nanoparticles possessed a particle size around 22.8 ± 4.3nm. A simple test carried out in the field showed that the nanoparticle suspension passed through a Fisher filter paper (P5) (particle interception: >1μm) without any retention of solid particles observed. It is well known that Fe nanoparticles could continuously dissolve in water because of corrosion and lose reactivity. The successful preparation of the nanoparticles on site maximally maintained the particle reactivity and therefore their lifetime for dechlorination.

**Iron Transport in the Test Area.**

Soil mobility is a critical characteristic of iron nanoparticles for their proactive destruction of chlorinated solvents in soil and groundwater. In order to monitor the migration of the nanoparticles, total iron concentration was measured at two down-gradient monitoring wells MW-1 and MW-2 throughout the test. Figure 5 shows the injection of the nanoparticle
suspension and the groundwater sample collection from monitoring well MW-1. The dark color of the gathered groundwater sample from MW-1 visually demonstrates the migration of the nanoparticles from the injection well IW-1 to the monitoring well MW-1.

Figure 5. (a) Injection of the nanoparticle suspension and (b) groundwater sample collection from monitoring well MW-1.

Transport properties of the stabilized nanoparticles were then quantified by comparing the elution of injected Fe relative to SO$_4^{2-}$ and tracer Br$^-$ in monitoring wells MW-1 and MW-2, as shown in Figure 6. During the pilot test, Fe migration from injection well IW-1 to up-gradient monitoring well MW-3 was not visually observed. Therefore, the Fe concentration change in MW-3 was not followed. Following the injection, the gravity-fed Fe suspension was significantly diluted by the groundwater, as indicated by only ~ 27% of the injected Br$^-$ concentration was observed in monitoring well MW-1. The peak concentration of the total Fe in MW-1, however, was determined to be ~ 15% of the injected concentration, which
suggested that some portion of the Fe particles were retained in the aquifer between IW-1 and MW-1. The comparison between Fe and Br$^-$ elution curves suggested that ~37.4% of the injected Fe transported to MW-1. Therefore, ~62.6% of the injected Fe was left in the soil between IW-1 and MW-1. In comparison, non-stabilized Fe particles would be completely intercepted on the injection well wall, as indicated in Figure 3. It is noteworthy that the breakthrough curves for Br$^-$ and SO$_4^{2-}$ almost coincide, which suggests that the SO$_4^{2-}$ ions from particle preparation can also be used as a tracer in the field study.

Figure 6. The transport of iron nanoparticles from injection well IW-1 to monitoring well MW-1 (a) and MW-2 (b). The inset in (a) shows the Fe migration in 1 day after injection. The background total iron concentrations in MW-1 and MW-2 were less than 1 mg/L and the
background SO$_4^{2-}$ concentrations were less than 5 mg/L.

Much less Br$^-$ and Fe concentrations were observed in MW-2. However, the presence of a peak Fe concentration of ~ 3% (C/C$_0$) still suggests the migration of Fe particles from well MW-1 to MW-2. The comparison between Fe and Br$^-$ elution curves suggested that ~ 24.0 % of the Fe eluted from MW-1 transported to MW-2, which accounted for ~ 9% of the injected Fe.

The filtration of colloids within porous media is generally determined by three major mechanism: 1) Brownian or molecular diffusion by which random motion of colloidal particle is brought about by thermal effects; 2) convective fluid flow wherein particles flow with water; and 3) gravitational effects producing vertical movement of particles. Filtration caused by Brownian motion tends to dominate for small particles (e.g. <0.1 μm) whereas filtration induced by gravity outweighs Brownian diffusion for large particles (e.g. > 1μm). The hydrodynamic diameter of CMC-stabilized Fe nanoparticles was lab-determined to be ~ 22.8 nm with a percentage of 89%. Therefore, Brownian motion should be the primary mechanism of Fe nanoparticle filtration in the soil in this study. The soil-retained nanoparticles in the test area were expected to form a reactive barrier through the aquifer. This barrier is expected to not only degrade the aqueous phase chlorinated hydrocarbon contaminants in groundwater but also proactively attack the contaminants adsorbed in the source zone soil.

Effects of Nanoparticle Injection on Groundwater Chemistry

The ORP of water extracted from monitoring well MW-1 reduced from base line of -40 mv to -254 mv following the injection. The ORP remained low to 2-3 days when negligible amounts of Fe were detected in MW-1, as shown in Figure 7. Calculations suggest that over 71 grams of iron nanoparticles were immobilized in the aquifer between IW-1 and MW-1, which resulted in the strong reducing environment. The decrease of ORP is attributable to the consumption of oxidants by the nanoparticles as they migrated within the aquifer. The reducing of ORP provides a favorable environment for reductive dechlorination.

![figure](image_url)

**Figure 7.** Change of oxidation and reduction potential (ORP) in monitoring well MW-1.
Chlorinated Solvent Transformation during the Field Test

Normalized concentration of chlorinated solvents ($C/C_0$) versus time were plotted to assess the reactivity of the stabilized nanoparticles. As shown in Figure 8, PCE, TCE and PCB 1242 concentrations in MW-1 increased significantly following the injection and then declined rapidly before exhibiting varying degrees of recovery. The increase of the chlorinated solvent concentrations in the beginning stage was also occasionally observed by other research groups on conducting similar field studies (17). They explained this phenomenon as that the injection process remobilized the contaminants from the unsaturated zone. The later sharp decline of chlorinated contaminant concentrations clearly suggests the rapid degradation of the chlorinated hydrocarbon contaminants. However, caution should be taken here that the decrease of contaminant concentration could be caused by the dilution of groundwater with the injecting of Fe suspension. In Figure 8, the curve $1-C_t(\text{Br})/C_0(\text{Br})$ versus time is used to represent the dilution effect of chlorinated solvents due to the injection. Clearly, much more decrease of PCE, TCE and PCB 1242 was obtained compared to the dilution at the first day after injection. After that, dilution did not exist while the chlorinated solvent concentrations remained at a very low level ($C/C_0 < 0.25$) for at least 4 days, indicating the significant chemical reduction of the contaminants. After 5 days, the concentrations of PCE, TCE and PCBs start to bounce back as the decrease of the Fe nanoparticle reactivity. This result is consistent with our lab findings that the reactivity of CMC-stabilized Fe-Pd nanoparticles exponentially decreased with time. For example, the TCE reduction rate with 9-day aged nanoparticles was only 2.8% of that with fresh nanoparticles. The exponential decrease of Fe-Pd nanoparticle reactivity is shown in Figure 9.

![Figure 8](image_url)

**Figure 8.** The concentration evolution of PCE, TCE and PCB 1242 in groundwater from MW-1 following the injection of Fe-Pd nanoparticle suspension.
It is noteworthy from Figure 8 that the concentration of TCE and PCE started to decrease again after their recovery at 12 days after injection. For example, at 29 days after injection, the concentrations of PCE and TCE in MW-1 were 497 ppb and 72 ppb compared to the concentration of 1225 ppb and 1655 ppb before injection. This part of degradation is attributed to the enhanced biodegradation of TCE and PCE. As well recognized, reactive Fe nanoparticles are a good H$_2$ source and H$_2$ is the preferred electron donor for microorganisms that biodegrade chlorinated solvents (18). Moreover, the CMC also provides an ideal nutrient for the growth of bacterial. The surprisingly good degradation of TCE and PCE demonstrated that the Fe left in the aquifer provided a steady-state H$_2$ concentration that is suitable for biodegradation of TCE and PCE in the groundwater. Interestingly, the PCB 1242 concentration remained constant after the recovery. This result conforms to the fact that PCB is extremely persistent to biodegradation.

Figure 10 depicts the concentration evolution of PCE, TCE and PCB 1242 in groundwater from MW-2 following the nanoparticle injection. It is noteworthy that the initial concentrations of PCE, TCE and PCB 1242 MW-2 were higher than that in MW-1, indicating some additional contaminant sources in the soil between MW-1 and MW-2. The concentrations of PCE, TCE and PCB 1242 declined rapidly following injection and later exhibited varying degrees of recovery. The chlorinated contaminants also underwent a second stage degradation after their recovery. The decrease of contaminant concentration in MW-2 can be attributed to: a) the reduced PCE, TCE and PCBs concentrations in the up-gradient monitoring well MW-1; b) further chemical reduction of the contaminants in groundwater flowing through MW-1 to MW-2 and proactive destruction of contaminants in the soil between MW-1 and MW-2; and c) enhanced biodegradation of chlorinated contaminants with H$_2$ generated from Fe corrosion.
Figure 10. The concentration evolution of PCE, TCE and PCB 1242 in groundwater in MW-2 following the nanoparticle treatment.

SUMMERY AND CONCLUSIONS

The successful field experiments of the stabilized Fe-Pd nanoparticle technology for in situ destruction of chlorinated organic contaminants confirmed the great promise of this in situ remediation technology. The stabilized nano-materials can be gravity-fed into contaminant source zones without disturbing the aquifer soil. Because of the superior reaction kinetics, complete remediation of contaminated sites can be achieved in a time scale much shorter than current technologies. Given the urgent needs for cost-effective technologies for destruction of chlorinated organic contaminants in contaminated soils and groundwater, this in situ technology holds very promising application in the future as a cost-competitive soil and groundwater remediation alternative.

LITERATURE CITED


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