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Degradation of carbon tetrachloride in the presence of zero-valent iron

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Efforts to achieve the decomposition of carbon tetrachloride through anaerobic and aerobic bioremediation and chemical transformation have met with limited success because of the conditions required and the formation of hazardous intermediates. Recently, particles of zero-valent iron (ZVI) have been used with limited success for *in situ* remediation of carbon tetrachloride. We studied a modified microparticulate product that combines controlled-release carbon with ZVI for stimulation of *in situ* chemical reduction of persistent organic compounds in groundwater. With this product, a number of physical, chemical, and microbiological processes were combined to create very strongly reducing conditions that stimulate rapid, complete dechlorination of organic solvents. In principle, the organic component of ZVI microparticles is nutrient rich and hydrophilic and has high surface area capable of supporting the growth of bacteria in the groundwater environment. In our experiments, we found that as the bacteria grew, oxygen was consumed, and the redox potential decreased to values reaching −600 mV. The small modified ZVI particles provide substantial reactive surface area that, in these conditions, directly stimulates chemical dechlorination and cleanup of the contaminated area without accumulation of undesirable breakdown products. The objective of this work was to evaluate the effectiveness of ZVI microparticles in reducing carbon tetrachloride under laboratory and field conditions. Changes in concentrations and in chemical and physical parameters were monitored to determine the role of the organic products in the reductive dechlorination reaction. Laboratory and field studies are presented.

Introduction

Carbon tetrachloride was formerly used widely as a fumigant, dry cleaning agent, solvent, and fire extinguisher. However, its primary function was in chlorofluorocarbon production, until it was banned in the 1970s because of its carcinogenic properties and environmental effects.[1] Today, carbon tetrachloride is a common contaminant in groundwater and soils.

The decomposition of carbon tetrachloride through bioremediation in anaerobic[2] and aerobic[3,4] conditions has met with limited success. The difficulties seem to result from the toxicity of carbon tetrachloride to microorganisms, as well as the production of hazardous intermediates such as chloroform[5] and methylene chloride. Recently, the use of micro- and nanoscale particles for *in situ* remediation has been considered as an alternative for the treatment of carbon tetrachloride[6–8] and other chlorinated compounds.[9–11] The theoretical potential benefits of these micro-/nanoscale particles include their abilities to flow with groundwater and to promote rapid degradation of organic contaminants, as well as—in some cases—the immobilization of dissolved metals.

Nanoparticles of zero-valent iron (ZVI) have been considered for *in situ* remediation of carbon tetrachloride.[7] The mechanisms at first glance appear to be very simple, but more detailed observation reveals complex pathways and products in the reductive transformation of carbon tetrachloride. In these studies, depending on the type of iron present and the relative availability of electrons, hydrogen, nucleophiles, and even oxygen, products have ranged from toxic hexachloroethane, tetrachloroethane, trichloromethane, and dichloromethane to relatively innocuous carbon monoxide, carbon dioxide, and methane. In most circumstances, the dominant toxic product of reductive degradation of carbon tetrachloride is chloroform. Yields of chloroform in different iron systems range from 20% to 80%.[6]

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Environmental impact

Carbon tetrachloride is a widespread contaminant in the environment and it was banned in the 1970s because of its carcinogenic properties and environmental effects. In addition, carbon tetrachloride is one of the most persistent volatile organic chemicals in the environment. Due to these properties, characterization and remediation of carbon tetrachloride is very important. We are presenting a new method for decomposition of carbon tetrachloride *in situ* by injection of modified zero-valent iron microparticles into the vadose zone. In this study, a number of physical, chemical and microbiological processes combined to create very strong reducing conditions that stimulate rapid and complete dechlorination to harmless products minimizing risk to human health.

Recent advances in ZVI include a commercially available microparticle product that combines controlled-release carbon with ZVI for stimulation of *in situ* chemical reduction of persistent organic compounds in groundwater. In this product, a number of physical, chemical, and microbiological processes combine to create very strongly reducing conditions that can stimulate rapid and complete dechlorination of organic solvents. In principle, the organic component of ZVI microparticles is nutrient rich and hydrophilic and has high surface area capable of supporting the growth of bacteria in the groundwater environment. As bacteria grow, oxygen is consumed, and the redox potential in the groundwater decreases to values approaching −600 mV. The small ZVI particles provide substantial reactive surface area that, at this potential, directly stimulates chemical dechlorination. In addition, indigenous heterotrophic bacteria can ferment carbon and release a variety of volatile fatty acids that diffuse from the site of fermentation into the groundwater plume and serve as electron donors for the bacteria and media supporting the reaction.

The objective of this work was to evaluate the effectiveness of the modified ZVI microparticles in reducing carbon tetrachloride under laboratory and field conditions. Parameters such as reaction rates were determined to elucidate the possible mechanistic pathways of the reaction. Changes in concentration and chemical and physical parameters were monitored to follow the fate of organic products and the progress of reductive dechlorination. A field study at a site contaminated with carbon tetrachloride is also presented.

Experimental methods

Reagents

A standard solution of carbon tetrachloride (100 mg ml^{-1} in methanol) from Chem Service (West Chester, Pennsylvania, USA) was used to prepare a solution with an initial concentration of 100 μg ml^{-1} of the analyte. These solutions meet or exceed all requirements and guidelines set forth in 40 Code of Federal Regulations Part 136. The stock solutions were stored at 4 °C, and dilutions were prepared daily as needed. All standard solutions and dilutions were made by using ultra-resi-analyzed methanol from J.T. Baker (Phillipsburg, New Jersey, USA). Two different ZVI products were obtained from Adventus Americas, Inc. (Freeport, Illinois, USA), specifically EHC and EHC-M. Both products are patented combinations of controlled-release, complex carbon plus ZVI.

Instrumentation

The analytical equipment used for this investigation consisted of a gas chromatograph (HP-6890; Agilent Technologies, Wilmington, Delaware, USA) with a mass spectrometer (HP-5892, Agilent). Heated lines were used to interface an HP-2016 autosampler (Agilent) to the gas chromatograph.

Batch studies

Laboratory studies were conducted through batch testing. All batch analyses were done in the same manner throughout the analysis. A series of 20-ml containers were filled with water, ZVI (EHC or EHC-M) material, and an aliquot of carbon tetrachloride. Deionized water (nanopure-diamond; Barnestead International, Dubuque, Iowa, USA) was used except where specified otherwise. For liquid samples, the ratio of liquid : ZVI material was maintained at 100 : 1 by volume using 10.0 ml of solution and adding 0.1 g of ZVI material to each one. For soil samples, the ratio of soil : ZVI material was 5 : 1 using 10.0 ml of DI water, 0.5 g of soils and 0.1 g of ZVI to each vial. Samples were placed in 20-ml sealed containers directly into the autosampler, and each sample was measured at times from 0 h to a maximum of 220 h. One sample was used in each experiment as a reference standard to quantify losses in each experimental set. The reference standard changed with time, decreasing from the initial 100% recovery to values averaging 92% of the original amount in the sample at the maximum time of 220 h. Concentrations changes were within the instrumental error. Decreases in sample concentrations due to the effect of the ZVI were easily quantified.

Samples

Soil samples came from a site in Kansas, USA, contaminated with carbon tetrachloride. Soil samples were collected from a well boring core at the location where the major contamination had been found, at a depth of 51 ft below ground level (BGL). The core sample was dried and homogenized prior to use by passage through a 16-mesh (0.0394-in.) sieve. Uncontaminated water from the site was collected for use in the experiments.

Field study

At the site in Kansas (Fig. 1 and 2), modified ZVI as EHC material was injected into the subsurface in well-characterized areas with high concentrations of carbon tetrachloride. Site characterization had previously identified three areas with carbon tetrachloride concentrations as high as >1200 μg L^{-1} in groundwater (at MW02 in 2006) and 219 μg kg^{-1} in soil (at boring SB12 in April 2003). MW02 was an injection point while PMP8 was a monitoring point. The area of highest concentrations around MW02 was selected for the pilot study. Samples were collected in the field in 20-ml vials after the injection to monitor the concentration of carbon tetrachloride and other physical and chemical parameters. Samples were preserved at 4 °C until analysis. All analyses were done according to standard methodologies.[12,13]

Results and discussion

In previous studies using zero-valent iron to decompose carbon tetrachloride contamination in the ground, the end product of dechlorination was chloroform.[6] Bioremediation has been used as an alternative route for decomposition of carbon tetrachloride, but its mechanisms are complex, and the pathways are difficult to follow. For example, previous studies using bacteria in an iron-nitrate environment had some positive results in the laboratory, but the conditions were difficult to reproduce in the field.[9] The application of ZVI would have a greater chance of success if the particles injected could be modified to set up an environment capable of completely reducing carbon tetrachloride to harmless products.

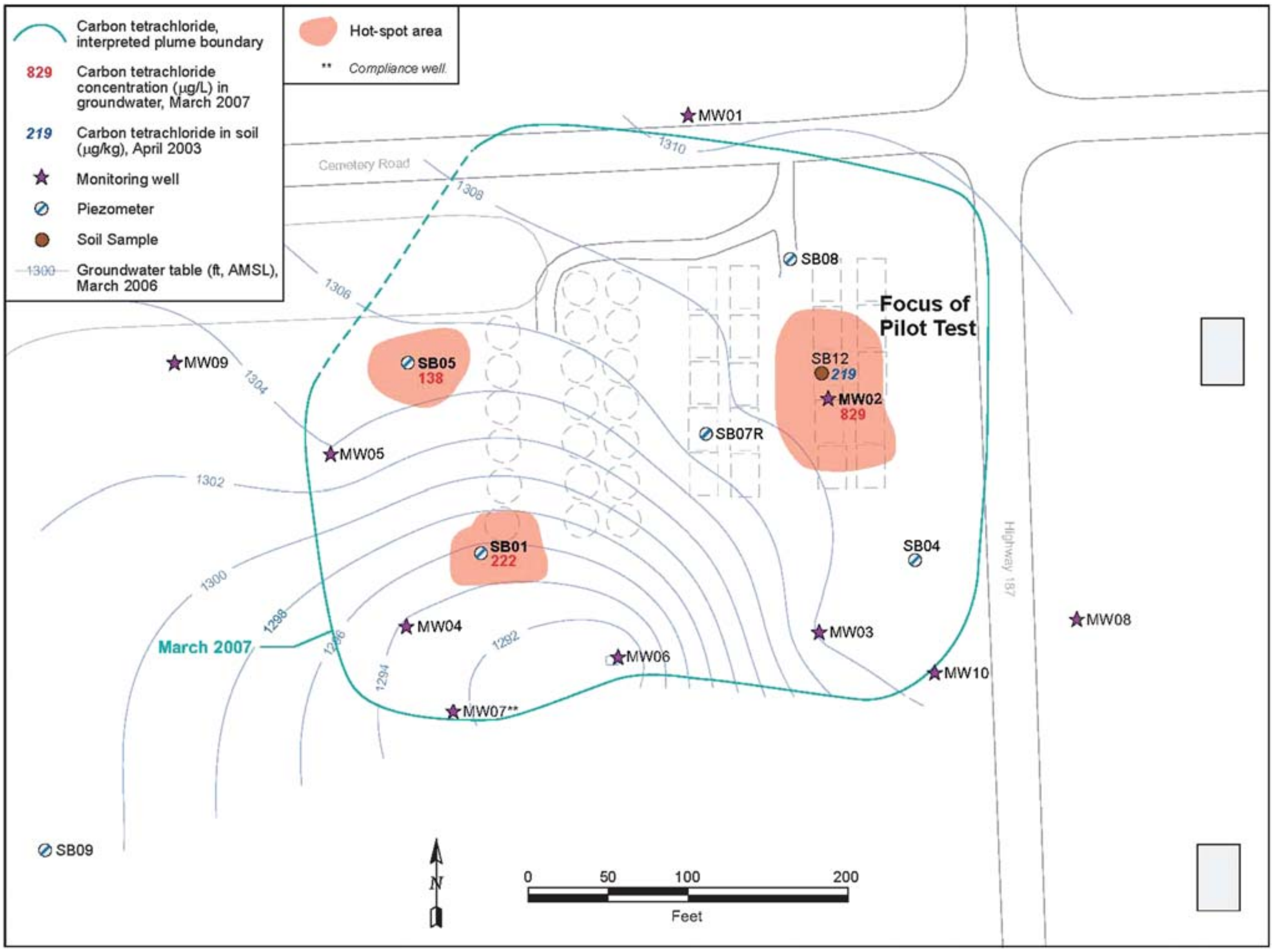

Fig. 1 Concentrations of carbon tetrachloride in water and soil, interpreted groundwater elevations, and interpreted lateral boundary of the contaminant in groundwater at the study site in Kansas.

Initial testing in our laboratory showed reduction of carbon tetrachloride by the commercial ZVI material. Rates of reaction depended on the experimental conditions. Fig. 3 shows evidence of dechlorination and formation of chloroform (typically accounting for 10—20% of the initial amount of carbon tetrachloride). The rest of the carbon tetrachloride went into different pathways, with possible formation of relatively harmless products such as formic acid and carbon monoxide. When carbon tetrachloride had disappeared almost completely from the solution, the small amount of chloroform remaining decomposed to form dichloromethane, as indicated in Fig. 3.

Effects of pH on the reduction of carbon tetrachloride by ZVI

Iron characteristically remains in lower valance states at lower pH values. At neutral pH values, iron is easily oxidized to form iron oxide. We evaluated the effect of pH on the decomposition of carbon tetrachloride by ZVI at four pH levels (Table 1).

In hydrochloric acid solution ($pH = 1.1$), almost 80% of the carbon tetrachloride introduced was decomposed, and minor production of chloroform was observed (Fig. 3)—not in the expected 1 : 1 ratio $CCl_4 : CHCl_3$. After 90 h, formation of small amounts (less than 1 $\mu g\ L^{-1}$) of dichloromethane was observed. Calculation of the average rate of reaction for each pH condition yielded the reaction half-lives shown in Table 1. The results indicate that the half-life of the reaction for decomposition of carbon tetrachloride increases with increasing pH. Thus, pH plays an important role in degradation of carbon tetrachloride by the modified ZVI. In the field, the pH is almost neutral (7.2), and hence a longer time will be required to decompose carbon tetrachloride.

Decomposition of carbon tetrachloride by ZVI in the presence of soil and water from a contaminated site

Soil samples for this study were selected from the core for monitoring well MW02 at the contaminated site (Fig. 1), at the center of the contaminant plume and at 51 ft BGL. In addition, water from the same aquifer system was used in laboratory mixtures to mimic conditions in the field. One laboratory reaction mixture contained soil from the contaminated area and ZVI material in a 5 : 1 ratio, with sufficient deionized water ($pH = 5.2$) to achieve a liquid : solid ratio of approximately 100 : 1 (by volume) as described in the experimental area. This reaction started slowly, with only small changes in the concentration of carbon tetrachloride over time. The reaction half-life was 73 h

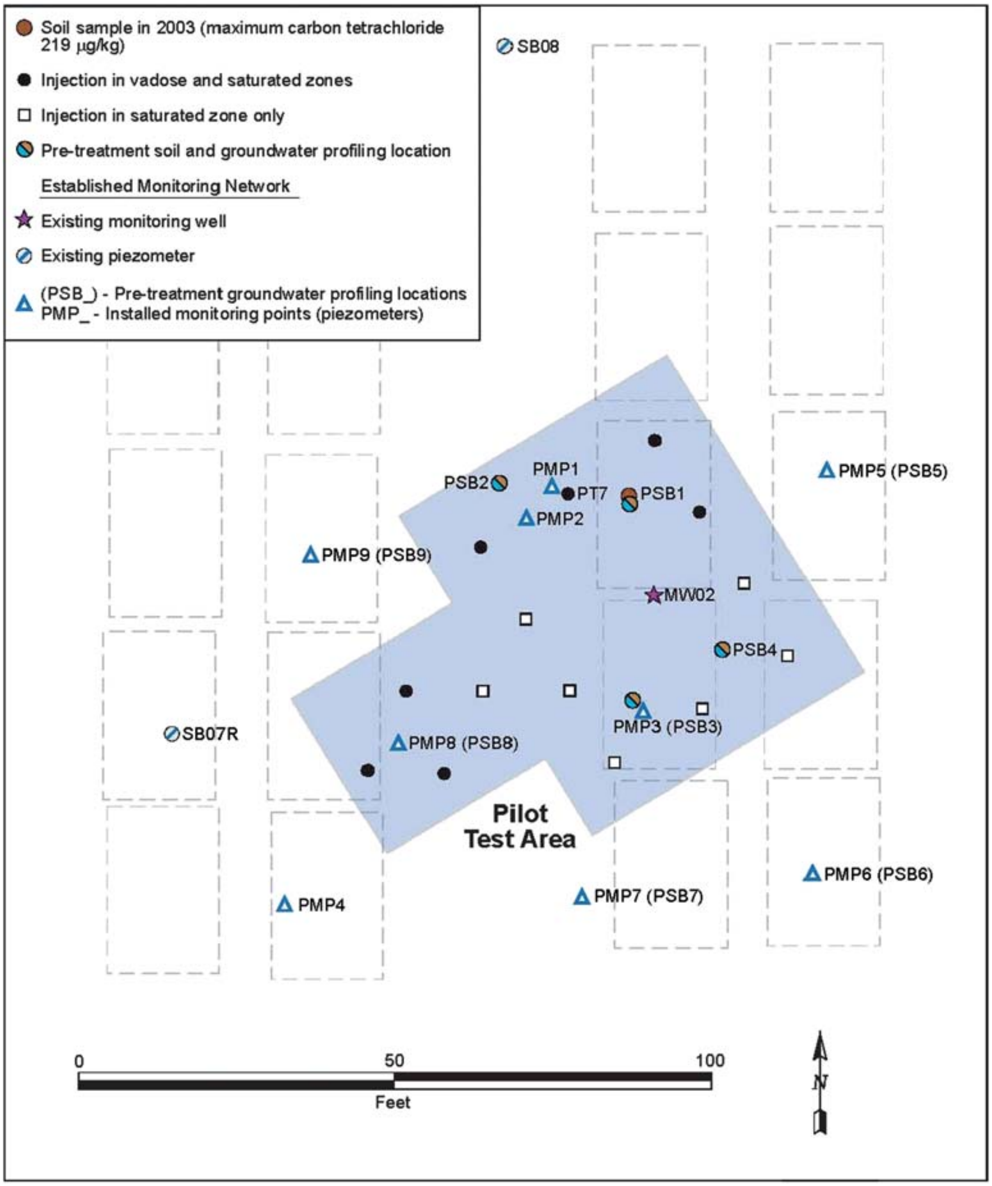

Fig. 2 Injection points in the saturated and vadose zones and monitoring network in the pilot test area at the study site in Kansas.

(Table 1). A subsequent experiment (Fig. 4) combined ZVI and carbon tetrachloride with soil and water (pH = 7.2) from the contaminated area. At neutral pH, the reaction rate was even slower than with deionized water, with a half-life of 145 h (Table 1). The results suggest that at the beginning, some of the free iron reacted to produce chloroform, but at longer times the decomposition was driven mainly by bacteria in the soil and water. The bacteria would use the organic material surrounding the ZVI microparticles as a food source, creating better

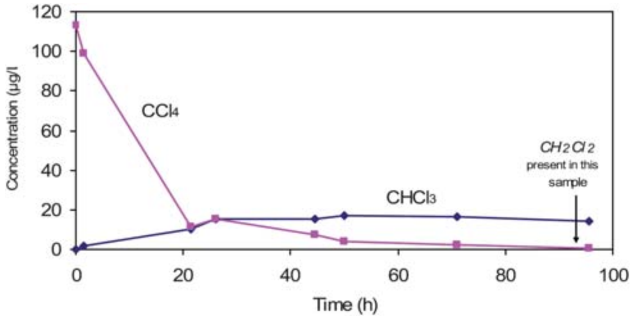

Fig. 3 Decomposition of carbon tetrachloride and formation of chloroform by ZVI in a laboratory reaction mixture with hydrochloric acid solution, pH = 1.1.

Table 1 Carbon tetrachloride degradation half-life and pH in laboratory batch tests

pH	Half-life/h	Description[a]
1.1	6	Hydrochloric acid
3.1	12	Acetic acid buffer
5.2	73	Soil + deionized water
7.2	77–145	Soil + groundwater

[a] Soil was from the contaminated aquifer zone; groundwater was from a nearby drinking water well.

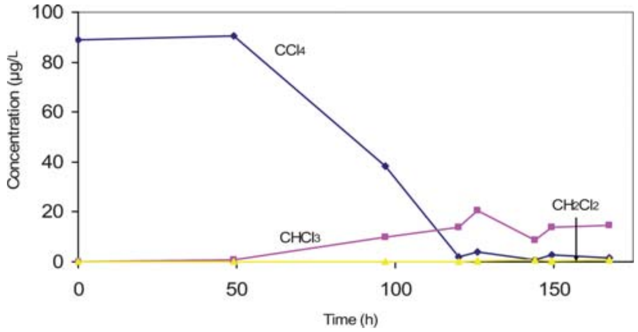

Fig. 4 Decomposition of carbon tetrachloride and formation of chloroform by ZVI in a laboratory reaction mixture containing soil and water from the contaminated site, pH = 7.2.

conditions for the reaction of iron with carbon tetrachloride. Almost 90% of the original carbon tetrachloride was decomposed in 140—160 h. Our hypothesis is that bacteria in the soil and water added to this reaction mixture used the organic material coating the iron microparticles to (a) decrease the oxygen levels; (b) decrease the oxidation-reduction potential (ORP), setting up a reducing environment; (c) release a variety of volatile fatty acids that could be used as electron donors; and (d) decrease the pH of the solution.

To understand the mechanism of degradation of carbon tetrachloride by ZVI microparticles, we studied changes in the pH and ORP of a laboratory reaction mixture containing ZVI, carbon tetrachloride, and soil and water from the contaminated site. In this system we observed changes in pH from 7.2 to 6.9, not significant enough to explain the changes in the reaction rate and the rapid decomposition of carbon tetrachloride observed when soil and water from the contaminated area were present (Fig. 4). In the laboratory, ORP seemed to increase and decrease randomly as the reaction progressed. Similar behavior was reported by Adventus (E. Dimitrovic, unpublished data). In contrast to our laboratory results, monitoring data for the pilot test at the Kansas site showed a significant decrease in ORP, to values as low as −548 mV, with the expected decrease in pH values for samples at MW02. No significant changes were observed at PMP8 where no injection of material was made.

To determine whether active bacterial metabolism was supporting the decomposition of carbon tetrachloride by modified ZVI in the last reaction mixture described above, we added sterilized soil and water from the contaminated site to an experimental batch with carbon tetrachloride and the commercial ZVI material. If bacteria in the native soil and water samples dramatically affected the decomposition of carbon tetrachloride by ZVI, then sterilization of soil and water should slow or even prevent decomposition. Soil samples were sterilized by heating in an oven to 80 °C on four consecutive days. Water samples were sterilized by boiling for 1 h at 100 °C. The commercial ZVI material is not sterile and was used with no treatment. Heating the ZVI coated with organic material can cause decomposition of the material and oxidize the iron, therefore reducing the effectiveness of the product.

The results for the reaction mixture with sterilized soil and water were similar to those shown in Fig. 4 for unsterilized media. These results do not rule out a role for bacteria in the decomposition of carbon tetrachloride; however, the results demonstrate that the decomposition is not dependent on the present of live bacteria in groundwater and soil from the contaminated site. The results demonstrate significant complexity in the reaction system.

Field activities – pilot project

The main purpose of this investigation was to evaluate the effectiveness of the modified ZVI microparticles in decreasing the potential future concentration of carbon tetrachloride in the groundwater in the contaminated area. The site selected for the investigation was the well-characterized area shown in Fig. 1. The pilot test was designed to address one of three hot-spot areas at the site, specifically the one centered on MW02 and the soil boring SB03. These are the locations of the highest concentrations of carbon tetrachloride identified in soil and groundwater at the investigation site. A three-dimensional grid pattern of direct-push injection points was used to distribute the modified ZVI material (in slurry or aqueous form) throughout the volume of the contaminated aquifer in this area, as well as in the vadose zone. The injection locations are shown in Fig. 2.

One important factor in this study is that the modified ZVI products tested can decompose carbon tetrachloride to compounds other than chloroform (which is the undesirable result typically observed in other studies). The ZVI products release an organic material to change the reaction conditions, and the ZVI acts as a chemical reducing agent. This product initiates a number of physical, chemical, and microbiological processes that combine to create very strongly reducing conditions *in situ* and stimulate rapid and complete dechlorination of carbon tetrachloride. These processes include (a) biological reduction (consumption of oxygen and other electron acceptors); (b) chemical reduction of the oxidized pollutants, either directly *via* the reduced metal or indirectly *via* the formation of hydrogen used by the bacteria as an electron donor; and (c) direct chemical oxidation due to the ZVI oxidation-reduction reactions, *via* beta-elimination reactions and additional oxygen scavenging processes that decrease the ORP of the system.

After injection of the ZVI material into the subsurface, concentrations of carbon tetrachloride were monitored for 16 months. Results are in Fig. 5 and 6. As Fig. 5 shows, at MW02 the concentration of carbon tetrachloride decreased almost

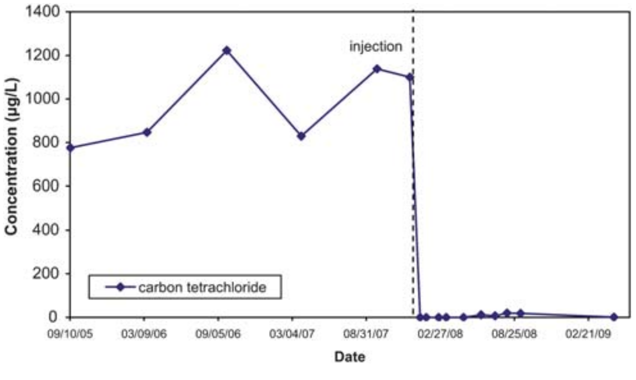

Fig. 5 Concentrations of carbon tetrachloride observed at MW02, in the highly contaminated area, after injection with the modified ZVI product.

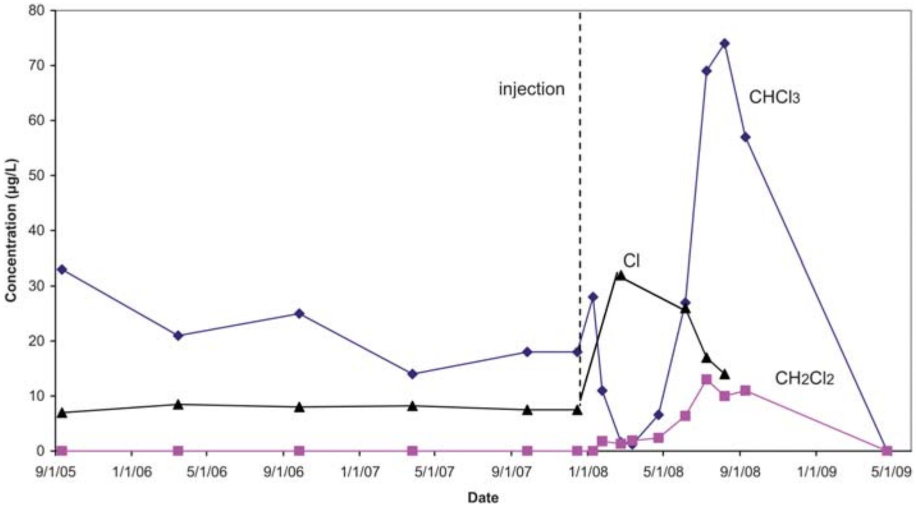

Fig. 6 Concentrations of chloroform ($CHCl_3$), dichloromethane (CH_2Cl_2), and chloride (Cl^-) observed at MW02, in the highly contaminated area, after injection with the modified ZVI product.

immediately from 1130 µg L^{-1} to "not detected" (ND). At PMP8, a monitoring well with no direct injection of the material, concentrations were reduced initially by more than 98% (Table 2). Concentrations increased in the next months, to high values of 20 µg L^{-1} at MW02 and 287 µg L^{-1} at PMP8, and then decreased again. Concentrations were ND (MW02) and 3.2 µg L^{-1} (PMP8) in the last analysis performed during the 16-month period shown. Both values were below maximum concentration limits (MCL's).

Other compounds such as chloroform, dichloromethane, and chloride showed initial increases in concentrations (as expected) and then decreases (Table 2 and Fig. 6). In addition, site conditions changed: decreased ORP, pH, and dissolved oxygen (DO) and increased iron(II) and chloride concentrations. Decreases in the concentrations of nitrate (at MW02) and DO (at both MW02 and PMP8; Table 2) suggest an increased bacteria population and an enhanced effect of the ZVI microparticles, as expected for the system. Increases in iron(II) and chloride concentrations were

Table 2 Analytical results for volatile organic compounds in groundwater samples collected during pilot testing, with field parameters recorded during sampling.[a,b]

	Concentration/µg L^{-1}					Concentration/mg L^{-1}		
Date	CCl_4	$CHCl_3$	CH_2Cl_2	ORP/mV	pH	DO	NO_3^-	Cl^-
Samples collected at MW02 (Fig. 1 and 2)								
09/26/07	1138	18	ND	156	7.0	3.4	7.5	8.0
01/09/08	0.3	28	ND	−218	5.8	0.17	—[c]	—
01/24/08	ND	11	1.8	89	5.8	0.96	—	—
02/23/08	ND	1.6	1.3	45	5.6	2.4	ND	32
03/12/08	ND	1.2	1.9	−42	5.6	0.28	—	—
04/23/08	ND	6.6	2.4	−54	5.7	0.11	—	—
06/05/08	12	27	6.4	−119	6.0	0.09	ND	26
07/09/08	6.8	69	13	−49	6.1	1.6	ND	17
08/07/08	20	74	10	−75	5.9	0.3	ND	14
09/09/08	18	57	11	−74	6.1	0.4	—	—
04/24/09	0.7	ND	ND	−131	6.7	0.6	—	—
10/08/09	ND	ND	ND	−138	6.9	0.4	—	—
Samples collected at PMP8 (Fig. 2)								
11/15/07	2646	103	2.5	—	6.95	4.3	4.1	36
01/09/08	30	606	3.4	−548	6.8	0.08	—	—
01/24/08	31	430	28	−208	7.2	1.01	—	—
02/23/08	287	374	25	−122	7.0	0.3	1.9	28
03/12/08	122	292	20	—	—	—	—	—
04/23/08	62	415	29	−186	6.9	0.18	—	—
06/05/08	77	355	24	−190	7.4	0.06	—	—
07/09/08	67	339	23	−135	6.9	0.08	—	—
08/07/08	105	317	17	−158	7.6	1.3	8.7	0.3
09/09/08	72	125	3.4	−129	7.1	0.03	—	—
04/24/09	3.2	5.6	1.9	−139	7.0	0.8	—	—

[a] Abbreviations: CCl_4, carbon tetrachloride; $CHCl_3$, chloroform; CH_2Cl_2, dichloromethane; ORP, oxidation-reduction potential; DO, dissolved oxygen; NO_3^-, nitrate; Cl^-, chloride. [b] ND, not detected at an instrument detection limit of 0.1 µg L^{-1}. [c] Not analyzed.

expected, according to the mechanism described by Matheson and Tratnyek.[14]

The conditions established by the combined physical, chemical, and biological processes in the ZVI system created a very strongly reducing environment that stimulated rapid, complete dechlorination of carbon tetrachloride. The conditions (physical, chemical and biological processes) combined to create very strong reducing conditions that should generally stimulate rapid and complete dechlorination of organic solvents. At this point, the bacterial growth set up optimal chemical conditions in which the large reactive surface area of the ZVI microparticles stimulated chemical dechlorination, as shown in Fig. 5 and 6 and summarized in Table 2.

Conclusion

Modified ZVI microparticles showed significant potential for the *in situ* decomposition of carbon tetrachloride in prepared samples and a field test. In use, the ZVI coated with an organic layer combined a number of physical, chemical, and microbiological processes to create very strongly reducing conditions that stimulated rapid and complete dechlorination of carbon tetrachloride.

Preliminary results for batch experiments using soil and water from the contaminated site showed that carbon tetrachloride was decomposed by the modified ZVI products in the presence of the environmental materials. The reaction began slowly, but it accelerated as the appropriate conditions were established by the combination of factors mentioned previously. Concentrations of carbon tetrachloride in our laboratory studies decreased by more than 90%.

The modified ZVI technology offers the possibility of *in situ* remediation of carbon tetrachloride at contaminated sites. Our pilot test showed great reduction in the carbon tetrachloride concentrations after *in situ* injection of the material at one of the highly contaminated areas (MW02). Concentrations were below the regulatory level of 5.0 $\mu g\ L^{-1}$ after 16 months of observation. However, practical problems experienced in injection of the ZVI material into the subsurface might be a limitation to wide application of this technology.

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