

A field evaluation of enhanced reductive dechlorination of chlorinated solvents in groundwater, New York Metropolitan Area

Eric Rodriguez · Kevin A. McGuinness · Duke U. Ophori

Abstract An initial assessment of an old manufacturing site with groundwater impacted by trichloroethene (TCE) contamination in the metropolitan New York area showed that the TCE was being removed naturally by reductive dechlorination. However, complete dechlorination was not expected at the site because the process was progressing too slowly under transitional to aerobic conditions at a degradation constant of -0.0013 and a TCE half life of 533 days. A pilot test was conducted at the site in which a carbohydrate substrate (molasses) was injected into the groundwater to create an In-Situ Reactive Zone (IRZ). Post-pilot test groundwater sampling and analysis indicated that an IRZ was created successfully as the total organic carbon (TOC) content and conductivity increased significantly while oxidation-reduction (REDOX) potential and dissolved oxygen (DO) decreased. The created IRZ caused enhanced reductive dechlorination of TCE at the site, found to proceed with a degradation constant of -0.0158 and a TCE half life of 44 days.

Keywords Field · Experiment · Enhanced Reductive Dechlorination · Groundwater

Introduction

Various waste sources have discharged organic chemicals into groundwater in many regions of the United States that require remediation. The process of natural attenuation, which depends on naturally occurring biodegradation of contaminants at field sites (Wiedemeier and others 1996, 1999), is frequently relied upon to restrict the spread of organic pollutants in groundwater. In fact, natural attenuation is the leading remedy for contamination from underground storage tanks (MacDonald 2000), and is in use as a remedial strategy at 25% of Superfund Sites (Delvin and others 2002).

In the case of groundwater contaminated by chlorinated aliphatics, remediation by microbial reductive dechlorination is a well-documented process that occurs given the appropriate groundwater environment (Bouwer and McCarty 1983; Vogel and McCarty 1985; Freedman and Gosset 1989; DiStefano and others 1991, 1992; de Bruin and others 1992; Wiedemeier and others 1996; Ballapragada and others 1997; Fennel and others 1997; Carr and Hughes 1998; Carr and others 2000; Morse and others 1998; Azadpour-Keeley and others 2001). Perchloroethene (PCE) and trichloroethene (TCE) are the most frequently detected organic contaminants in groundwater (US EPA 1993). The first microbiologically mediated reductive dechlorination of PCE and TCE was observed in the early 1980s, and the first evidence of complete dechlorination of PCE to ethene under methanogenic conditions was reported in 1989 (Sutherson 2002). According to Sutherson (2002), the first level of the treatment hierarchy for chlorinated ethenes is intrinsic bioremediation, or natural biodegradation, whereby indigenous microflora destroy the contaminants of concern naturally without any form of stimulation or enhancement. Support for this statement is also evident in the studies by Fathepure and others (1987), Holliger and others (1993), Holliger and Schumacher (1994), Sharma and McCarty (1996), Krumholz and others (1996), Gerritse and others (1996), and Maymó-Gatell and others (1997). However, Wiedemeier and others (1996) state that natural groundwater conditions are not always favorable for complete reductive dechlorination; therefore, natural attenuation is not always the appropriate method for complete remediation of chlorinated aliphatics in groundwater.

Where a strongly reducing natural groundwater environment is not present, Sutherson (2002) contends that

Received: 21 July 2003 / Accepted: 23 September 2003
Published online: 6 December 2003
© Springer-Verlag 2003

E. Rodriguez · K.A. McGuinness
ARCADIS G&M, 1200 MacArthur Boulevard,
Mahwah, New Jersey, USA

D.U. Ophori (✉)
Department of Earth and Environmental Studies,
Montclair State University, Upper Montclair, NJ 07043, USA
E-mail: Ophorid@mail.montclair.edu
Tel.: +1-973-6557558
Fax: +1-973-6554072

complete and effective reductive dechlorination of chlorinated volatile organic compounds (CVOCs) can still be accomplished. This is done by artificially driving an aquifer to a strongly reduced state that is maintained throughout the remedial process. The injection of a reagent solution (electron donor) to serve as a carbohydrate substrate can enhance microbial activity (biostimulation) by providing a carbon source (Smatlak and others 1996; Ballapragada and others 1997; Carr and Hughes 1998; Carr and others 2000; Sutherson 2002). Electron donors are compounds capable of donating electrons during REDOX reactions, and microorganisms obtain energy by transferring these electrons from donors to electron acceptors (Wiedemeier and others 1996). Biostimulation causes indigenous heterotrophic microorganisms to readily degrade the carbohydrates introduced into the groundwater. The metabolic degradation process utilizes available dissolved oxygen and other alternative electron acceptors in the groundwater, and as a result drives the system to a more anaerobic and reduced state. Under this condition, the bacterial population adjusts, and facultative species begin to use alternative electron acceptors in the absence of oxygen (Sutherson 2002). Populations of obligately anaerobic species dominate, and a bacterial community capable of fermenting carbohydrate sugars develops. Hydrolysis and fermentation of carbohydrates ultimately result in the production of acetate and hydrogen, which serves as the most desirable sources of energy for bacteria using sulfate and carbon dioxide (CO₂) as electron acceptors. Methanogens use CO₂ as an electron acceptor, and are among the most noted metabolic groups of obligately anaerobic bacteria responsible ultimately for the resulting enhanced reductive dechlorination (ERD) (Wiedemeier and others 1996; Sutherson 2002). In this study, a site impacted with CVOCs was evaluated to determine if natural attenuation was occurring. A pilot test was then conducted, in which a carbohydrate solution was injected into groundwater wells at the site, in an attempt to create strongly anaerobic and reducing conditions that might enhance reductive dechlorination. Finally, a post-test evaluation of the site was performed to ascertain: (1) if a strongly anaerobic and reducing zone was created successfully, (2) if reductive dechlorination was enhanced, and (3) if so, to estimate the rate of enhancement.

Site description

The site occupies approximately 0.73 ha of land (Fig. 1), in the metropolitan New York area. A review of topographic maps indicates that the site slopes gently southward with high bedrock ridges to the east and west. The two ridges trend in the north-south direction. The average ground surface elevation at the site is 30.48 m above sea level. Locally, the site is underlain by fill material consisting of sand, silt, gravel, bricks, marble fragments, and boulders (Fig. 2). Prior to the development of the site, the area historically operated as a marble quarry. Following

Fig. 1

Site plan, groundwater wells, potentiometric surface map, and distribution of trichloroethene at the site

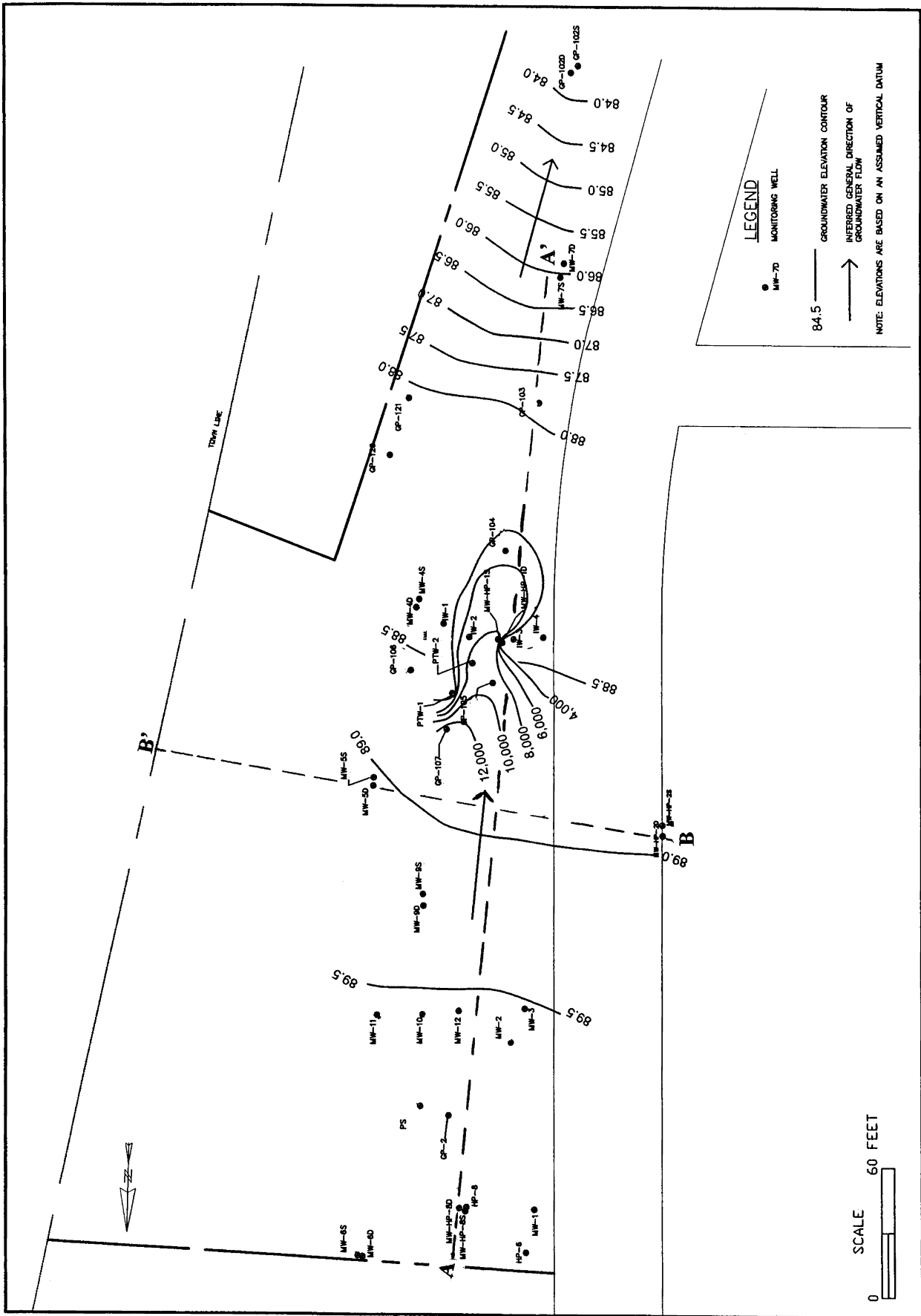
cessation of quarry operations, the area was backfilled to the existing elevation, using non-native fill material. The thickness of the fill material varies from 0 to 3.7 m. An unconsolidated, predominantly fining downward, sand unit underlies the fill material. The bedrock is encountered generally between 1.5 and 16.5 m beneath the site. Regionally, the bedrock is composed of the Manhattan Formation Schist, Inwood Marble, and Fordham Gneiss (Hall 1968).

Manufacturing operations at the site were initiated in 1951 and ceased in 1998. Operations consisted of electroplating and the use of degreasers, which are believed to be the source of a CVOC plume, mainly TCE, at the site. The site plan illustrating monitoring wells is included on Fig. 1. An initial review of available site-specific data showed that high concentrations of TCE (up to 13,000 ppb) were present in the upper 3 m of the aquifer (see Fig. 1). Dissolved oxygen ranged from 0.47 to 7 mg/L, indicating aerobic to slightly anaerobic groundwater conditions at the site. That *cis*-1,2-DCE (up to 1,700 µg/L) occurred, a daughter product of TCE which was not a source contaminant at the site, indicated that reductive dechlorination was already occurring. However, because of the aerobic to slightly anaerobic conditions, complete dechlorination was not expected to occur naturally.

Pre-pilot test evaluation

General

The focus of this study was to create conditions that would enhance or drive reductive dechlorination to completion at the site. Prior to creating such anaerobic conditions, it was necessary to assess the existing natural background conditions of groundwater at the site. The conditions would assist in the creation and implementation of an in-situ reactive zone (IRZ), defined as an area in a groundwater system where strongly reducing and anaerobic conditions have been created for the purpose of reducing chlorinated compounds in groundwater. These data would also serve as the background with which post-test results could be compared. The background evaluation was performed to identify key electron acceptors and donors available, and to establish existing oxidation-reduction potential (REDOX) conditions. These data were obtained by collecting and analyzing groundwater samples from wells, and by collecting wellhead field parameters during low-flow well purging (USEPA 1998). In addition to the background evaluation, a site hydrogeological assessment was also conducted to determine site lithology, lithologic permeability/hydraulic conductivity, effective porosity, groundwater flow gradients, directions and velocities, and CVOC plume distribution.



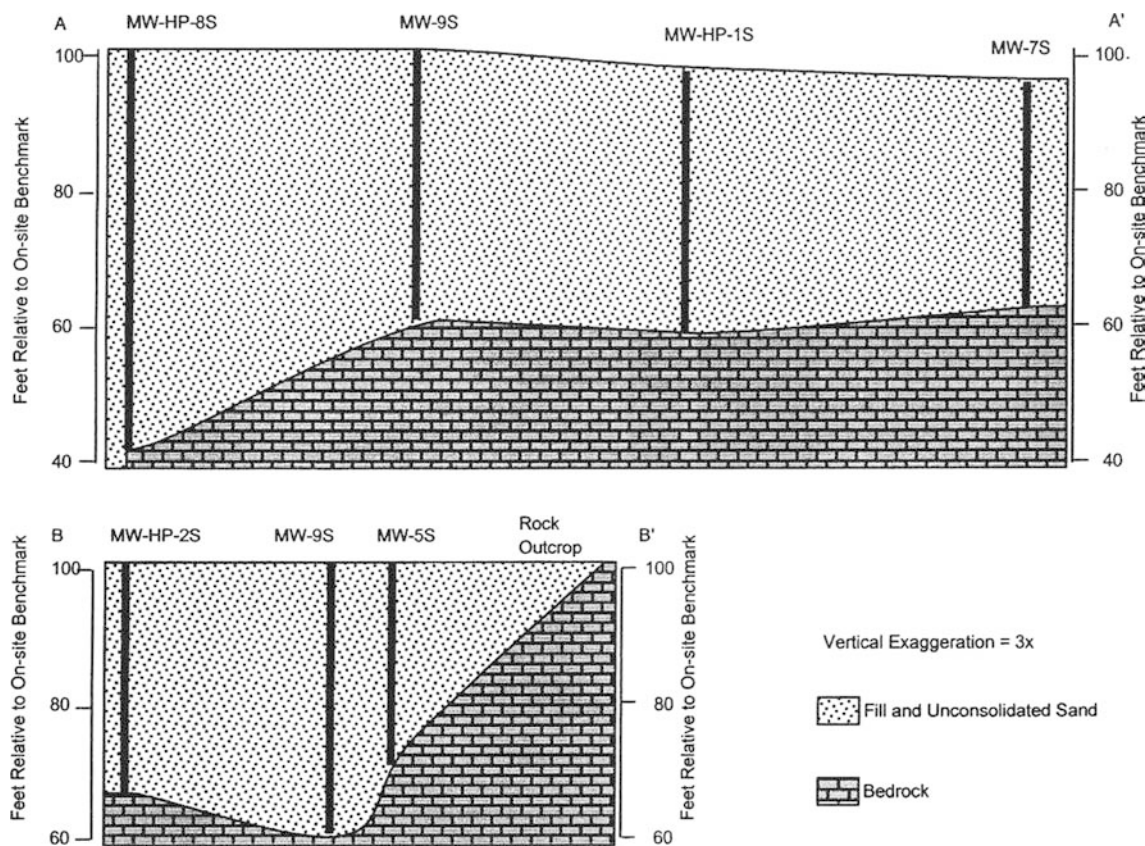


Fig. 2

Stratigraphic cross-section A-A' and B-B' through study area (see trace of sections in Fig. 1)

Groundwater flow

Groundwater levels in wells were measured to characterize the groundwater flow field. Results of these measurements indicate that groundwater flows to the south and southwest at the site (see Fig. 1). Available data were used to estimate horizontal hydraulic conductivity values that vary from 1.8 to 2.1 m/day in the unconsolidated unit. Based on lithology, effective porosity was estimated to be 0.2, with which horizontal seepage velocities were then calculated as (Driscoll 1986):

$$V_x = Ki/n \quad (1)$$

where V_x =seepage velocity (m/day), K =hydraulic conductivity (m/day), i =hydraulic gradient (m/m), and n = effective porosity (dimensionless).

Horizontal seepage velocities were estimated to range from 0.06 m/day in the north to 0.15 m/day in the south in the unconsolidated sediments. Using these seepage velocities, travel times were determined for selected wells in relation

to their distances from well GP-107 through which the substrate would be injected. The equation that was used in calculating travel time is (Driscoll 1986):

$$T = L/V_x \quad (2)$$

where T =travel time between point x and the injection well (days), and L =distance between point x and the injection well (m).

The calculated travel times between well GP-107 and three other wells are shown in Table 1. These travel times were to be used in tracking the anticipated movement of the IRZ to be created.

Groundwater quality

Groundwater sampling was performed using the low-flow methodology (USEPA 1998). Wells were purged using a Grundfos Rediflow 2 submersible pump at a purge rate between 0.2 and 0.5 L/min. Trichloroethene (TCE) was found to be the diagnostic constituent of concern at the site. The highest concentrations of total CVOCs in groundwater were detected in the upper unconsolidated unit between the depth range of 3 to 6 m. Concentrations of TCE ranged from not detected to 28,000 ppb.

Table 1
Travel Times from injection point gp-107 to selected wells

Well ID	Estimated travel time (months)	Encompassment of IRZ (months)
PTW-1	1.2–1.4	1.5
PTW-2	3.6–4.2	5
MW-HP-1S	8.4–9.8	10
GP-104	15.3–17.8	ND

ND, Not determined

Biogeochemical parameters

Field parameters were collected during low flow purging using a flow-through-cell. A YSI 600XL water meter was used to measure water-quality field parameters such as DO, REDOX, temperature, specific conductance, and pH. Samples were submitted to a certified laboratory for analysis, except for ferrous iron and sulfide that were analyzed directly in the field using a HACH spectrophotometer.

The field parameters and biogeochemical analysis were used to determine the DO and REDOX conditions of the site, and to evaluate the presence of electron acceptors and donors. Dissolved oxygen is the most thermodynamically favored acceptor used by microbes for the biodegradation of organic carbon. After depletion of DO, microbes will preferentially use nitrate as an electron acceptor, followed by iron (III), sulfate (sulfanogenesis), and carbon dioxide (methanogenesis) in that order (Wiedemeier and others 1996). Reductive dechlorination is most effective in the sulfanogenesis and methanogenesis stages, thus a preferential depletion of DO, nitrate, and iron (III) usually allows efficient reductive pathways.

During the pre-test assessment, one up-gradient well (MW-HP-8S), three side-gradient wells (GP-106, MW-2, MW-4S), seven mid-plume wells (GP-107, PTW-1, GP-105, MW-HP-1S, MW-HP-1D, GP-104), and three distal-plume wells (GP-103, MW-7S, GP-102S) (see Fig. 1), were sampled. These wells were selected because they provide adequate coverage to characterize the groundwater environment and chemistry throughout the site as recommended by Wiedemeier and others (1995).

A summary of relevant field and analytical data from this assessment (Table 2) shows DO and REDOX values which indicate aerobic and oxidizing groundwater conditions in the up-gradient well, transitional to aerobic conditions in the side-gradient and mid-plume wells, and anaerobic to aerobic conditions in the distal-plume wells. Sufficient concentrations of electron acceptors such as nitrate, manganese, Fe(III), sulfate and carbon dioxide are available for microbial respiration, once oxygen is depleted, to support reductive pathways. However, these acceptors may undergo competitive exclusion with respect to reductive pathways (Wiedemeier and others 1996). Thus, it is important to monitor depletion of the acceptors and the increase of associated byproducts to assess the level of reductive dechlorination that may occur, especially at the sulfanogenesis and methanogenesis stages.

Table 2

Field and analytical biogeochemical data

Location	Electron acceptors								
	DO (mg/L)	REDOX (mV)	NO ₃ (mg/L)	Mn(IV) (ug/L)	Fe(III) (ug/L)	S ₀₄ (mg/L)	C ₀₂ (mg/L)	TCE (ug/L)	TOC (mg/L)
Upgradient	7	137.6	6.43	20.2	200	61.2	24.98	28.2	10.7
Sidegradient	0.86–6.61	137.6–184	3.1–5.06	5.2–502	21.6–117.0	43.9–44.7	28.96–30.62	4.6–100	3.39–19.4
Mid-plume	0.54–5.91	56.0–182	2.45–6.99	2.3–90.1	0–3,440	57.6–127	16.76–51.27	150.0–13,000	2.47–8.88
Distal plume	0.47–2.29	–196.4	1.59–4.47	122–1,680	0–13,700	39.2–52.8	40.5–102.87	330.0–1,390	3.5–4.92

Historical degradation rates

Historical concentration data on TCE were reviewed to determine the natural rate of degradation at the site prior to initiating the pilot test. Concentrations of TCE from well MW-HP-1S were plotted and an exponential trend line was fit to the data (Fig. 3), using the method suggested by Sutherson (1997). Data from this well were used because it is the only well in the pilot test area with at least three data points to be used in the pilot test. The data were collected between July 1998 and July 2000. It may be observed from Fig. 3 that TCE concentrations have decreased over the two years of sampling, due supposedly to natural attenuation processes. The presence of cis-1,2 DCE at the site and in the pilot test area supports that some reduction of TCE was already occurring, as cis-1,2 DCE was not a source contaminant. However, based on the aerobic and oxidizing nature of the environment as indicated by the pre-pilot test assessment, only limited reductive dechlorination would be possible as complete degradation of CVOCs may only occur under strongly reducing conditions (Wiedemeier and others 1996). The goal of the pilot test was to transform the DO and REDOX environment and deplete the electron acceptors so that more efficient pathways of reductive dechlorination such as sulfanogenesis and methanogenesis would ultimately be used. A degradation constant of -0.0013 was calculated for TCE from the trend line in Fig. 3. Using this degradation rate and an initial concentration derived from the best-fit exponential line, a natural degradation half-life was estimated for TCE with the equation (Sutherson 1997):

$$T = \ln((C_o/2)/C_o)/K \quad (3)$$

where T =half life (days), C_o =initial concentration at time 0, and K =degradation rate.

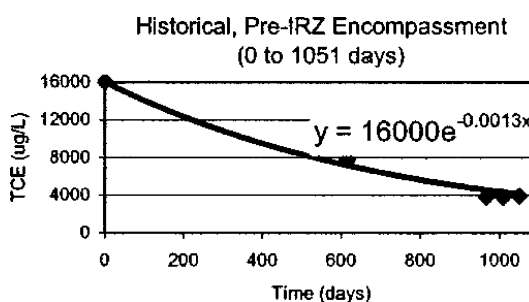


Fig. 3

Pre-test degradation trend for TCE in well MW-HP-1S

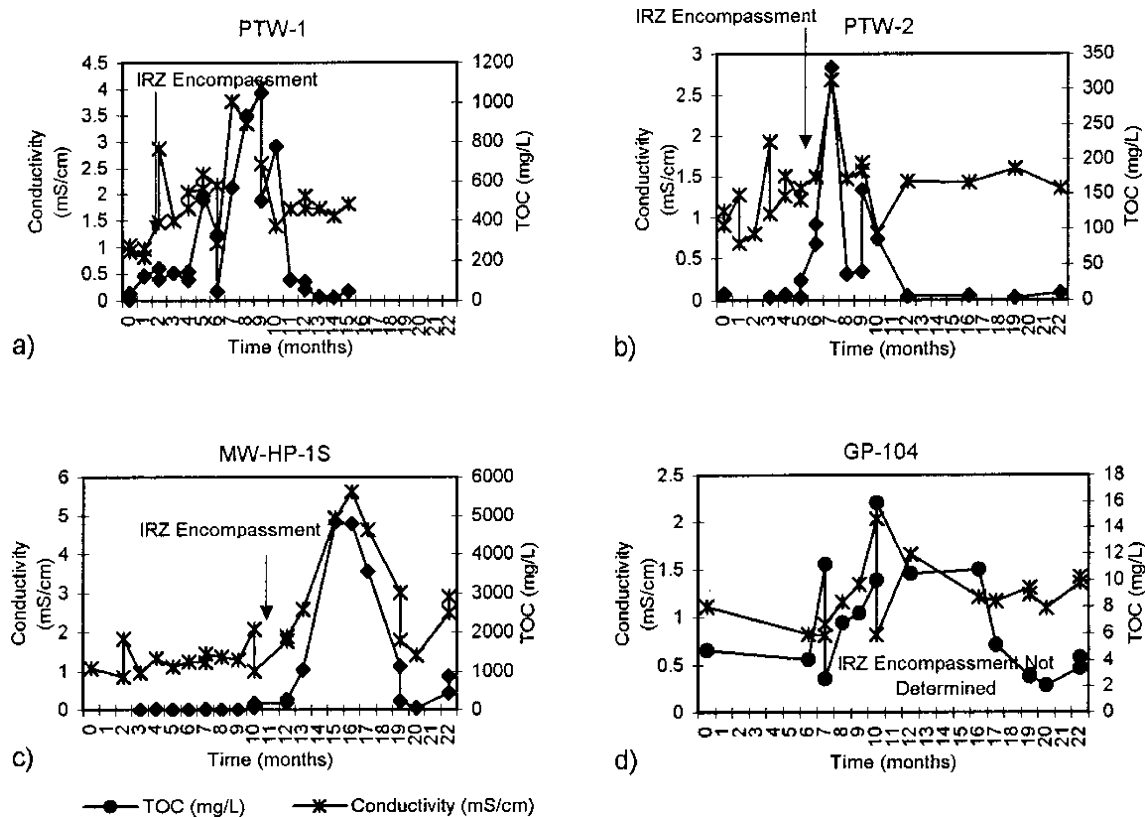


Fig. 4

Post-test patterns of conductivity and TOC in four different wells

The calculated initial concentration was 16,000 ppb, and the half life for TCE using the site-specific data obtained from well MW-HP-1S was 533 days. Although only a few data points are used in this calculation, the rate constant estimated for TCE is within the published range (0.0001 to 0.021) reported by Wiedemeier and others (1996).

The pilot test

Test scope

A 20-month in-situ bioremediation pilot test was conducted by attempting to create an in-situ reactive zone (IRZ) that would possibly enhance reductive dechlorination (ERD) of CVOCs in groundwater at the site. The creation of the IRZ was accomplished by injecting a carbohydrate substrate (molasses) into the groundwater to increase microbial activity and thus to deplete the electron acceptors. Monitoring well GP-107 was selected as the substrate injection point because it is located in the center of the TCE plume area (see Fig. 1) that has historically shown elevated concentrations of TCE. Well GP-107 is also located in close proximity to several existing monitoring points in the down-gradient directions. The upper portion of the aquifer was targeted because it is where the highest TCE concentrations were historically detected. The substrate injections were performed on a biweekly schedule to create and maintain the IRZ. Fifty substrate injection

events were performed between September 2000 and August 2002.

The concentration of substrate used for the first three injections into well GP-107 had a water to molasses ratio of 20:1, with a volume of approximately 0.38 m³. By the fourth injection, the ratio was adjusted to 10:1, and the volume was changed to 0.76 m³ at the tenth injection. In an effort to expand the IRZ, injections were initiated in monitoring well GP-105, which is side-gradient to GP-107 at the twentieth injection. Due to a decrease in the water table and the shallow well construction of GP-107, injections were ceased at GP-107 after injection 32 (month 14), and injections were initiated at well PTW-1 which is constructed approximately 1 m deeper and down-gradient from GP-107.

Substrate injections were performed using a centrifugal pump. The water and molasses were mixed using the pump and stirring rod in 0.21-m³ drums. Following a thorough mixing of the solution, it was injected under low pressure (approximately 2 to 12 psi) into the injection point. Prior to each injection, field data and groundwater samples were collected for the analysis of pH, DO, REDOX potential, specific conductance, total organic carbon (TOC) and dissolved organic carbon (DOC). Results from these analyses were continuously reviewed throughout the pilot program to adjust the reagent strength and volume to ensure that the injections would not initiate excessive fermentation processes that can lower the pH.

To track the establishment, growth and progress of the IRZ, performance monitoring of select wells (PTW-1, PTW-2, GP-104, MW-HP-1S) immediately down-gradient and side-gradient of well GP-107 was conducted on a biweekly schedule. This allowed parameters such as DO,

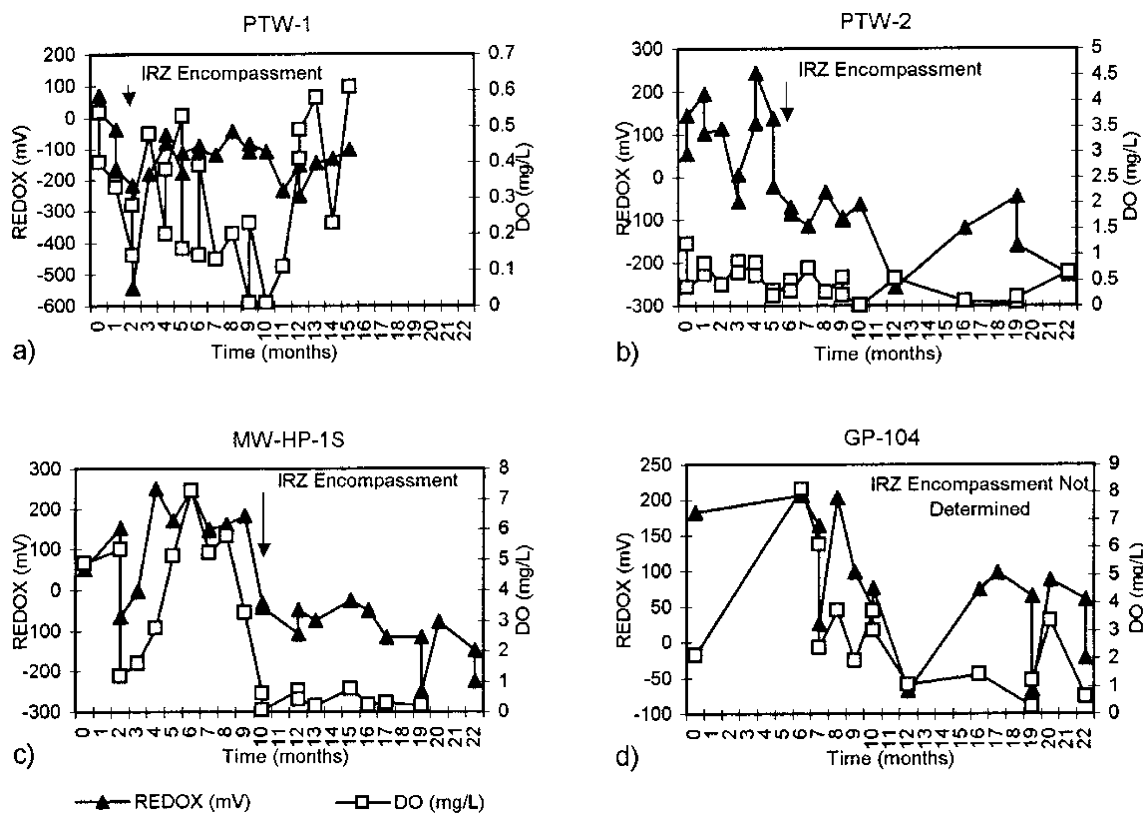


Fig. 5

Post-test patterns of REDOX and DO in four different wells

REDOX potential, specific conductivity, TOC and DOC to be monitored. These wells which are within and immediately surrounding the IRZ were sampled and analyzed for a targeted list of specific electron acceptors and byproducts to document that anaerobic microorganisms were depleting the acceptors, and that reduced byproducts (i.e., sulfide, ferrous iron, dissolved iron, methane) were present and accumulating. Daughter products of TCE such as cis-1,2 DCE, vinyl chloride, and ethene were also analyzed to track the anticipated increase of these compounds. This synergy of data collected is sufficient to document the occurrence of reductive dechlorination and its level of occurrence.

Test results

Establishment of in-situ reactive zone (IRZ)

Substrate injections were performed to create an IRZ for the purpose of treating TCE and other CVOCs. Reducing conditions were established at the initial injection point GP-107 two weeks after the first substrate injection was performed. The minimum target TOC concentration of 1,000 mg/L was reached approximately 1.5 months after the first injection. The created IRZ encompassed an area down-gradient of GP-107 that included wells PTW-1, PTW-2, and MW-HP-1S, after 1.5, 5 and 10 months of the first injection respectively. Encompassment of the IRZ is characterized by increases in TOC and conductivity, and by decreases in DO and REDOX potential. Figure 4 shows when increased TOC and conductivity occurred as a

consequence of carbohydrate solution injections, and Fig. 5 illustrates when significant decreases in DO and REDOX occurred from the increase in microbial respiration. As a check on the encompassment of the IRZ, the travel times estimated earlier with Eq. (2) were compared with the encompassment time of the IRZ. Both sets of travel times compare very well (see Table 1), indicating that the encompassment resulted from the injection events at GP-107.

Evidence of enhanced reductive dechlorination (ERD) Results of the pilot test provided evidence that ERD was occurring at the site due to the alteration of the groundwater environment. Factors for evaluating the occurrence of ERD include depletion of electron acceptors and increase in their byproducts as illustrated by biogeochemical monitoring results, a decrease in parent (source) TCE concentrations, and the accompanying increase in daughter products. Analytical results indicated that concentrations of TCE decreased in wells PTW-1, PTW-2, MW-HP-1S, and GP-104 while daughter products, primarily cis-1,2 DCE, vinyl chloride, and ethene increased in concentration. Based on the field data and TOC results summarized in the preceding section, the IRZ has encompassed monitoring points PTW-1, PTW-2, and MW-HP-1S, and is believed to be the catalyst for the ERD of TCE. The monitoring results from the three wells encompassed by the IRZ were similar, thus only those from PTW-2 are summarized here. Monitoring well PTW-2 is located approximately 9.2 m downgradient of injection well GP-107. Concentrations of TCE detected in well PTW-2 (downgradient of well PTW-1) showed a

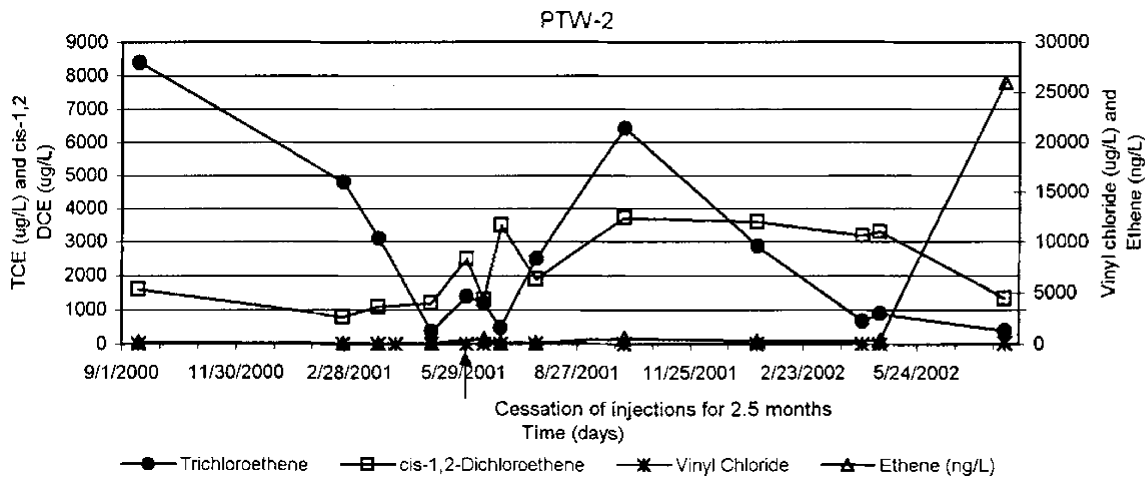


Fig. 6

Distribution of post-test TCE and daughter products in well PTW-2

significant decrease from 8,400 ug/L (pre-pilot) to 400 ug/L (post-pilot) (Fig. 6). In May and June 2001, concentrations of TCE had decreased to 380 and 480 ug/L, respectively, and subsequently increased to 2,500 (July 2001) and then to 6440 ug/L (October 2001). Note that the pilot test was conducted in the mid-plume area, therefore a mass of TCE continues to flow into the study area, which may be responsible for the TCE concentration rebound. Additionally, a temporary cessation of injections occurred to quantify how long the organic carbon in the upgradient injection well (GP-107) would remain during injection #20, which may be partially responsible for the rebound. However, following initiation of injections, concentrations of TCE again decreased significantly.

With the decrease of TCE, concentrations of cis-1,2-DCE increased from 1,600 (pre-pilot) to 3730 ug/L (October 2001) providing evidence of ERD of TCE and not TCE dilution processes. Following October 2001, cis-1,2 DCE decreased to 1340 ug/L at the conclusion of the pilot test demonstrating that continued reductive dechlorination is occurring. This process is further supported by the detection of vinyl chloride (118 ug/L) during the last groundwater sampling event. Concentrations of ethene have also illustrated a significant increasing trend from 209 (pre-pilot test) to 26,000 ng/L (post-pilot test) demonstrating that the mass of TCE in groundwater has been reduced and that the final degradation product (ethene) has been achieved. The complete degradation sequence (TCE to ethene) for dechlorination of TCE has been observed.

Field data collected at well PTW-2 indicate anaerobic and reducing conditions characterized by low dissolved oxygen (<1 mg/L) and REDOX (<0 mV) concentrations (see Fig. 5b). Anaerobic and reducing conditions were achieved during the fifth month of the pilot test and remained throughout the test. Biogeochemical indicators supporting ERD include sulfate and nitrate reduction. Nitrate was found to reduce from 6.47 to 1.7 mg/L while nitrite increased from not detected to 3.1 mg/L. Also, sulfate was reduced from 107 to 48 mg/L while sulfide has increased from 0.006 to 0.07 mg/L (Fig. 7). Methane concentrations

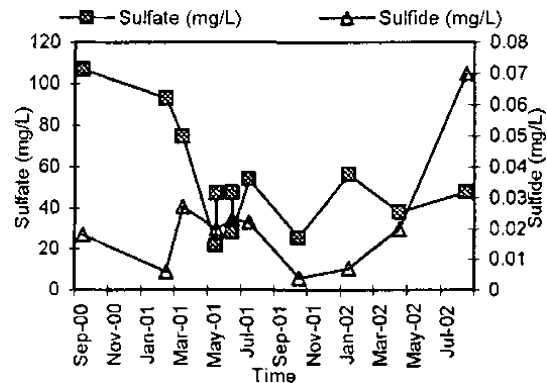


Fig. 7

Sulfate and sulfide data from well PTW-2

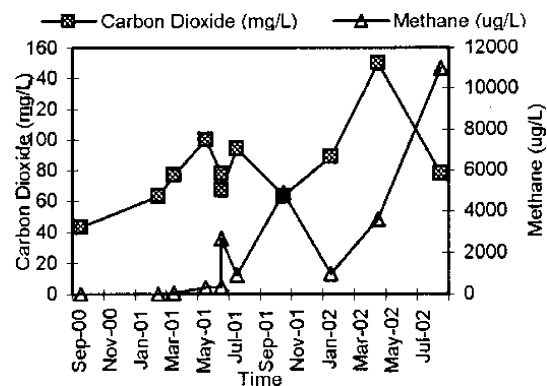


Fig. 8

Carbon dioxide and methane data from well PTW-2

have continually increased, suggesting that the environment has approached and achieved methanogenic conditions (Fig. 8). However, concentrations of carbon dioxide have also increased throughout the pilot test. Note that as stated by Wiedemeier and others (1996), it is possible for acetate to split, forming both methane and carbon dioxide. This appears to be the case in Fig. 8 where methane and carbon dioxide increase simultaneously. Also, carbon dioxide is continually being released by the reduction of other compounds as a final byproduct. Therefore, as TCE and other compounds are reduced, carbon dioxide may also accumulate.

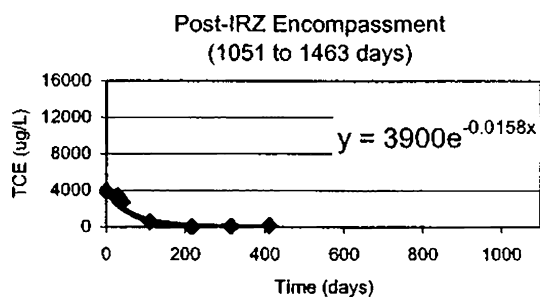


Fig. 9

Post-test degradation trend for TCE in well MW-HP-1S

Comparison of historical and pilot test degradation rates. The pre-pilot test data indicated that limited reductive dechlorination was already occurring at the site. To determine if the pilot test ERD increased TCE degradation, a post-pilot test degradation rate was obtained for TCE using information from well MW-HP-1S. As done previously, the Sutherson (1997) method was used as illustrated in Fig. 9. The calculated post-pilot test degradation constant and half life are -0.0158 and 44 days, respectively. Compared to the pre-test constant and half life of -0.0013 and 533 days, it is evident that the reduction of TCE has been enhanced significantly.

Conclusions

The main purpose of this study was to attempt to create an In-Situ Reactive Zone (IRZ) in groundwater at an old manufacturing site that was contaminated by trichloroethene (TCE) in the metropolitan New York area. This was to be achieved by injecting a carbohydrate substrate (molasses) into groundwater wells at the site under controlled and monitored conditions. It was hoped that the introduction of the carbohydrate substrate would stimulate increased microbial activity to cause depletion of available electron acceptors as a consequence of increased respiration by microbes. This would produce strongly anaerobic and reducing conditions that are necessary to enhance reductive dechlorination of TCE for a complete bioremediation of contaminated groundwater at the site. Preliminary analysis of field data at the site indicated that reductive dechlorination of TCE was occurring naturally but slowly under transitional to aerobic groundwater conditions. The rate of occurrence was marked by a degradation rate constant of -0.0013 and a TCE half-life degradation rate of 533 days.

The accompanying pilot test in which molasses was injected into groundwater wells at the site successfully demonstrated the establishment of an IRZ. Field and analytical data showed significant increases in TOC and conductivity, and decreases in REDOX and dissolved oxygen that characterized the existence of the IRZ. Groundwater advective travel times calculated on the basis of purely hydrogeologic parameters correlated very well with travel times obtained from biogeochemical data from

the pilot test, supporting that the IRZ was caused by the injection of the carbohydrate substrate.

There was evidence of ERD of TCE with the injection of the carbohydrate substrate. This included continued anaerobic and reducing conditions with sufficient presence of organic carbon, increases in concentrations of TCE daughter products (cis-1,2 DCE, vinyl chloride, and ethene), depletion of electron acceptors (e.g., nitrate, sulfate), and increased concentrations of byproducts of electron acceptors (e.g., nitrite, sulfide). At locations down gradient of the injection wells, concentrations of carbon dioxide (CO_2) first showed evidence of an increasing trend, possibly supporting methanogenesis in which acetate is split to produce methane and CO_2 . The CO_2 concentrations subsequently stabilized and decreased slightly, suggesting that CO_2 was again being used as an electron acceptor. These conditions showed that the groundwater environment in the area of the IRZ was transitioned to methanogenic conditions favorable for rapid and possibly complete degradation of CVOCs.

Data were collected to estimate the degradation rate constant and half life of TCE after the injection of the carbohydrate substrate. The calculated constant and half life were -0.0158 and 44 days, respectively. A comparison of these post-test values with the pre-test values of -0.0013 and 533 days shows that the pilot test successfully demonstrated a strong enhancement of reductive dechlorination of TCE.

It may be concluded from this study that TCE mass can be destroyed, at a greater than the natural rate, by enhancing reducing conditions of a groundwater environment using a carbohydrate substrate, molasses.

References

- Azadpour-Keeley A, Keeley JW, Russel HH, Sewell GW (2001) Monitored natural attenuation of contaminants in the subsurface: processes. *Ground Water Monit R* 21:97–107
- Ballapragada BS, Stensel HD, Puhakka JA, Ferguson JF (1997) Effect of hydrogen on reductive rechlorination of chlorinated ethenes. *Environ Sci Tech* 31:1728–1734
- Bouwer EJ, McCarty PL (1983) Transformations of 1- and 2-carbon halogenated aliphatic organic compounds under methanogenic conditions. *Appl Envir Microbiol* 45:1286–1294
- Carr CS, Hughes JB (1998) Enrichment of high-rate PCE dechlorination and comparative study of lactate, methanol, and hydrogen as electron donors to sustain activity. *Environ Sci Tech* 32:1817–1824
- Carr CS, Sanjay G, Hughes JB (2000) Effect of dechlorinating bacteria on the longevity and composition of PCE-containing nonaqueous phase liquids under equilibrium dissolution conditions. *Environ Sci Tech* 34:1088–1094
- Delvin JF, McMaster M, Barker JF (2002) Hydrogeologic assessment of in situ natural attenuation in a controlled field experiment. *Water Resour Res* 38(1):3-1–3-11
- de Bruin WP, Kotterman MJ, Posthumus MA, Schraa G, Zehnder AJ (1992) Complete biological reductive transformation of tetrachloroethene to ethane. *Appl Envir Microbiol* 58:1996–2000
- DiStefano TD, Gossett JM, Zinder SH (1991) Reductive dechlorination of high concentration of tetrachloroethene to ethane by

- an anaerobic enrichment culture in the absence of methanogenesis. *Appl Environ Microbiol* 57:2287–2292
- DiStefano TD, Gossett JM, Zinder SH (1992) Hydrogen as an electron donor for dechlorination of tetrachloroethene by an anaerobic mixed culture. *Appl Environ Microbiol* 58:3622–3629
- Driscoll FG (1986) *Groundwater and wells*. Johnson Filtration Systems, St. Paul, Minnesota, 1089 pp
- Fathepure BZ, Nengu JP, Boyd SA (1987) Anaerobic bacteria that dechlorinate perchloroethene. *Appl Environ Microbiol* 53:2671–2674
- Fennell DE, Gossett JM, Zinder SH (1997) Comparison of butyric acid, ethanol, lactic acid, and propionic acid as hydrogen donors for the reductive dechlorination of tetrachloroethene. *Environ Sci Tech* 31:918–926
- Freedman DL, Gossett JM (1989) Biological reductive dechlorination of tetrachloroethylene and trichloroethylene to ethylene under methanogenic conditions. *Appl Environ Microbiol* 55:2144–2151
- Gerritse J, Renard V, Gomes TMP, Lawson PA, Collins MD, Gottschal JC (1996) *Desulfotobacterium* sp. strain PCE1, an anaerobic bacterium that can grow by reductive dechlorination of tetrachloroethene or ortho-chlorinated phenols. *Arch Microbiol* 165:132–140
- Hall LM (1968) *Bedrock geology in the vicinity of White Plain, New York*. University of Massachusetts, Amherst, Massachusetts
- Holliger C, Schumacher W (1994) Reductive dehalogenation as a respiratory process. *Antonie van Leeuwenhoek* 66:239–246
- Holliger C, Schraa G, Stams AJ, Zehnder AJ (1993) A highly purified enrichment culture couples the reductive dechlorination of tetrachloroethene to growth. *Appl Environ Microbiol* 59:2991–2997
- Krumholz LR, Sharp R, Fishbain SS (1996) A freshwater anaerobe coupling acetate oxidation to tetrachloroethylene dehalogenation. *Appl Environ Microbiol* 62:4108–4113
- MacDonald J (2000) Natural attenuation for groundwater cleanup. *Environ Sci Technol* 34:346A–353A
- Maymó-Gatell X, Chien Y-t, Gossett JM, Zinder SH (1997) Isolation of a bacterium that reductively dechlorinates tetrachloroethene to ethane. *Science* 276:1568–1571
- Morse JJ, Alleman BC, Gossett JM, Zinder SH, Fennell DE, Sewell GW, Vogel CM (1998) A treatability test for evaluating the potential applicability of the reductive anaerobic biological in situ treatment technology (RABITT) to remediate chloroethenes – DRAFT. Department of Defense, Environmental Security Technology Certification Program, Arlington, Virginia
- Sharma PK, McCarty PL (1996) Isolation and characterization of a facultatively aerobic bacterium that reductively dehalogenates tetrachloroethene to cis-1,2-Dichloroethene. *Appl Environ Microbiol* 62:761–765
- Smatlak CR, Gossett JM, Zinder SH (1996) Comparative kinetics of hydrogen utilization for reductive dechlorination of tetrachloroethene and methanogenesis in an anaerobic enrichment culture. *Environ Sci Tech* 30:2850–2858
- Sutherson SS (1997) *Remediation engineering, design concepts*. CRC Press, Boca Raton, Florida
- Sutherson SS (2002) *Natural and enhanced remediation systems*. CRC Press, Boca Raton, Florida
- U.S. Environmental Protection Agency (1993) Evaluation of the likelihood of DNAPL presence at NPL sites. EPA 540-R-93-073, U.S. EPA, Office of Solid Waste and Emergency Response, Washington, DC
- U.S. Environmental Protection Agency (1998) *Groundwater sampling standard operating procedures*. U.S. Environmental Protection Agency, Region II, New York
- Vogel T, McCarty PL (1985) Biotransformation of tetrachloroethylene to trichloroethylene, dichloroethylene, vinyl chloride, and carbon dioxide under methanogenic conditions. *Appl Environ Microbiol* 49:1080–1083
- Wiedemeier TH, Wilson JT, Kampbell DH, Miller RN, Hansen JE (1995) Technical protocol for implementing intrinsic remediation with long-term monitoring for natural attenuation of fuel contamination dissolved in groundwater (volumes I and II). San Antonio, Texas: Air Force Center for Environmental Excellence Technology Transfer Division, Brooks AFB
- Wiedemeier TH, Swanson MA, Moutoux DE, Gordon EK, Wilson JT, Wilson BH, Kampbell DH, Hansen JE, Haas P, Chapelle FH (1996) Technical protocol for evaluating natural attenuation of chlorinated solvents in groundwater. Air Force Center for Environmental Excellence, Technology Transfer Division, San Antonio, Texas
- Wiedemeier TH, Rifai HS, Newell CJ, Wilson JT (1999) *Natural attenuation of fuels and solvents in subsurface*. Wiley, New York, 632 pp