Thermal DNAPL Source Zone Treatment Impact on a CVOC Plume

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Abstract

The tetrachloroethene (PCE) source zone at a site in Endicott, New York had caused a dissolved PCE plume. This plume was commingled with a petroleum hydrocarbon plume from an upgradient source of fuel oil. The plume required a system for hydraulic containment, using extraction wells located about 360 m downgradient of the source. The source area was remediated using in situ thermal desorption (ISTD). Approximately 1406 kilograms (kg) of PCE was removed in addition to 4082 kg of commingled petroleum-related compounds. The ISTD treatment reduced the PCE mass discharge into the plume from an estimated 57 kg/year to 0.07 kg/year, essentially removing the source term. In the 5 years following the completion of the thermal treatment in early 2010, the PCE plume has collapsed, and the concentration of degradation products in the PCE-series plume area has declined by two to three orders of magnitude. Anaerobic dechlorination is the suspected dominant mechanism, assisted by the presence of a fuel oil smear zone and a petroleum hydrocarbon plume from a separate source area upgradient of the PCE source. Based on the post-thermal treatment groundwater monitoring data, the hydraulic containment system was reduced in 2014 and discontinued in early 2015.

Introduction

Dense nonaqueous phase liquids (DNAPL) have created significant environmental concerns. Soil and groundwater contaminated with DNAPL are relatively slow to remediate naturally, with typical plume life expected to be hundreds of years. The longevity of source zones is primarily caused by the environmental stability of the DNAPL, its immobility in the subsurface, low dissolution rate into moving groundwater, and its low vaporization rate when located below the groundwater table at typical ambient temperatures (Hunt et al. 1988; Mercer and Cohen 1990; Pankow and Cherry 1996). As such, DNAPL source zones release contaminants for decades or centuries and can sustain long dissolved plumes with downgradient impacts on the environment. Payne et al. (2008) describe the evolution of plumes from the time of source initiation (DNAPL release) through the plume expansion phase to the time of source elimination. Most chlorinated solvent plumes have existed for decades and are far from the depletion stage, meaning that substantial source mass is present and that the plume can be sustained for decades or longer unless the DNAPL source is treated.

Thermal treatment has been proven effective for source zone treatment, with the reduction of soil concentrations from hundreds or thousands of mg/kg to target levels ranging between 0.10 and 10 mg/kg, depending on site-specific

objectives (Davis 1997; BERC 2000; EarthTech and SteamTech 2003; McGee 2003; LaChance et al. 2004; Heron et al. 2005, 2013, 2014; Johnson et al. 2009). Typical mass removal percentages exceed 99% (equal to two orders of magnitude) and in some instances, more than 99.9%, equal to three orders of magnitude (Heron et al. 2005, 2013).

However, the reduction of source zone concentrations of the contaminants of concern (COC) to below target levels does not directly translate into site closure when a dissolved plume is present downgradient of the source, often due to back-diffusion from low-permeability zones (Liu and Ball 2002; Kavanaugh and Rao 2003; Chapman and Parker 2005; Parker et al. 2008; Seyedabbasi et al. 2012). Such dissolved plumes have typically evolved over decades of seepage of water through the source and the slow dissolution of COCs and have reached a semi-steady state size and shape where natural attenuation processes balance out the supply of COCs to the plume. Figure 1 illustrates these mechanisms.

Natural attenuation processes include dilution, dispersion, sorption, diffusion, and degradation (Christensen et al. 2001). The first four processes are physical and can cause the plume to spread perpendicular to the dominant groundwater flow direction and into low-permeability zones above and below the core of a plume. After decades of plume development, diffusion of COCs into clay and silt layers may lead to a significant fraction of the mass being present in low-permeability zones with limited groundwater flow (Liu and Ball 2002; Payne et al. 2008). Diffusion of COCs into coarse sand- and gravel-sized soils and sorption onto
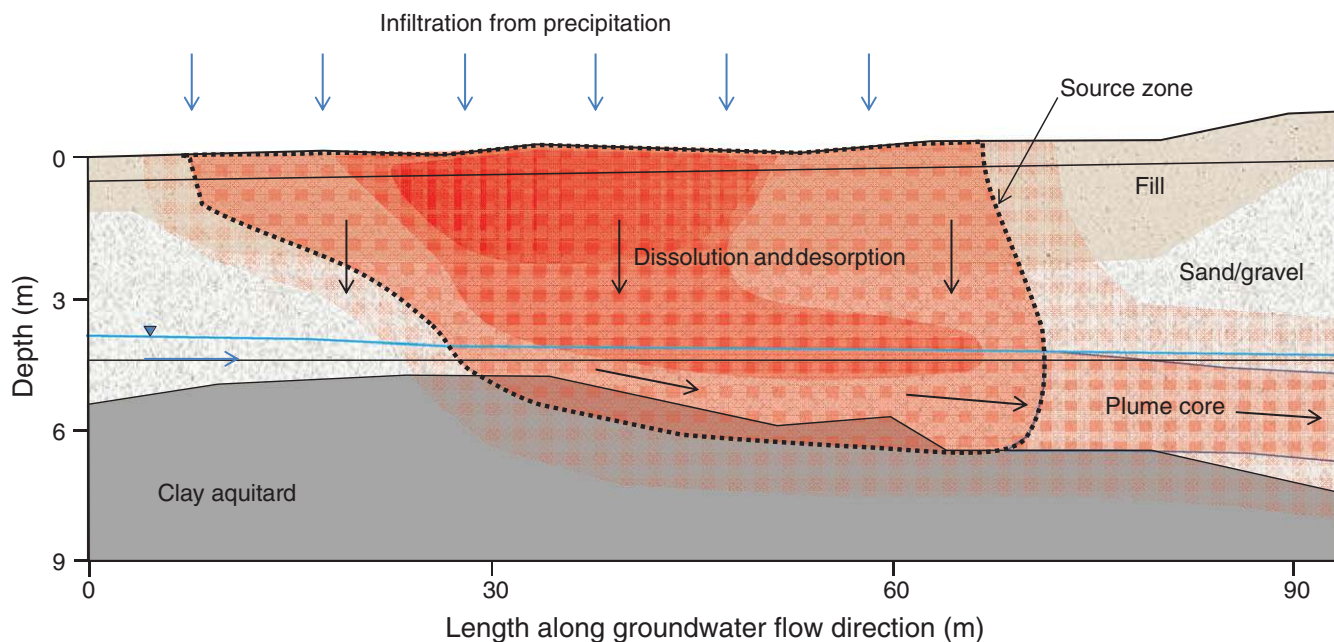
Figure 1. Conceptual site model for the DNAPL-impacted site with a downgradient dissolved plume emanating from the source/smear zone.

and within those coarser soils can also lead to significant storage of mass in higher-permeability zones. For some sites, back-diffusion of COCs stored in the solid phase of the aquifer may continue to supply mass to a plume many years after the core of the plume has been remediated, as modeled and discussed by Seyedabbasi et al. (2012). It is uncertain whether this COC mass flux from the solid phase of the aquifer can sustain the plume or whether the degradation reactions occurring will be enough to overcome the mass flux released to the plume.

The degradation reactions may be abiotic or biotic. Biological degradation reactions are highly dependent on the presence of microbial populations, redox conditions, electron donors, and nutrients required to sustain the activity. For chlorinated volatile organic compounds (CVOCs), such as PCE and Trichloroethene (TCE), the most effective degradation has been observed under anaerobic, methanogenic conditions, whereas degradation is generally much slower under aerobic conditions. Anaerobic conditions are typically created when a source zone releases organic material that is easily degraded under aerobic or slightly anoxic conditions (Christensen et al. 2001). Such material can be landfill leachate, petroleum hydrocarbons, wood-treating chemicals such as creosote, or tar produced at manufactured gas plants.

As a result of these complex processes, it is not simple to predict how much of an effect a successful source removal action can have on an associated groundwater plume. The impact is governed by a complex interplay of physical dilution and dispersion, diffusion, sorption, and degradation reactions.

Some studies indicate that source removal can have minimal impact on a plume, primarily due to back-diffusion of COCs out of low-permeability zones (Seyedabbasi et al. 2012). In this study, we postulate that a very positive impact can be had on CVOC plumes by the following logic:

1. Thermal treatment can remove more than 99% of the PCE mass in the source zone, if properly delineated.
2. The reduction in PCE mass in the source zone can reduce the mass discharge of PCE into the downgradient plume by several orders of magnitude.
3. After reduction of the PCE mass discharge from the source zone, natural attenuation processes can lead to the shrinkage of the PCE plume as the remaining PCE is reduced by physical and/or biodegradation processes.
4. At the site in Endicott, the groundwater flow is sufficiently fast to allow for plume attenuation in a period of 5 years following thermal treatment.

This paper presents the results of a full-scale remediation of a PCE DNAPL-impacted source zone using thermal conduction heating (TCH) combined with vacuum extraction, which is otherwise known as in situ thermal desorption (ISTD). Estimates of the impact on mass discharge of PCE are provided, and groundwater plume data for PCE and the degradation products are used to document the effect.

Background

Site Description and History

The former Ideal Cleaners property (Site) is located at 1900 North Street in the Village of Endicott, Broome County, New York. The Site currently consists of an open asphalt-paved parking area with smaller lawn areas. The area surrounding the Site to the west, north, and east includes roadways and commercial or industrial properties, while the area south of the Site consists of residential properties (Figure 2). Dry-cleaning operations were present at the Site from about 1965 to 1985. In 1985, IBM purchased the Site for use as a parking lot. Historical dry-cleaning operations at the property by previous owners apparently resulted in the
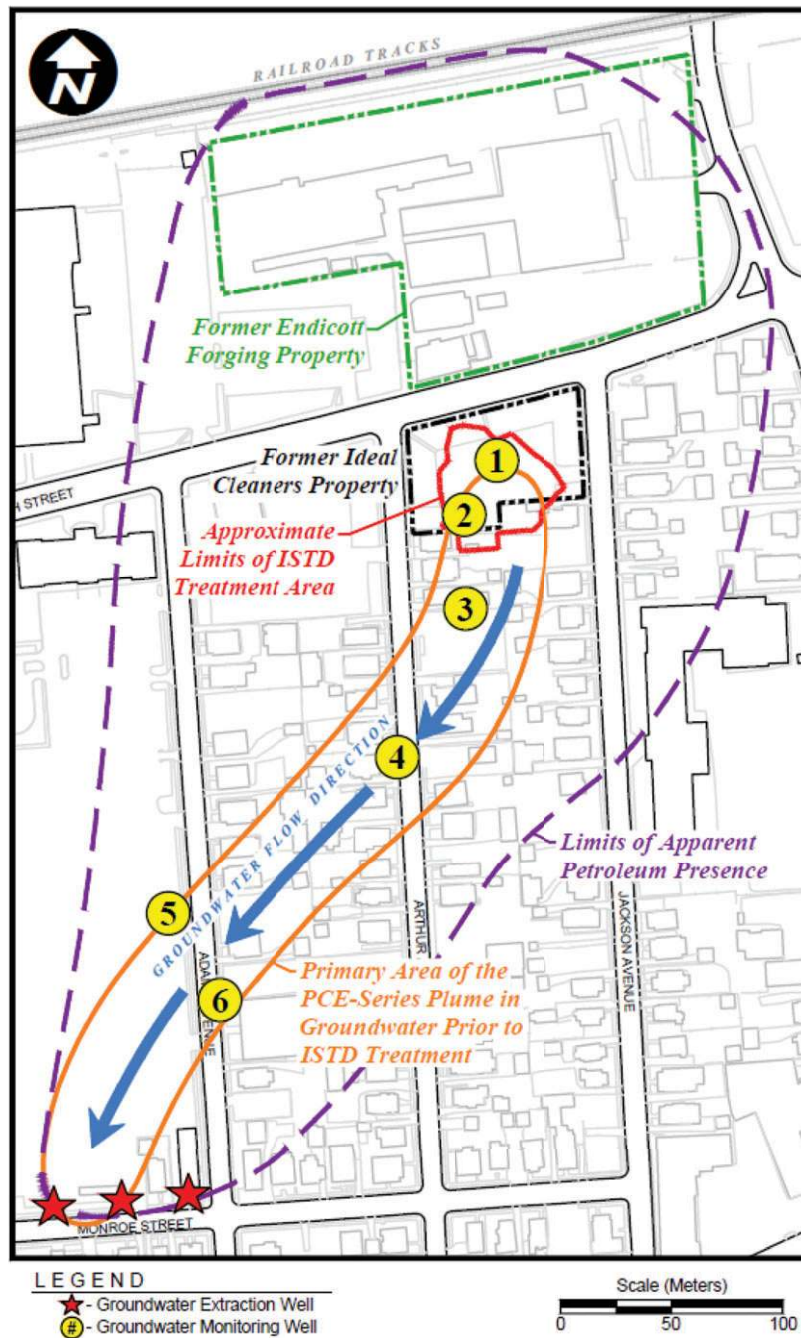
Figure 2. Site map depicting PCE-Series source area (ISTD Treatment Area) and PCE-Series plume, with monitoring well locations shown.

release of PCE into the soil and groundwater at the Site. The PCE-series plume required a pump-and-treatment system for hydraulic containment, using extraction wells located about 360 m downgradient of the source. The pump-and-treatment system began operations in 1985 and expanded operations in 1989, 1992, and 2006. In 2002, the Site was sold to a third party with IBM retaining responsibility for the soil and groundwater cleanup.

Site Geology/Hydrogeology

Geological conditions at the Site include a downward sequence of soil fill, sand interbedded with sand and gravel and sandy silt (glaciofluvial outwash sand and gravel),

and silt with a thin lamina of clay (glaciolacustrine silt). A thin zone of cinder fill is also present beneath some of the asphalt-paved portions of the Site. Where saturated, the outwash sand and gravel constitutes an upper aquifer, with the lacustrine silt serving as an underlying aquitard.

The water table in the source area is approximately 5 to 6 m (17 to 20 ft) below existing grade. Average hydraulic conductivity in the upper aquifer sand and gravel is estimated at about 4.6×10^{-2} cm/sec (40 m/day). Under groundwater pumping conditions, the hydraulic gradient varies between 0.005 and 0.02, and the average porosity is estimated at 35%. Based on these aquifer characteristics, seepage velocities of 0.6 to 2.3 m/day are estimated. Applying these seep-

age velocities to the approximate 360 m (1,200 ft) flow path from the former PCE DNAPL-impacted source zone to the downgradient groundwater extraction wells yields a range in travel time of about 5 to 20 months. Assuming an average seepage velocity of 1.5 m/day, this yields a mean travel time estimate of about 8 months.

Nature and Extent of Contamination

A source area associated with past disposal (probably due to leaks or spills) of PCE has contaminated the soil from the near surface to the glaciolacustrine silt layer that forms the base of the Upper aquifer. Of significance is the fact that the high percentage of thermally altered carbonaceous material in the cinder fill layer resulted in concentrations of sorbed COCs on the order of 100 to 1000 mg/kg that served as a long-term reservoir for source area mass flux to groundwater. A relatively thin (generally less than 3 m) water-bearing zone carries PCE from the source zone to the downgradient plume, as depicted in the conceptual site model in Figure 1. The plume exhibits a distinctive chlorinated ethene chemical signature characterized by the presence of PCE and/or its degradation products TCE, cis-1,2-DCE, and vinyl chloride (hereinafter referred to as the "PCE-series plume"). The PCE-series plume is captured by groundwater extraction wells located to the northwest of the intersection of Adams Avenue and Monroe Street (Figure 2). Extracted groundwater is treated in IBM's Adams Avenue Groundwater Treatment Facility.

As depicted in Figure 2, a larger plume with petroleum has emanated from the upgradient Former Endicott Forging property. Historical releases of fuel oil from this property and historical water level fluctuations have resulted in a widespread oil smear zone that extends south in the direction of the groundwater flow. Fingerprinting of light nonaqueous phase liquid (LNAPL) collected from within the large petroleum hydrocarbon plume indicates the presence of weathered No. 2 fuel oil, consistent with the historic bulk storage and usage at the former forging facility. This LNAPL plume flows through the PCE source zone. Field explorations and testing indicate that the oil smear zone is about 1 to 2 m thick in the source zone and downgradient PCE-series plume area (GSPC and GSC 2010).

Results of water quality monitoring between late 2003 and 2008, prior to the PCE source removal, suggest that the PCE-series plume was stable or slowly declining with degradation occurring throughout the area of the plume. The larger LNAPL plume/oil smear zone has contributed to the anaerobic conditions found throughout the PCE-series plume.

Interim Remedial Measures and Supplemental Site Investigations

Interim remedial measures (IRMs) and supplemental site investigations completed prior to the implementation of the thermal treatment source removal include 1) hydraulic containment of the PCE-series plume via groundwater extraction and treatment; 2) installation of sub-slab depressurization systems on structures in the area of the plume where vapor intrusion was identified as a potential concern;

3) completion of a multiphased field investigation program to develop site-specific soil cleanup standards and provide a detailed source delineation; and 4) development, screening, and evaluation of potential source removal IRMs including detailed and comparative analyses of excavation versus ISTD treatment alternatives.

The multiphased field exploration and testing program included a combination of membrane interface probe (MIP) and laboratory analyses of soil samples to provide a high density of data concerning the nature and extent of PCE presence in soil and the creation of an accurate three dimensional (3D) visualization of PCE mass distribution in the source area. The investigation program included a fraction of organic carbon analyses and laboratory experiments to derive site-specific sorption partition coefficients used to develop the source removal soil cleanup goal of 0.56 mg/kg for PCE. The overall volume of soil with PCE greater than 0.56 mg/kg was estimated to be 7493 m³ (9800 cubic yards [yd³]), including approximately 5811 m³ (7600 yd³) in the vadose zone, 994 m³ (1300 yd³) in the oil smear zone, and 275 m³ (360 yd³) in the saturated zone below the oil smear zone and in the upper portion of the lacustrine silt. The relative distribution of PCE mass in the vadose zone, oil smear zone, and the saturated zone/silt was estimated to be approximately 71%, 28%, and 1%, respectively. A significant portion of the PCE mass was particularly identified in the portion of the vadose zone consisting of cinder fill (GSPC and GSC 2008).

IBM's evaluation of potential remedial alternatives for the PCE source area resulted in the selection of ISTD treatment as an IRM. Remedial goals were 0.56 mg/kg for PCE in soils by average, with a maximum single sample value of 5.6 mg/kg. ISTD treatment was selected over excavation based on the following:

- Reduction of toxicity, mobility or volume with treatment – istd results in the ultimate destruction of CVOC mass, whereas excavation results in offsite land disposal and long-term liability of CVOC mass within a significant volume of soil.
- Implementability - ISTD at the Site was determined to be far less complex to implement with fewer logistical and administrative considerations than an excavation adjacent to a residential neighborhood and surrounded by roadways with heavy traffic. Power was available locally to support the thermal remedy.
- Short-Term Effectiveness – ISTD had much less potential for short-term impacts to the community and the environment contrasted with excavation that was projected to have significant onsite disturbances and heavy truck traffic (nearly 1000 truckloads of soil for offsite land disposal and nearly 1000 truckloads of clean soil fill material) through a residential neighborhood.
- Cost - The remedial alternative assessment produced two feasible options, excavation and ISTD. Excavation of the material was difficult in this particular mixed residential setting and would require sheeting and shoring, vapor mitigation, and dust control among addressing a host of other health and safety concerns related to excavations of this size. Excavation was estimated at

$9.6M. With ISTD, the costs of treating the same footprint (and actually more volume considering the entire soil column) was estimated at $5.4M. The actual cost of implementing ISTD was reasonably consistent with estimates made at the remedial options alternative stage.

The PCE source removal by ISTD achieved the NYSDEC's 6 NYCRR Part 375-6 "unrestricted use" Soil Cleanup Objectives. In November 2010, NYSDEC issued a record of decision (ROD) that selected no further action with the continued operation of upper aquifer groundwater plume remediation systems and vapor intrusion mitigation systems as the remedy (New York State Department and Environmental Conservation 2010). The ROD specified that the groundwater plume remediation systems should remain in operation until groundwater quality standards for site-related constituents have been achieved or the NYSDEC determines that natural attenuation processes will be sufficient to attain those standards over time (NYSDEC 2010). The long-term cleanup goals for PCE, TCE, and cis-1,2-DCE in groundwater is 5 μg/L. For vinyl chloride, it is 2 μg/L.

Methods and Results

ISTD Laboratory Treatability and Field Pilot Scale Testing

The ISTD source removal IRM was completed in three phases consisting of a laboratory treatability study, a field pilot scale test in the area of highest contaminant mass, and full-scale ISTD implementation, which also included the pilot test area. The first two phases were performed to 1) evaluate the site-specific effectiveness of ISTD to remove CVOCs from different site soils and 2) support the full-scale design of the ISTD IRM.

Laboratory treatability tests were conducted using four samples from each of the four stratigraphic layers in the PCE source area (16 samples total):

- Cinder fill layer samples from 2 to 6 ft below grade.
- Soil fill layer with ash samples from 6 to 8 ft below grade.
- Sand/gravel and oil smear zone samples from 18 to 20 ft below grade.
- Silt/clay samples from 20 to 22 ft below grade.

Soils were heated at temperatures between 100 and 250 °C for periods between 3 and 14 days. Results indicated that the remedial objective could be met at 100 °C, except for the cinder fill layer where either a longer period of treatment or treatment at a temperature of 150 °C would be required. Based on these marginal results, a decision was made to conduct a field pilot test in the area of the source zone with the highest concentration of COCs and presence of the cinder fill.

A total of 21 heater wells, six multiphase extraction (MPE) wells, and one vacuum extraction well (VEW) was installed. Soil vapor and groundwater were extracted from the wellfield under vacuum through MPEs and the VEW and conveyed to an aboveground treatment system through granular-activated carbon prior to being discharged to the environment. An estimated 1300 kg (2,700 lbs) of PCE and an additional 400 kg (900 lbs) of petroleum hydrocarbons

was recovered as vapor and dissolved in collected NAPL. Soil samples were collected and analyzed before, during, and after treatment to monitor the progress and effectiveness of ISTD in the removal of PCE. Based on the analytical data results, all of the four stratigraphic units, with the exception of the cinder fill layer, achieved strict compliance with the remedial goals. Ten of the 12 samples in the cinder fill unit did meet the remedial goals. Two samples remained above the treatment goal of 5.6 mg/kg for a single sample. In total, the average concentration of PCE across all four stratigraphic units was reduced by greater than 99% (two orders of magnitude).

Adjustments to the full-scale design, including an improved shallow soil vapor extraction design, an improved insulating vapor cover, and a longer heating duration were adopted based on these results.

ISTD Full-Scale Field Implementation

A total of 257 heater wells, 19 multiphase extraction wells, and 72 vapor extraction wells was installed in the contaminated area and included the pilot test area. Well designs are shown in the supporting information, and the layout is shown in Figure 3. Note that the ISTD heater well depths were varied across the site to follow the deepest PCE soil concentrations above the treatment goal. This minimized the treatment volume and saved energy for the heating process.

Soil vapor and groundwater were extracted from the wells and conveyed to a multiphase effluent treatment system consisting of cooling and phase separation followed by vapor phase and liquid phase carbon vessels for treatment. Mass removal in each of the treatment phases were estimated based on flow rates and volumes and analytical data from vapor, water, and NAPL samples (using EPA standard methods) as well as the screening of the vapor concentrations using a photo-ionization detector.

Figure 4 shows the summary of the thermal operations. Thermal treatment lasted approximately 200 days. The energy input of approximately 3.4 million kWh resulted in the heating of the target volume to above 100 °C, with some shallower zones (the cinder fill) locally exceeding 125 °C, per the design. Extraction of fluids, primarily steam and groundwater, during heating totaled approximately 30% of the injected energy (1 million kWh) and was sufficient to maintain hydraulic control of the source area and to contain and extract the released contaminants. More than 3800 kg (8,000 lbs) of chemical mass was removed during the full-scale treatment, half of this in the vaporized form with extracted steam and air and the rest as NAPL pumped from the MPE wells. Combined with the pilot study, a total of over 1400 kg (3100 pounds) of chlorinated VOCs and over 4100 kg (9000 pounds) of other VOCs and NAPL were removed from the site soils (data not shown). Toward the end of heating, the mass removal rate had decreased to modest levels (Figure 4).

Soil Concentrations Before and After ISTD Treatment

Soil samples were collected and analyzed before, during, and after treatment to monitor the progress and effectiveness of the ISTD treatment. The soil data before and after treatment are provided in Figure 5 on a logarithmic scale. Table 1 shows the values from the smear zone and
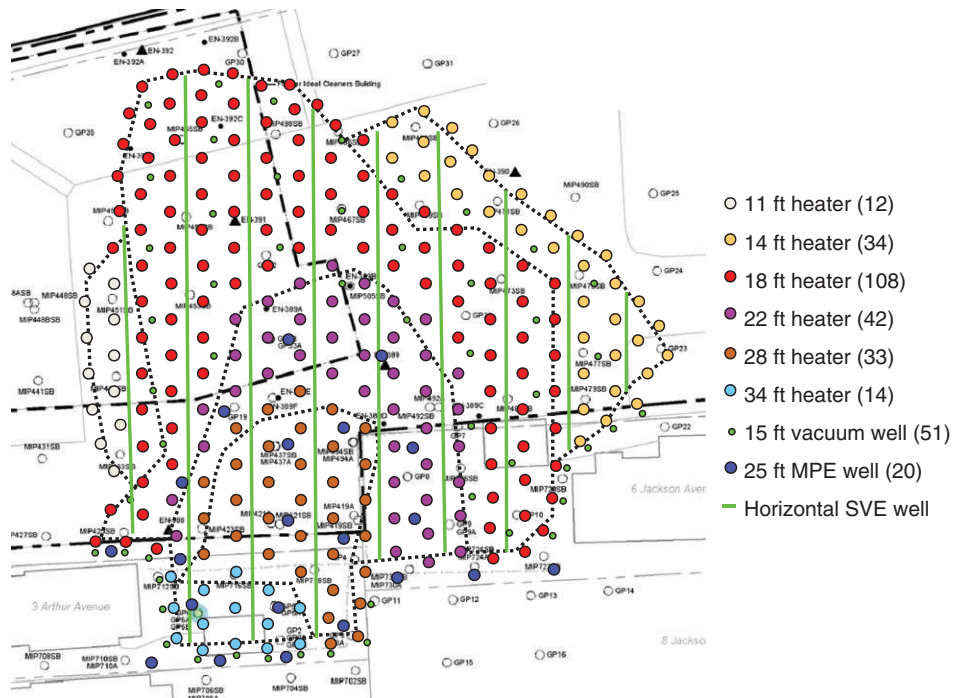
Figure 3. Treatment zone map with varying depths and borings and wells used for ISTD treatment.
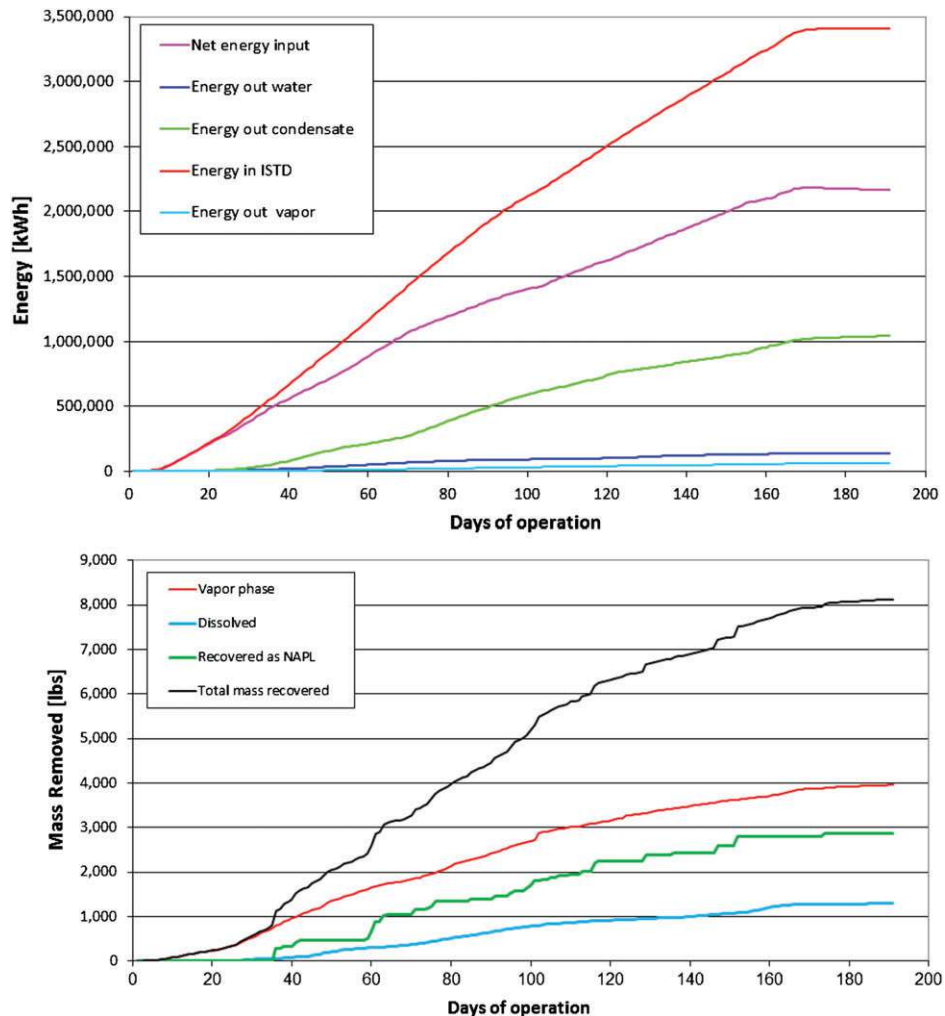

Figure 4. Thermal treatment performance data. Energy balance and PCE mass removal.
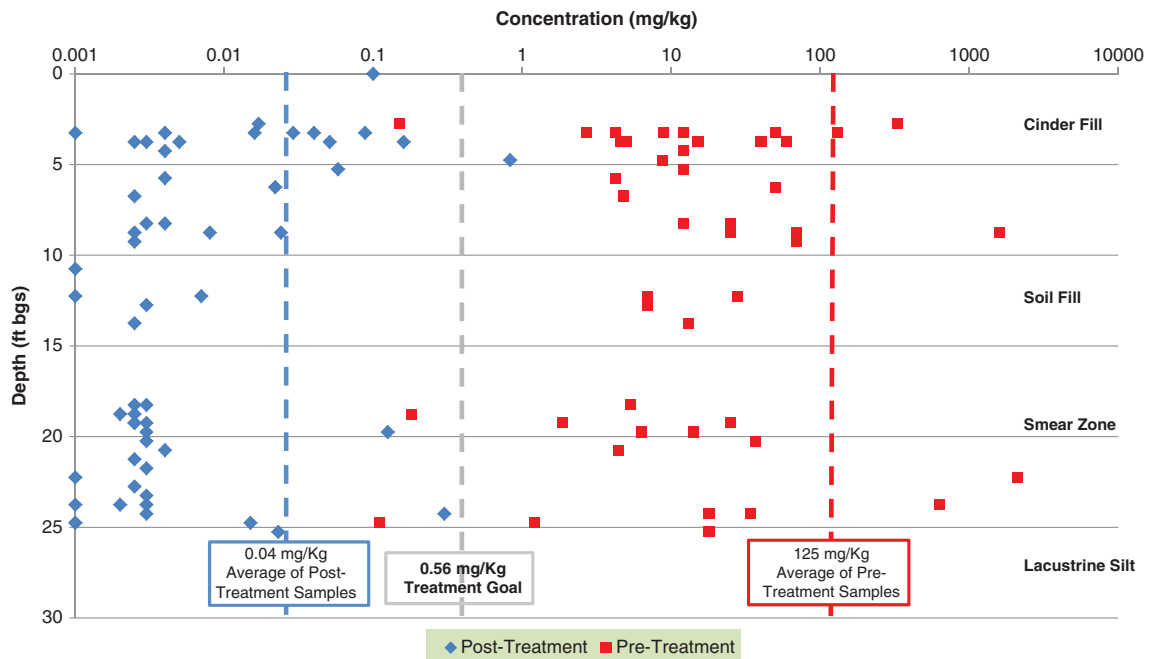
Figure 5. Soil concentrations before and after thermal treatment.

below the groundwater table; these values are used for mass discharge calculations. Soil sampling techniques that were documented to not lead to the loss of VOCs during sampling

of hot soils were used (Gaberell et al. 2002). Based on the analytical data provided by the 55 samples taken (12 of which were from the saturated zone feeding the plume), all four stratigraphic units achieved compliance with the IRM's remedial action objectives. The average PCE concentration in the post-treatment samples was 0.04 mg/Kg, and the highest single sample concentration was 0.83 mg/Kg, both well below the treatment goals. The reduction in average soil concentrations from 125 to 0.04 mg/kg corresponds to a 99.97% reduction in mass (four orders of magnitude).

Mass discharge rate estimates

Based on groundwater concentrations in the smear zone near the start of the plume core, mass discharge estimates for PCE in the dissolved state were estimated (Table 2). Mass discharge was estimated based on cross-sectional area, groundwater migration rates, and average groundwater concentrations

Table 1

Soil Concentrations of PCE in the Smear Zone and Below the Groundwater Table Before and After Thermal Treatment and Estimated Average Reduction Percentage

| Sample | Depth (ft Bags) | PCE Soil Concentration (mg/kg) | | |
		Before Treatment	After Treatment	
PST27M2#	24.5 to 25	0.11	0.001	
PST28L4#	23.5 to 24	630	0.001	
CS5K4	21.5 to 22	2100	0.003	
CS11L1	22 to 22.5	2100	0.001	
CS14K1	20 to 20.5	37	0.003	
CS15J4	19.5 to 20	14	0.125	
CS17J4	19.5 to 20	6.3	0.003	
CS19K2	20.5 to 21	4.4	0.004	
CS22J3	19 to 19.5	1.85	0.0025	
CS27J2	18.5 to 19	0.18	0.0025	
CS29J3	19 to 19.5	25	0.0025	
CS35J1	18 to 18.5	5.3	0.003	
CS43J1	18 to 18.5	not sampled	0.0025	
CS44J2	18.5 to 19	not sampled	0.002	
CS46J3	19 to 19.5	not sampled	0.003	
Average		410.3	0.0106	mg/kg
Percentage reduction			99.9974	%

Table 2

Estimated PCE Mass Discharge Before and After Thermal Treatment

Mass Discharge Estimates	Before Treatment	After Treatment	
Estimated leaching concentration	3	0.0036	mg/L
Plume width	50		m
Plume depth	2		m
Seepage velocity	1.5		m/day
Porosity	35		%
Groundwater volume flow	52.5		m³ day
PCE mass discharge	157.5	0.19	g/day
PCE mass discharge	57	0.069	kg/yr

in the smear zone. Before thermal treatment, groundwater would leave the source zone at PCE concentrations averaging 3 mg/L, equalling an estimated mass discharge of 57 kg of PCE per year. After thermal treatment, this mass flux was reduced to 0.069 kg/yr or by a factor of approximately 800 (2.9 orders of magnitude). This strong reduction in PCE mass discharge to the core of the PCE-series plume would then facilitate plume shrinkage, as discussed below.

MNA Field Implementation

IBM implemented an Monitored Natural Attenuation (MNA) program in the former PCE source area and downgradient PCE-series plume area consisting of quarterly monitoring for VOCs supplemented by semiannual monitoring of dissolved gases, transformation indicator parameters, inorganics, and dechlorinating bacteria. The purpose of the quarterly sampling for VOCs was to monitor for a potential rebound in PCE-series constituents in the former

PCE source area and for changes in the nature and extent of the downgradient PCE-series plume. The purpose of the semiannual monitoring for other parameters was to provide a basis to track trends in conditions of the plume, including the oxidation-reduction potential (ORP), the presence of electron acceptors, the presence of electron donors, and the presence of dechlorinating bacteria.

Distribution of PCE-Series Constituents

The six primary groundwater monitoring well locations used to monitor for a potential rebound in PCE-series constituents in the former PCE source area and for changes in the nature and extent of the downgradient PCE-series plume are shown in Figure 2. Well locations #1 and #2 are located within the ISTD treatment area. Well locations #3 through #6 are located along the plume axis in positions downgradient from the ISTD treatment area. Graphs depicting PCE-series concentrations versus time for groundwater monitoring wells

Figure 6. PCE-series groundwater concentrations in source area and plume area before and after thermal treatment. Monitoring well locations are shown in Figure 2.

in the former PCE source area and near the apparent axis of the groundwater plume are provided in Figure 6. The semi-log graphs depict the VOC concentrations using a log scale versus time in an arithmetic scale and include timelines for the pilot and full-scale ISTD thermal treatment.

Overall, groundwater monitoring at well locations in the former PCE source area indicate roughly three orders of magnitude decrease in pre- and post-thermal treatment CVOC concentrations. The 5 years of post-thermal treatment data also indicate groundwater concentrations below applicable New York State groundwater quality standards without a noticeable rebound or increasing trend. The semi-log graphs for plume area wells #3 through #6 indicate an increase in the rate of decline of the PCE-series concentrations in the plume following the completion of the PCE source removal. Concentrations of PCE-series constituents in groundwater samples from well #3 have declined one to two orders of magnitude, while concentrations of PCE-series constituents in groundwater samples from well locations #4 through #6 have declined two to three orders of magnitude. As depicted by

the PCE, TCE, cis-1,2-DCE, and vinyl chloride isoconcentration contour maps in Figure 7, the areal extent of PCE-series constituents in the PCE-series plume area has also diminished substantially over the past 5 years. The remaining constituents above applicable New York State groundwater quality standards are limited to cis-1,2-DCE and vinyl chloride in the area of well location #3 and a narrow plume of vinyl chloride that extends southwesterly to well location #6. The increase in the rate of decline in concentrations of PCE-series plume constituents suggests that the combined effects of physical dilution by groundwater flowing through the former source area and biodegradation are significantly greater than the rates of desorption and back diffusion, including under natural groundwater flow conditions with the extraction wells turned off.

Evidence of Plume Area Transformations

Decreases in PCE-series parent concentrations and/or PCE-series daughter product generation (expressed on a molar basis) serve as evidence of trends in transformations of the PCE-series groundwater plume. The isoconcentration
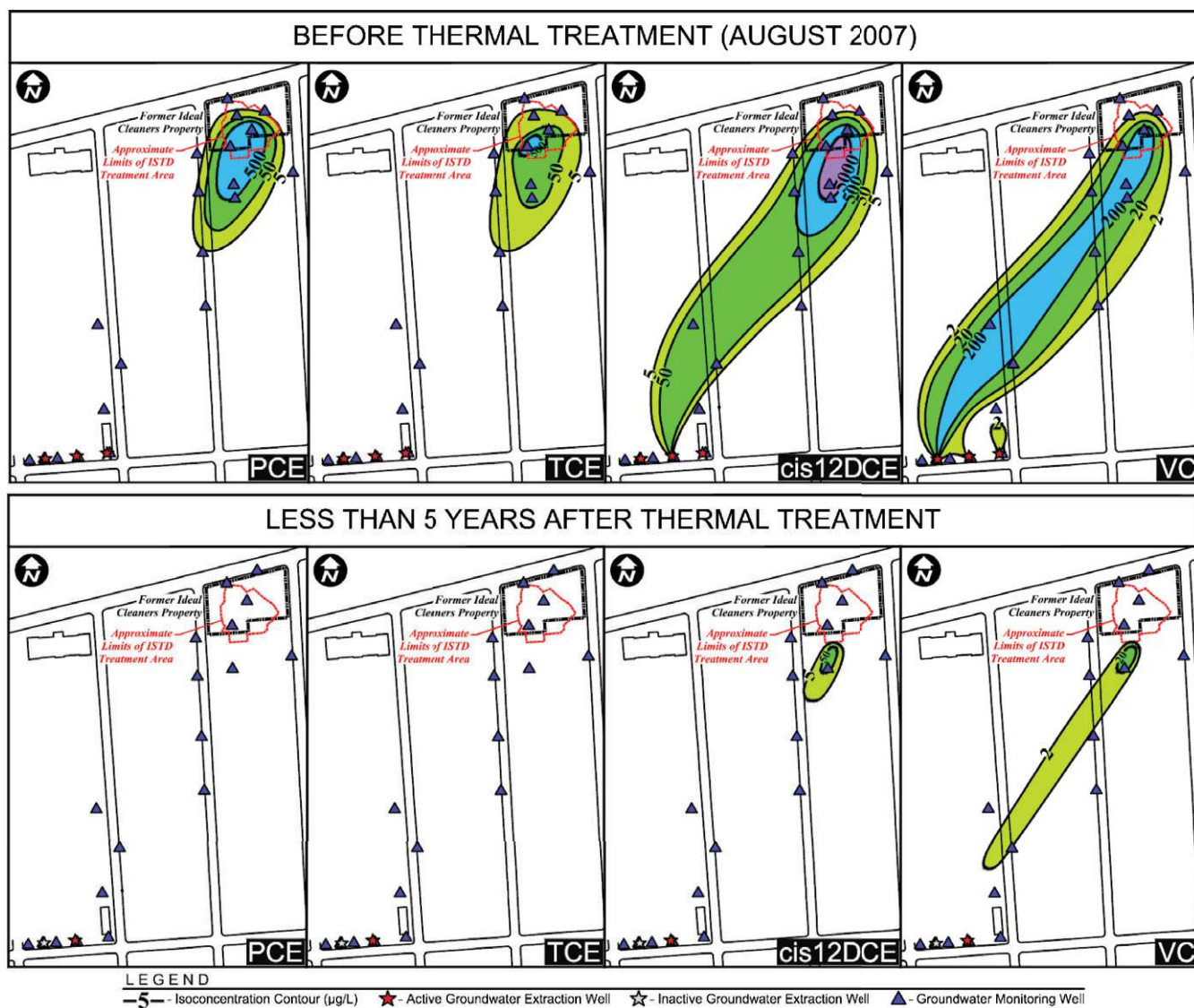

Figure 7. Dissolved plumes of PCE and its degradation products (TCE, *cis*-1,2 DCE, and VC) before and less than 5 years after thermal treatment.

contour maps for PCE and its daughter products indicate a relatively abrupt decline in PCE and TCE groundwater concentrations directly downgradient from the former PCE source area, whereas degradation of *cis*-1,2-DCE and vinyl chloride is less pronounced. This spatial pattern was evident before and after the source removal and is consistent with the relatively slow rate of dechlorination of *cis*-1,2-DCE and vinyl chloride as compared to PCE and TCE.

Over the past 5 years, the molar fractions of *cis*-12-DCE, vinyl chloride, and ethene in the plume area have indicated a shift in the speciation of the plume from *cis*-1,2-DCE to vinyl chloride and ethene. The data indicate a declining temporal trend for each constituent with distance along the plume, supporting an overall strong reduction in PCE-series mass (Groundwater Sciences P.C. and Groundwater Sciences Corporation 2014).

Monitoring of transformation indicator and general inorganic water quality parameters indicate that groundwater quality conditions favorable to anaerobic degradation have been maintained within the plume area. The geochemical conditions within the plume include negative ORP (typically -50 to -100 mV); low dissolved oxygen, typically less than 1 milligram per liter (mg/L); and low nitrate, typically less than 1 mg/L. Throughout the monitoring period, temporal variations in pH have been limited with values that are close to neutral, which likely reflects the natural background buffering capacity of the upper aquifer groundwater with alkalinity values generally between 400 and 600 mg/L. A review of the relative concentrations of iron, manganese, and sulfate and the presence and concentration of methane (typically less than 1 mg/L) suggest that sulfate reduction is probably a more active mechanism than iron/manganese reduction or methanogenesis. These degradation pathways likely vary both spatially and temporally due to the heterogeneity of the texture of the aquifer solids and seasonal variability in recharge and saturated thickness. Many of the
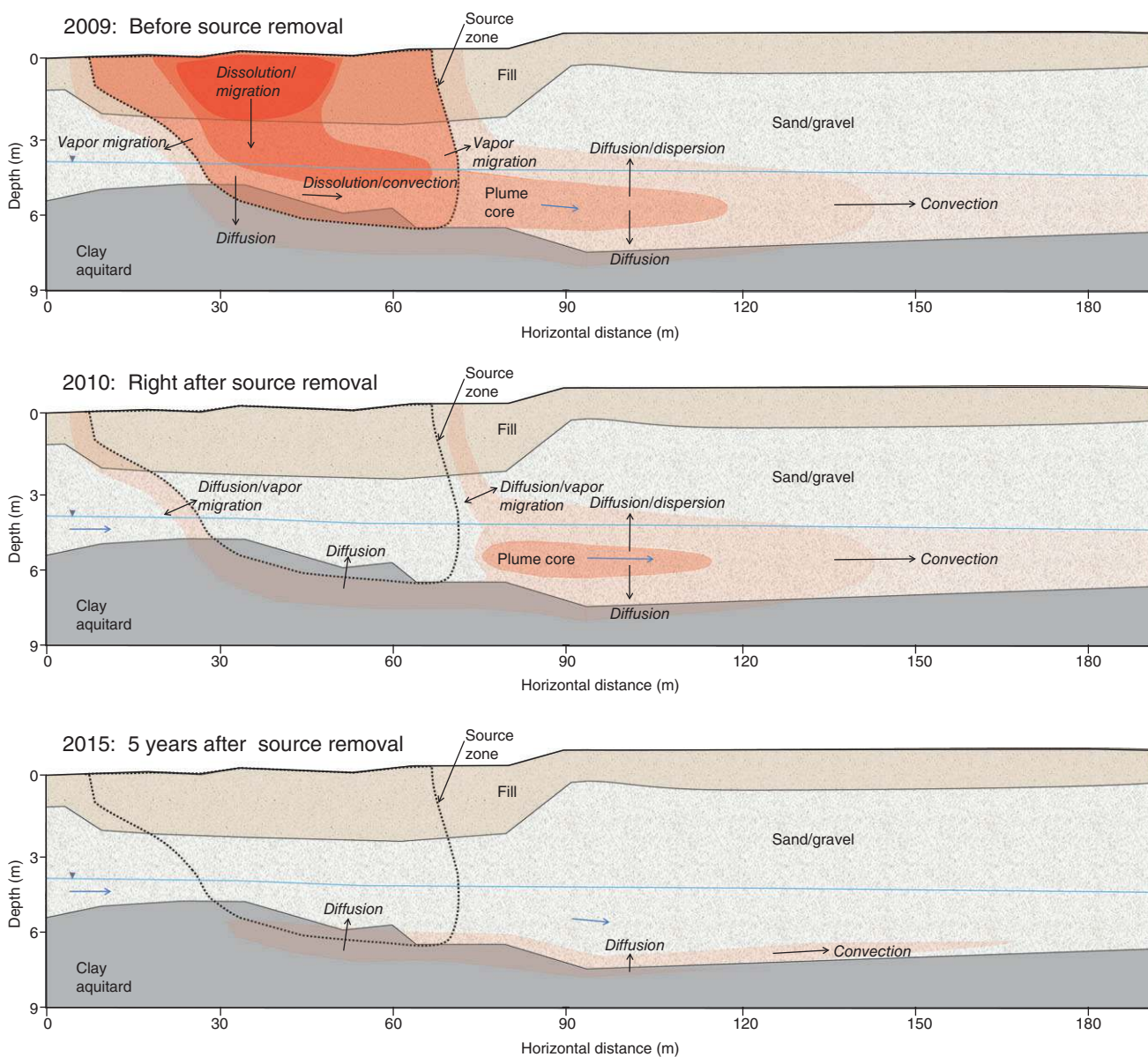
Figure 8. Conceptual model of natural attenuation processes leading to rapid plume shrinkage after source zone mass reduction. The conceptual situations are depicted for before and right after thermal treatment and 5 years after treatment.

transformation and general inorganic water quality parameters exhibit some temporal variability without a discernible increasing or declining trend. This variability is likely due to variations in seasonal water levels relative to the oil smear zone and to the sampling of fully-screened wells that may span both reducing and more localized oxidizing zones. The low concentrations of methane and the seasonal recharge of more oxygenated water is consistent with microbial analyses of groundwater samples in October 2007, May 2011, and August 2011 that indicate spatial and temporal variations in populations of dechlorinating bacteria (*Dehalococcoides spp*), which are generally lower in number than expected given the overall rate of PCE-series plume degradation (see the table in Supplemental Information).

Discussion and Recommendations

Figure 8 illustrates the site conceptual model before, during, and after thermal treatment. The ISTD source treatment removed approximately 1400 kg of PCE mass from the source zone. This resulted in a significant reduction in the mass flux into the downgradient PCE-series dissolved plume in the upper aquifer, estimated to be an 800-fold reduction (2.9 orders of magnitude) in mass discharge compared to conditions prior to ISTD treatment. Conditions in the aquifer were favorable for PCE degradation (mostly anaerobic), and over the past 5 years, since completion of the ISTD source removal, the downgradient PCE-series plume has been nearly eliminated. Concentrations of PCE-series constituents in the plume that are above applicable groundwater quality standards no longer extend to downgradient extraction wells formerly used for hydraulic containment of the plume.

Our hypothesis is that a combination of biological degradation and other attenuation mechanisms result in the removal/attenuation of dissolved PCE-series mass at a greater rate than the rate of back-diffusion and desorption mass transfer mechanisms under actual groundwater recharge and groundwater flow velocities. In other words, the natural attenuation processes are robust enough to overcome the back-diffusion from zones not affected directly by the source treatment—particularly the clay layer at the base of the aquifer. For this site, the presence of favorable geochemical conditions and the pattern of the PCE and degradation product concentrations indicate that biological activity plays a major role in the attenuation of the chemicals.

In settings where attenuation is already occurring within a plume at substantial rates, the reduction of the net mass flux from source areas can result in significantly accelerating cleanup timeframes of the associated groundwater plumes. Back diffusion is not necessarily a barrier to reaching groundwater goals as clearly demonstrated by this example.

At the time of this article, groundwater concentrations in the PCE-series plume were reduced such that the operation of the groundwater extraction and treatment system formerly used to contain the plume has been discontinued with the concurrence of the State Regulatory Agency, and a monitored natural attenuation remedy is now in place. The operation and maintenance of the groundwater extraction and treatment system has been estimated at $125K annually.

Supporting Information

The following supporting information is available for this article:

Table S1. Results of Microbial Analyses (CENSUS—cells/mL) for *Dehalococcoides spp.* Well locations are shown in Figure 2.

Figure S1. Cross-section view of the PCE source zone, showing ISTD hearer borings and extraction wells.

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