Groundwater
Monitoring&Remediation

How Effective Is Thermal Remediation of DNAPL Source Zones in Reducing Groundwater Concentrations?

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Abstract

Dense nonaqueous phase liquid (DNAPL) source areas containing chlorinated volatile organic compounds (cVOCs) such as trichloroethene (TCE) and perchloroethene (PCE) often give rise to significant dissolved plumes in groundwater, leading to the closure of downgradient water supply wells and creating vapor intrusion issues in buildings located above the plume. Hydraulic containment via pump-and-treat has often been implemented to limit migration but must continue indefinitely. Removal of the DNAPL source area by means such as in situ thermal remediation (ISTR) offers the potential to diminish or end the need for hydraulic containment if the associated dissolved plume attenuates sufficiently following source removal. A question often raised is whether this occurs or whether the back diffusion of contaminants from secondary sources such as low-permeability lenses in the dissolved plume precludes it. The authors conducted DNAPL source removal using ISTR at dozens of sites. This paper presents a compilation of cases—10 separate DNAPL source areas at five project sites—where data indicate that the implementation of a thorough ISTR in a DNAPL source area can result in the attenuation of the associated dissolved plume, such that in several cases, long-standing pump-and-treat systems could be turned off. Our findings contrast with recent assertions that aggressive source remediation may not be justifiable because dissolved plume concentrations will not decline sufficiently. We show that the application of ISTR can result in the thorough removal of the DNAPL source, effective diminution of dissolved plume groundwater concentrations, and achievement of drinking water standards.

Introduction

In the late 1980s and early 1990s, researchers became aware of the importance of releases of dense nonaqueous phase liquids (DNAPL), such as chlorinated solvents, to the subsurface in giving rise to persistent dissolved contaminant plumes in groundwater (Huling and Weaver 1991; Pankow and Cherry 1996). While DNAPL sources tend to be relatively small in scale (e.g., in the 10s of meters, often similar to the size of the facilities from which the solvents were spilled or discharged), the associate dissolved plumes are often found to be quite long (e.g., up to several kilometers in length) and thereby can contaminate a large volume of groundwater. There are tens of thousands of DNAPL sites in the U.S. alone. Many early remediation practitioners and regulators charged with protecting groundwater employed pump-and-treat (P&T) systems as a means to hydraulically contain and prevent the migration of dissolved chlorinated volatile organic compound (cVOC) plumes. With the then new understanding of DNAPL behavior, however, P&T began to be recognized in most cases as having a very limited impact on reducing source area concentrations due, primarily, to low dissolution rates of the nonaqueous phase liquids. Under effective hydraulic containment, dissolved plumes would not continue to grow, but they would nonetheless persist for hundreds of years, rendering the groundwater nonpotable. It was postulated by some (e.g., Sale and McWhorter 2001) that unless a vast majority of the DNAPL were removed from a source area, the mass flux continuing to emanate from the residual DNAPL would prevent multiple order-of-magnitude reductions in the associated dissolved plume concentrations that are typically required to attain risk-based maximum concentration limits (MCLs). Some reductions in dissolved plume concentrations may occur as a result of natural attenuative processes, such as reductive biodegradation. Even where conditions in the plume are favorable to reductive dechlorination by microorganisms such as *dehalococcoides sp.*, which are capable of depleting cVOCs, the remaining primary and/or secondary source zones may continue to give rise to the plume.

Most available in situ remediation technologies at the time relied upon introducing a liquid reagent such as a chemical oxidant (in situ chemical oxidation or ISCO), reducing agent, electron donor, or surfactant to promote degradation of

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the source, but the efficacy of such fluid injection techniques was found to be only as good as their ability to contact the DNAPL, and rebounding dissolved plume concentrations were frequently observed (e.g., following ISCO injections) (Siegrist et al. 2010). In the late 1990s, some researchers (e.g., Rao et al. 2001) focused on the "architecture" of the DNAPL source zone, specifically whether the spatial distribution of the DNAPL, along with its geological and hydrogeological setting, would make the source zone more susceptible to being removed by in situ remediation technologies. Given subsurface heterogeneity and the associated complexity of DNAPL architecture in many cases, few in situ remediation technologies were viewed as robust enough to be able to achieve a high degree of DNAPL source zone removal. Early practitioners of in situ thermal remediation (ISTR), however, proposed that ISTR was robust enough to be able to remove a high percentage of the DNAPL source in a variety of geological settings if its boundaries had been well delineated (Udell 1996; Newmark and Aines 1997). Several ISTR technologies came into use in the late 1990s and early 2000s, including steam injection and electrical heating by either resistive or conductive means (Davis 1997). Compilations of data from numerous completed ISTR source zone remediations collected by 2007 (Kingston et al. 2010) showed high removals, in many cases comparable to what would have been removed had the sources been able to be thoroughly excavated.

Others, however, pointed to the multicompartmental nature of the dissolved plumes themselves to suggest that even thorough source zone removal may not be adequate to produce significant dissolved plume reductions in many cases (Sale and Newell 2010). They observed that secondary sources often exist within the dissolved plume, that is, lower-permeability lenses and layers into which chlorinated solvents had diffused during the early years after DNAPL release to the subsurface and then from which the cVOCs continued to back diffuse even after the source was removed. Chapman and Parker (2005) examined a dissolved plume isolated from its source zone by installation of steel sheeting around the entire delineated source. Even after such source isolation, viewed as equivalent to having excavated and removed the source, dissolved plume concentrations diminished only by one to two orders of magnitude, not nearly enough to approach drinking water standards. McGuire et al. (2006) reported on dissolved plume concentrations associated with numerous DNAPL source zones, indicating that reductions of one to two orders of magnitude were about as much as might be expected following source zone remediation by bioremediation, ISCO, or ISTR. In a recent State-of-the-Science Review, Sale et al. (2013) concluded that thermal remediation of low-permeability, large-scale DNAPL source zones was not necessarily justifiable.

The purpose of this paper is to report on the results of several ISTR source area remediations on the associated dissolved plumes. ISTR practitioners are typically tasked only with treating the delineated source zones and not with addressing the associated dissolved plumes. Thus, groundwater data have not often been available for the several dozen chlorinated solvent sites at which the authors have performed source area ISTR projects, despite the fact that the stipulated remedial goals within the source zones have been achieved at every site upon completion. Now, with the passage of several years, groundwater data have begun to become available in several cases given cooperation on the part of the responsible parties. Thus, this paper is able to include groundwater data associated with 10 separate source areas (situated at five separate project sites) where the authors designed, constructed, and operated ISTR systems. The results indicate that where the source zone delineation was deemed to have been complete (in nine of the 10 source areas) and thereafter where the source was thoroughly removed by ISTR, the resulting groundwater concentrations were reduced sufficiently (i.e., by >2 to 4 orders of magnitude) to achieve downgradient drinking water concentrations within approximately 5 to 10 years after thermal remediation.

Thermal Treatment Methodology

At each of the ISTR sites presented herein, the primary remediation technology employed by the authors was thermal conduction heating (TCH), also known as in situ thermal desorption (ISTD), a technology invented and initially developed by Shell Oil Co. (Stegemeier and Vinegar 2001). TCH, as practiced by the authors for the treatment of chlorinated solvent source zones, involves the installation of heater elements inside of 7.5 cm (3 in) dia. steel pipes, which are typically installed in vertical borings, often by direct push or rotosonic drilling methods. Typical spacing between TCH borings at cVOC sites is 4.3 to 4.9 m (14 to 16 ft). Electricity is used to power the heater elements, which deliver approximately 1 kW/m of heat over the desired depth interval. Operating temperatures of the heater elements, which are controlled thermostatically, range from near ambient to as high as 600 to 800°C. Heat flows from the heater element to the walls of the steel pipe by radiation, after which, it is transferred from the hot pipes to the surrounding soil primarily by thermal conduction. The relative invariance of soil thermal conductivity on the order of about two for dry soil over a wide range of soil types (Stegemeier and Vinegar 2001) as well as the nearly uniform delivery of power over the length of the heater means that heat is delivered quite uniformly regardless of soil heterogeneity. This leads to relatively uniform heating, provided the target treatment zone (TTZ) is not subject to excessive groundwater flux and associated cooling. Thermal designers employ numerical modeling to predict, for a given site, the optimal placement of heater wells, the need to control groundwater influx, and the amount of power and heating time that will be required. The target temperature for chlorinated solvent sites is most often the boiling point of water (e.g., 100°C at ambient pressure). Experience has indicated that generally, 20 to 30% of the pore water needs to be boiled off to accomplish effective volatilization, steam stripping, and removal of cVOCs from DNAPL source zones, which often require 3 to 5 months of heating, depending on design parameters. During this period, each soil pore is flushed between 300 and 600 times on average by the in situ-generated steam (Heron et al. 2013). TCH is particularly well suited to heating all types of soil above the water table; low- and moderate-permeability soil both above and below the water table; and most types of fractured rock. As the TTZ heats up, steam and contaminant vapors are generated and must be captured via a network of Soil Vapor Extraction (SVE) wells so that the extracted vapors can be collected and treated in an aboveground treatment system. A surface cover is generally installed at the ground surface to prevent fugitive emissions, provide insulation, and shed rainwater. Electric power is brought in off the grid. Further details on ISTD design and operation are available elsewhere (Baker et al. 2009; Heron et al. 2009, 2013).

Methods and Materials

The key attributes of each of the sites are summarized in the following two tables to facilitate the quick comparison between sites. Table 1 focuses on the source area, the thermal treatment utilized to treat the source, and the pre- versus post-treatment contaminant concentrations in the solid samples collected to document source zone reduction.

Table 2 summarizes the plume attributes and the methods used to monitor groundwater concentrations in the plumes.

Case Studies

Case 1: Ohio

At a manufacturing facility in central Ohio, investigation and remediation of chlorinated solvent source areas was undertaken by the responsible parties and overseen by the Ohio Environmental Protection Agency (OEPA) under the State of Ohio Voluntary Action Program. Spills and releases of TCE, 1,1,1-Tetrachloroethane (1,1,1-TCA), and PCE to site soils occurred over several decades of plant operations, resulting in elevated source zone soil concentrations and downgradient groundwater concentrations that exceeded drinking water standards. Three DNAPL source zones were delineated within ~100 m of each other within the plant property. All three were located on the grounds and parking areas just outside the active manufacturing building, and one of the three was only several meters from nearby residences. Site soils are predominantly silty clay derived from glacial till underlain by a glaciofluvial sand and gravel aquifer. The perched water table in the silty clay is generally within 0.6 and 1.2 m of the ground surface; that is, each of the three TTZs for ISTR extended both above and below the water table within the upper 4.6 m of the silty clay (Figure 1). Contaminant concentrations in all soil samples collected within the three source areas prior to and following ISTR (LaChance et al. 2004) are presented in Figure 2 and summarized in Table 1.

TerraTherm, Inc. utilized ISTD to treat the silty clay soil at each of the three source areas simultaneously. Heating began in May 2003 and ended in November 2003 after the

Table 1

Source Area Attributes

Project name, (oversight agency)	Source dimensions: area × depth = volume ($m^2 \times m = m^3$)	Source geology (major strata), type*	Number of TCH wells, depth × spacing (m)	Duration of heating (d), year completed, mass removed (kg)	Target temperature (°C)	Mean pre-treatment cVOC concentration (mg/kg)	Mean post-treatment cVOC concentration (mg/kg)	Reduction in soil concentration (%)
Ohio, (OEPA)	3 Source Areas: (a) 1318 × 4.6 = 6,063 (b) 289 × 4.6 = 1,329 (c) 224 × 4.6 = 1,030 Total = 8,422	Fractured Clay Till: V	Full-length: 138, 5 × 5.3 Short: 68, 1.3 × 2.7	150 to 180 Feb. 2004 NA	99	TCE: 99.7 1,1,1-TCA: 31.9 PCE: 1.51	TCE: 0.070 1,1,1-TCA: 0.045 PCE: 0.363	TCE: 99.9 1,1,1-TCA: 99.9 PCE: 76.0
Syracuse NY (NYSDEC)	3 Source Areas: (a) 1178 × 6.1 = 7,186 (b) 780 × 5.5 = 4,290 (c) 113 × 5.5 = 622 Total = 12,098	Clay marl/ Peat over Mixed Silt, Clay and Sand: III	288, 7.6 × 4.6	330 Oct. 2007 39,090	100	PCE: 2,864	PCE: 4.2	PCE: 99.9
Reerslev DK (Capital Region of Denmark)	2 Source Areas: (a1) 406 × 10 = 4,060 (a2) 236 × 8.75 = 2,065 (b1) 431 × 8.75 = 3,771 (b2) 215 × 7.5 = 1,613 Total = 11,509	Clay Till over Sand & Gravel:III	147, 9-11.5 × 4	169 Dec. 2009 2,400	100	PCE: 78	PCE: 0.01 (non detect in all samples 22 month after shutdown)	PCE: 99.9 – 100
Knullen DK (Region of Southern Denmark)	250 × 10 (top of treatment 4 m bgs) = 2,500	Clay Till over Sand & Gravel: III	45, 11 × 2.8 + 9 SEE wells	107 Oct. 2008 3,500	100	PCE: 337	PCE: 0.55	PCE: 99.8
Endicott NY (NYSDEC, NYSDOH)	1171 × 9.1 = 10,656	Cinder Fill over Sand over Lacustrine Silt: III	Full-length: 225, 9.1 × 3.7 Short: 32, 2.4 × 3.7	192 Apr. 2010 5,600	150 (cinder fill), 100 (balance)	PCE: 125	PCE: 0.04	PCE: 99.9

*Type categorization: Type III = Granular media with moderate to high heterogeneity; Type V = Fractured media with high matrix porosity (NRC 2005; Sale and Newell 2011); NA = Not Available; SEE = Steam Enhanced Extraction.

Table 2
Dissolved Plume Attributes

Project name, (oversight agency)	Plume dimensions: length width depth (m)	Plume geology (major strata), plume type*	Plume hydrogeology: depth to water table (m), groundwater generalized flux* (m/d), generalized conditions	Number of monitoring wells in the dissolved plume, including historic (abandoned) wells	Frequency of monitoring
Ohio (OEPA)	3,700 <200 ~20	Fractured Clay Till over Sand & Gravel: III	7.5 6-12 oxidizing	20	2x/year
Syracuse NY (NYSDEC)	3 Plumes: Each <100 < 50 ~15	Clay marl/Peat over Mixed Silt, Clay and Sand: III	1.0 0.008-0.13 reducing	3 Plumes: Area B-1: 2 Area B-3: 1 Area MW-3D: 2	4x/year
Reerslev DK (Capital Region of Denmark)	2,400 ~240 ~13	Sand & Gravel over Clay over Chalk: III over V	23 5.1 oxidizing	>8	1x/year Selected wells 2x/year
Knullen DK (Region of Southern Denmark)	>900 ~75 ~20	Clay Till over Sand & Gravel: III	5.5 0.01-0.02 oxidizing/reducing	>23	2x/year
Endicott NY (NYSDEC, NYSDOH)	360 50 2.4	Sand & Gravel with Silt Layers over Lacustrine Silt: III	4.0 1.5 reducing	~10	4x/year

*Type categorization: Type III = Granular media with moderate to high heterogeneity; Type IV = Fractured media with low matrix porosity; Type V = Fractured media with high matrix porosity (NRC 2005; Sale and Newell 2011).

agreed-upon soil remediation standards had been achieved. Treatment of the underlying groundwater plume was not a required goal of the ISTD project. At one of the TTZs, the responsible parties deployed air sparging/SVE following the completion of ISTD and operated it for several years to address the underlying sand and gravel beneath a long-standing storm drain, which was not delineated as a secondary source zone until several years following the ISTD project. Had it been identified prior to ISTD, it could have been readily incorporated into the thermal TTZ.

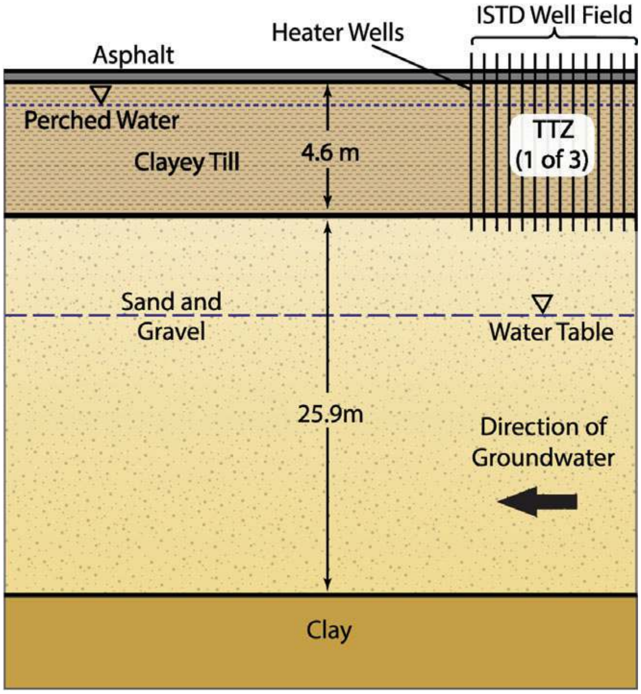


Figure 1. Ohio conceptual site model.

While at the Syracuse, New York site presented in this paper, each source area has its own distinguishable dissolved plume, the groundwater data for the three source areas at the Ohio site are presented together here because each of the three source areas contributed to the same dissolved plume in the underlying high-flux (6 to 12 m/d) sand and gravel aquifer (Figure 3). Twenty groundwater wells have been monitored in the upper 2.3 km portion of this dissolved plume. All 11 wells on the source property and all six wells within the uppermost 0.6 km (0.5 mi) of the plume are now below unrestricted potable use standards (UPUS) of 5 μg/l, that is, drinking water standards (TRC 2014). Figure 3 shows the locations of the off-property compliance wells relative to the source zones and where groundwater concentrations below UPUS have been attained for the requisite four successive sampling rounds. As the monitoring wells are so numerous, graphs of concentration versus time for each of the 20 monitoring wells are provided in the Supporting Information (Figures S1 through S20). Table 3 presents the maximum pre-ISTR groundwater concentrations and recent concentrations in monitoring wells within the source and in the first 0.6 km of the plume, showing that the nearfield plume has attained UPUS concentrations and maintained them through repeated sampling events. Downgradient portions of the >3-km long plume are generally showing very low/declining concentrations but have not yet all achieved UPUS. Groundwater data deeper in the system are not reviewed here because the deeper aquifer, which occurs about 30 m beneath the source property, is not contaminated and is separated from the shallow aquifer by an aquitard that extends beneath the plume (TRC 2014).

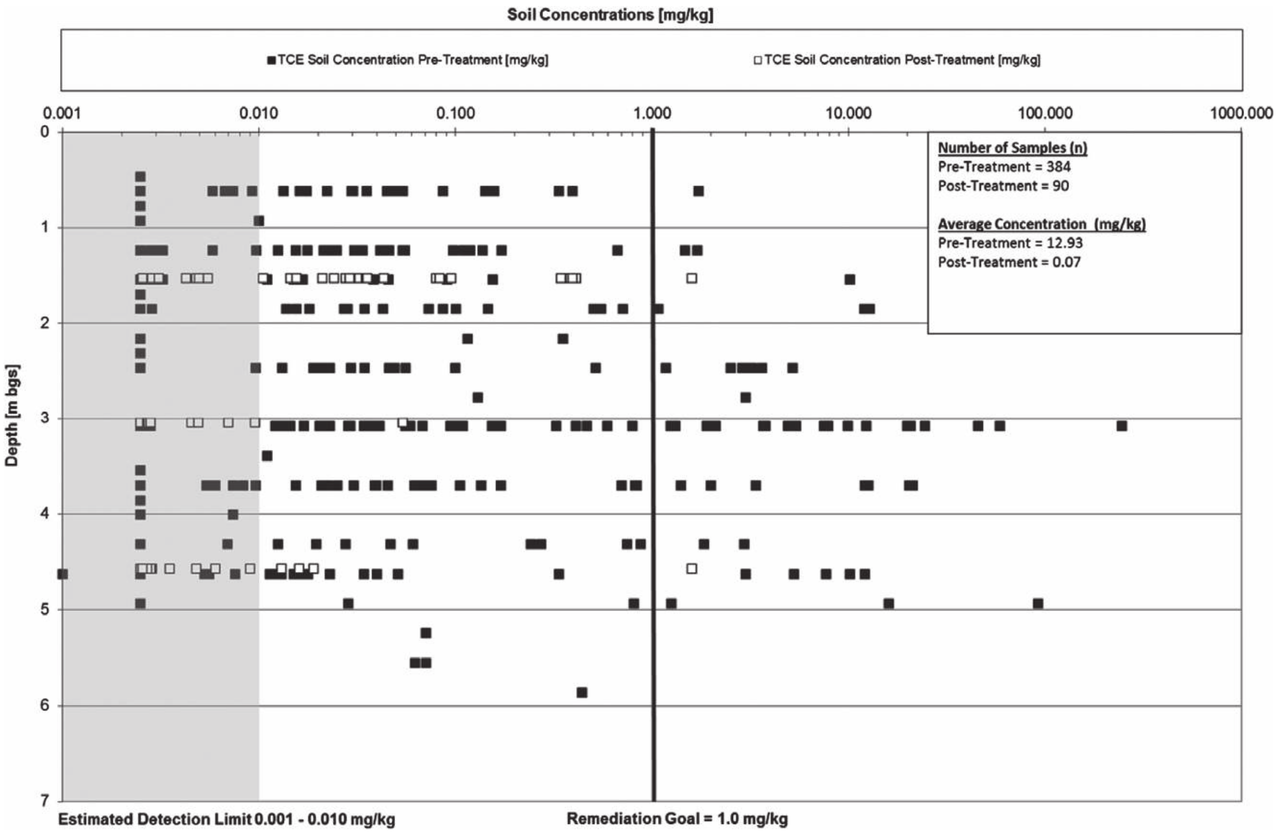


Figure 2. Ohio: Source areas soil concentrations pre- and post-thermal remediation.

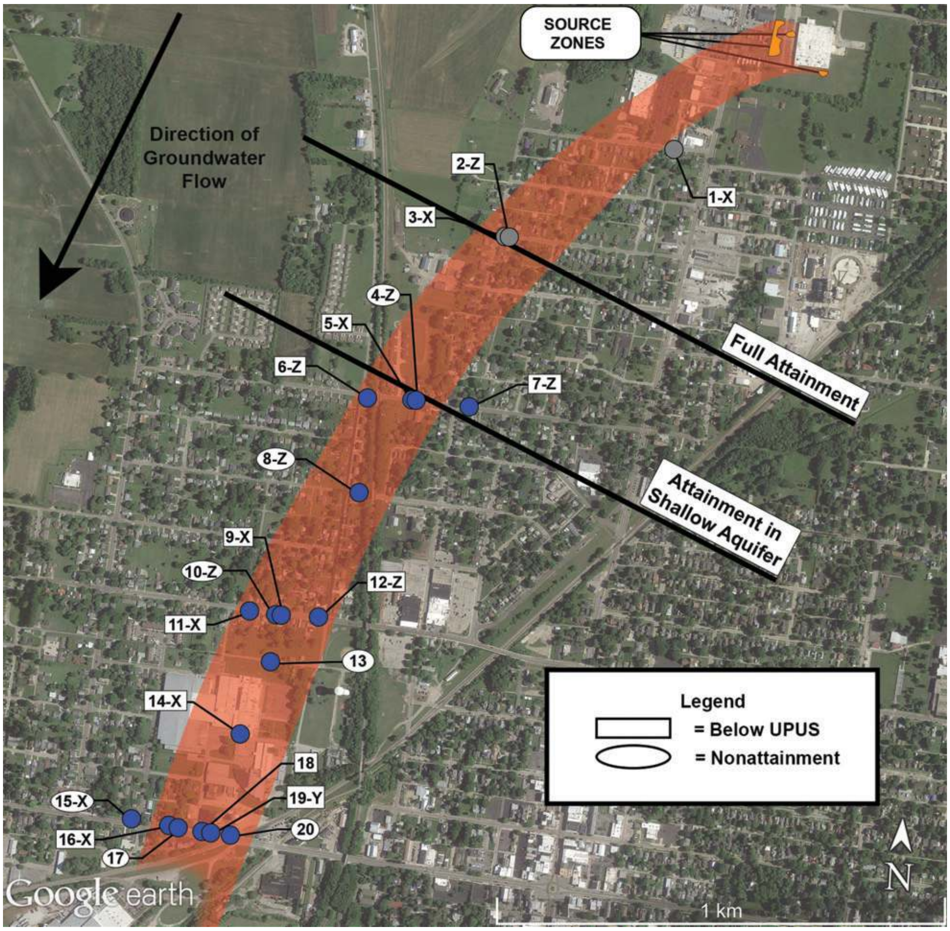


Figure 3. Ohio plume monitoring well locations. UPUS = unrestricted potable use standard.

In summary, the upper 1.0-km portion of the groundwater plume has been restored to drinking water standards after approximately 10 years following source removal, and the mid-field portions of the plume are close to being restored (Table 3).

Case 2: Syracuse, New York

A former facility on Midler Ave., Syracuse, New York manufactured industrial dry cleaning equipment. PCE was the primary cVOC spilled or released from the site, which is under the jurisdiction of the New York State Department of Environmental Conservation (NYSDEC), Site No. C734103. Four DNAPL source areas were delineated, with contamination residing in the following layers (from the ground surface): fill, clay and clay marl with interbedded peat, over mixed silty clay, silty sand, sand and gravel, and silt layers (Figure 4). It was decided to excavate the smallest of the four areas and place the excavated material over one of the larger areas. Delineation of the three source areas identified for thermal treatment was based upon those locations where pre-treatment soil samples had total cVOCs > 31,200 µg/kg (C&S Engineers 2006). Note that this standard was the least stringent of the cases presented in this paper. Three ISTD wellfields, as was the case in Ohio, were installed and operated simultaneously from November 2006 to October 2007. Contaminant concentrations in soil samples collected within the source areas prior to and following ISTR are presented in Figure 5 and are summarized in Table 1. As in Ohio, the authors' assigned task was to treat the source zones and not the associated groundwater plumes. The site owner's consulting firm, C&S Engineers, investigated the conditions in the dissolved plumes and concluded that they were conducive to monitored natural attenuation (MNA) (Heron et al. 2010).

TerraTherm, Inc. installed 288 ISTD wells and 25 vapor extraction wells in areas B1, B3, and MW3D. Because a large contaminant mass was anticipated, a thermal oxidizer was utilized to treat the extracted vapors. Altogether, 39,090 kg of contaminant mass was extracted and treated over a period of 11 months, and subsequently, NYSDEC accepted the achievement of the Specific Soil Cleanup Objectives.

The three source areas treated with ISTD (designated Areas B1, B3, and MW3) are shown in Figure 6 along with

Table 3
Ohio Site: Groundwater Concentrations Pre- and Post-Thermal Remediation

Compliance wells	Maximum pre-thermal concentration			Most recent year's concentration data			Consecutive sampling events below UPUS (<5 µg/l)
	TCE	1,1,1-TCA	PCE	TCE	1,1,1-TCA	PCE	
Source:		(µg/l)			(µg/l)		
All 11	**34**	**6.5**	2.1	1.9	0.3	<1.0	17
Plume:							
1-X	**469**	**15**	2.0	4.0	1.1	1.0	5
2-Z	**6.7**	**6.7**	**6.7**	1.0	1.0	1.0	15
3-X	**93**	**34**	3.3	2.7	1.2	1.0	5
4-Z	**83**	**29**	4.0	**9.3**	1.6	1.0	
5-X	**128**	**23**	2.0	3.0	0.6	1.0	5
6-Z	1.5	1.5	1.5	1.0	1.0	1.0	27
7-X	3.1	2.9	3.1	0.3	1.0	1.7	27
8-Z	**61**	**22**	2.0	**7.0**	1.1	1.0	
9	**53**	**18**	1.7	**5.0**	0.8	1.0	
10-Z	**53**	**20**	1.7	**5.0**	**8.8**	1.0	
11-X	**13**	**7.0**	1.0	1.3	0.4	1.0	9
12-Z	**5.1**	2.9	2.9	1.0	1.0	1.0	26
13	**30**	**10**	1.2	3.1	0.5	0.6	1
14-X	**15**	**5.1**	1.7	3.4	0.6	0.7	2
15-X	3.1	1.1	1.0	0.3	0.5	1.0	13
16-X	**11**	3.0	1.0	4.3	0.8	1.0	1
17	**11**	3.5	1.0	4.5	1.1	1.0	1
18	**16**	**7.6**	1.0	4.0	0.8	0.3	1
19-Y	**16**	**5.8**	1.0	**9.0**	1.6	1.0	
20	**6.6**	2.4	**10**	1.2	1.0	1.3	10

Values in boldface are >UPUS. UPUS = unrestricted potable use standard.

the locations of various downgradient monitoring wells referred to in the following paragraphs. A cross-section (C-C') representative of the three source areas and their associated dissolved plumes is depicted in Figure 4. PCE/TCE impacts within the source areas were relatively shallow (<6 m, primarily within peat and marl layers). The high Total Organic Carbon (TOC) content of the peat soil was expected to have a significant inhibitory impact on the mobility of the cVOCs and the partitioning of the cVOCs to groundwater (C&S Engineers 2006).

Area B1: This source area had pre-treatment soil concentrations as high as 2,500,000 µg/kg PCE. Total cVOC in groundwater was 28,710 µg/L at SB-13-2, 18 m (60 ft) downgradient from Area B1. MW-14D, which is 11 m (37 ft) from SB-13-2, has been almost clean over the last 2 years, with VC only slightly above the Class GA Standard of 5 µg/L (Figure 7a). MW-9D, which is about 60 m (200 ft) downgradient (and usually, although not always, slightly cross-gradient to the west), had very low pre-thermal PCE, 1,2-DCE, and vinyl chloride (VC) concentrations but has

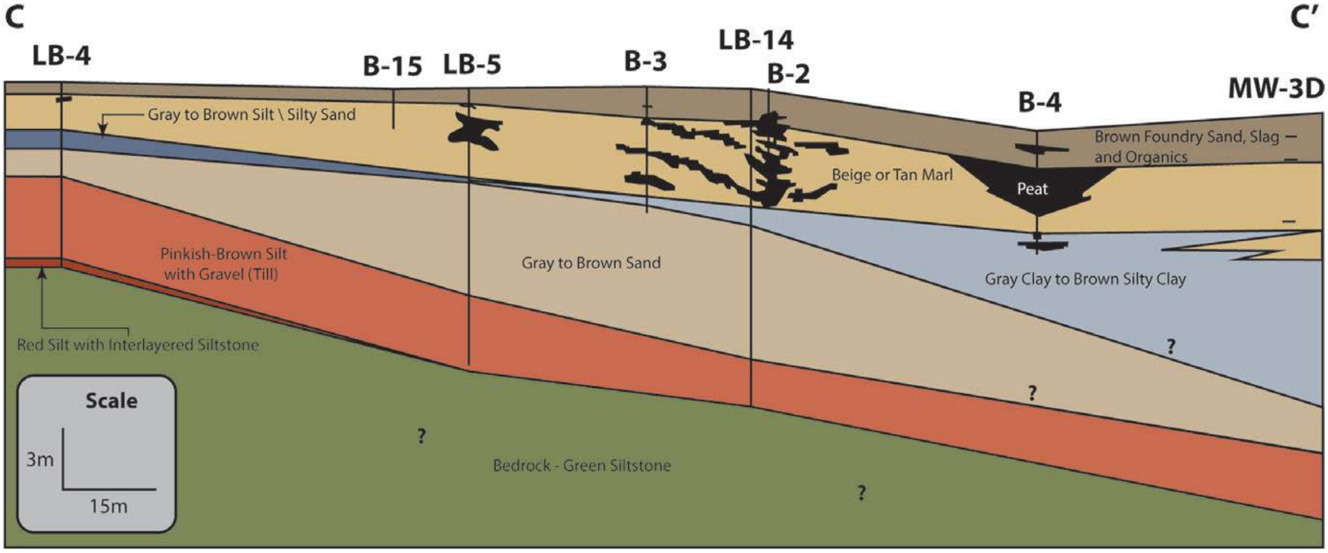


Figure 4. Syracuse, New York, conceptual site model.

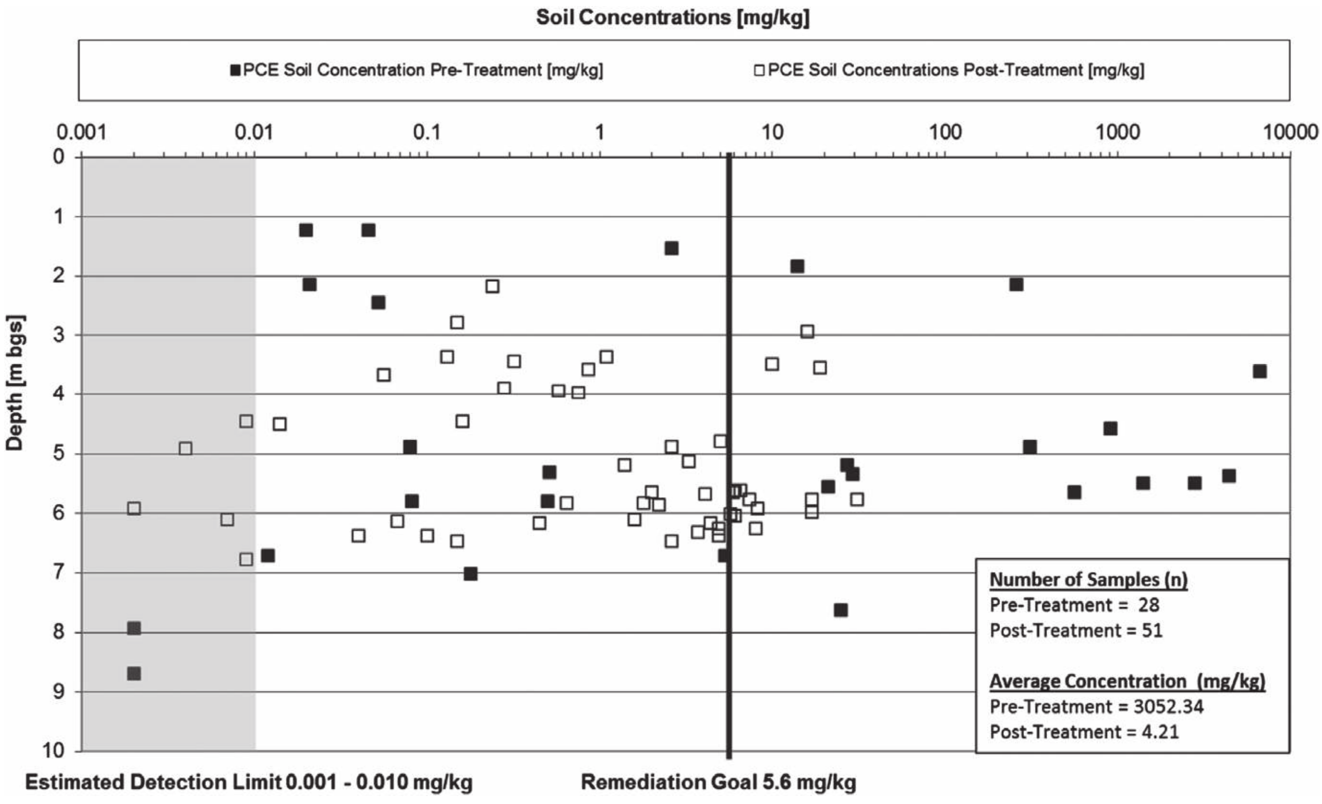


Figure 5. Syracuse, New York: Source areas soil concentrations pre- and post-thermal remediation.

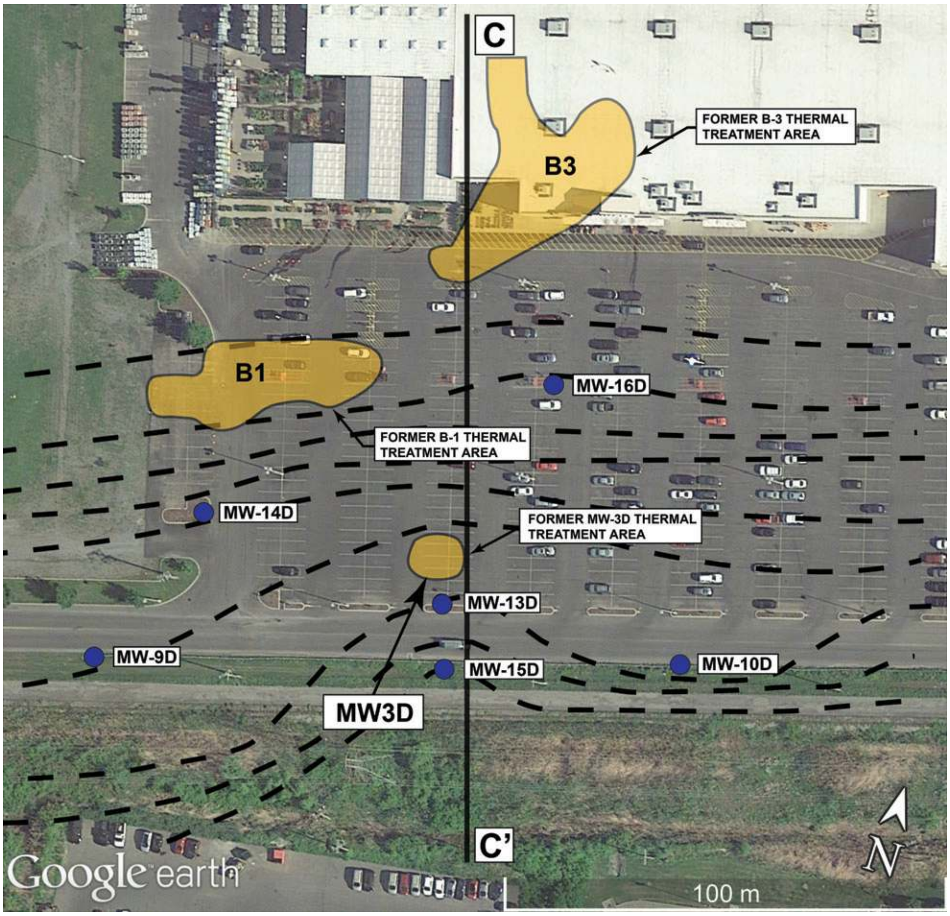


Figure 6. Syracuse, New York source/plume map.

been below the standard in the last 2 years for which data are available (i.e., 2013 to 2014).

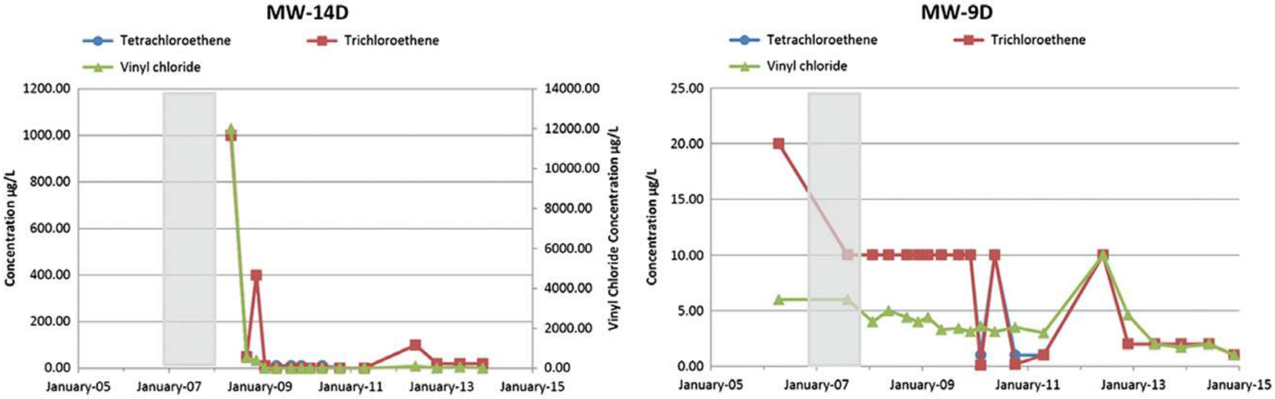
Area B3: The only pre-treatment groundwater concentrations are at SB-12-1 (~34 m [~112 ft] downgradient), where total cVOC was 2,161 μg/L. However, post-treatment groundwater data from MW-16D, only 6 m (20 ft) from where SB-12-1 was and which had somewhat elevated concentrations in 2008 when it was installed, has remained below standards since then (Figure 7b). *N.B.:* MW-10D, about 120 m (390 ft) south and 9 m (30 ft) cross-gradient to the east of Area B, has had low but significant 1,2-DCE and VC concentrations (in the hundreds of μg/L) even before thermal treatment that have not changed much over the years since thermal. As it is often cross-gradient and is situated within what was a portion of the former manufacturing facility, MW-10-D is not believed to be located in a plume that emanated from the former B3 source; so, it is omitted from Figure 7b.

Area MW3: This is a very small source area (10 x 12 m [33 x 39 ft]). MW-13D, which is 8 m (26 ft) downgradient of Area MW-3, had sub-1000 μg/L concentrations of 1, 2-DCE and VC pre-thermal, which then went up during thermal to as high as 3,400 μg/L for 1,2-DCE and 21,000 μg/L for VC, but which have remained as high as 1,900 μg/L and 3,200 μg/L, respectively, over the past 2 to 3 years (Figure 7c). MW-15D, which is ~20 m (66 ft) directly downgradient of Area MW-3 is clean, but no pre-treatment data are available for it (Figure 7c). It may be that the very small source area that was delineated at Area MW3 was too limited to fully encompass the DNAPL source at this location. Thus, the poor results for Area MW3 are the exception to the stronger results presented elsewhere in this paper, where ISTR fully removed the more generously-delineated sources. Alternatively, it may be that the high TOC and clay content at this site has contributed to significant back diffusion from secondary sources lying outside the delineated TTZ. Information concerning the basis for MNA is provided elsewhere (Heron et al. 2010).

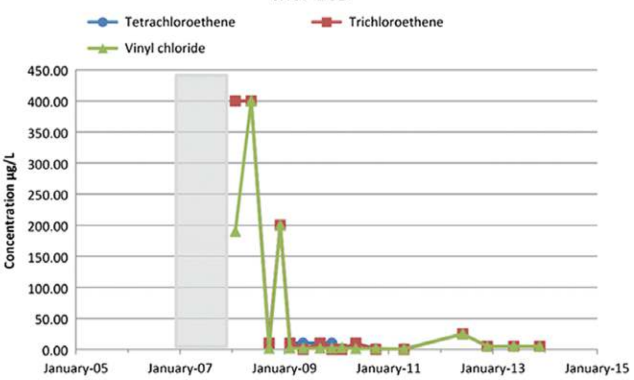
Case 3: Reerslev, Denmark

In Reerslev, Denmark, a source area (hotspot) associated with a former industrial dry cleaning firm was present in a low-permeability clay till layer, with PCE concentrations in soil as high as 700 mg/kg. The source was situated in a residential area with single-family houses and partly beneath an existing graveyard adjacent to a church listed on an historic registry. The contamination caused a serious risk to the Solhoej municipal groundwater production wellfield, one of the most important in Denmark, supplying drinking water to 50,000 homes in the Copenhagen metropolitan area. The low-permeability geology of the DNAPL source area and its location immediately adjacent to residences and the graveyard left only a few realistic remediation alternatives. In addition, very strict clean-up criteria were essential to reach the objective of eliminating the risk to the groundwater production wells (Baker et al. 2010).

(a) Area B1



(b) Area B3



(c) Area MW3

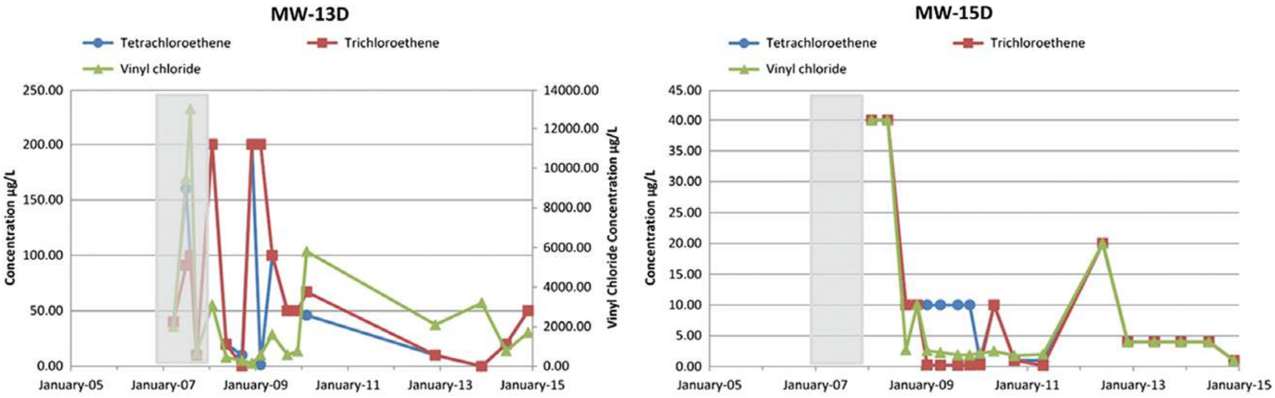


Figure 7. Syracuse, New York groundwater concentrations pre- and post-thermal remediation in plumes associated with each of the three source areas, Area B1, Area B2 and Area MW3. Shaded bar indicates period of thermal remediation.

Risk assessment calculations had shown that a large contaminant mass removal itself would not reach the goal of eliminating the risk to the valuable groundwater aquifer. To reach the goal of the remediation, all DNAPL at the site had to be removed, and the post-treatment soil concentrations of cVOCs had to be <1 mg/kg in the entire area. It was estimated that ~34.6 kg/y of contaminant mass was discharging from the source at the time when the source remediation technology was being selected, as indicated in Figure 8. By reducing the contaminant concentration within the 1,300 m^2 source area to 0.1 mg/kg, it was estimated that a 50-fold reduction, to 0.7 kg/y, of the mass discharge from the source would occur (Christensen et al. 2009).

The complex geology of the area consists of 8 to 10 m (26 to 33 ft) of clayey till underlain by an approximately 15 m (49 ft)-thick unsaturated zone consisting of alternating layers of coarse-grained glaciofluvial deposits. About 25 m (82 ft) below ground surface (bgs), a thin and discontinuous clay layer comprises the bottom of a shallow secondary aquifer with a seepage velocity of ~0.5 m/d. Beneath it is situated a very high-yielding primary aquifer in a thick layer of Danien bryozoan chalk (and having a seepage velocity of 5.1 m/d). Subslab ventilation of the houses was implemented in 2002 to prevent health risks to the families living in the vicinity. To prevent further spreading from the hotspot area, an SVE system was established in the unsaturated zone in 2005 simultaneously with a P&T system in the secondary aquifer. These measures effectively cut off the source from the plume; however, results from several groundwater model simulations clearly showed that due to diffusion limitations,

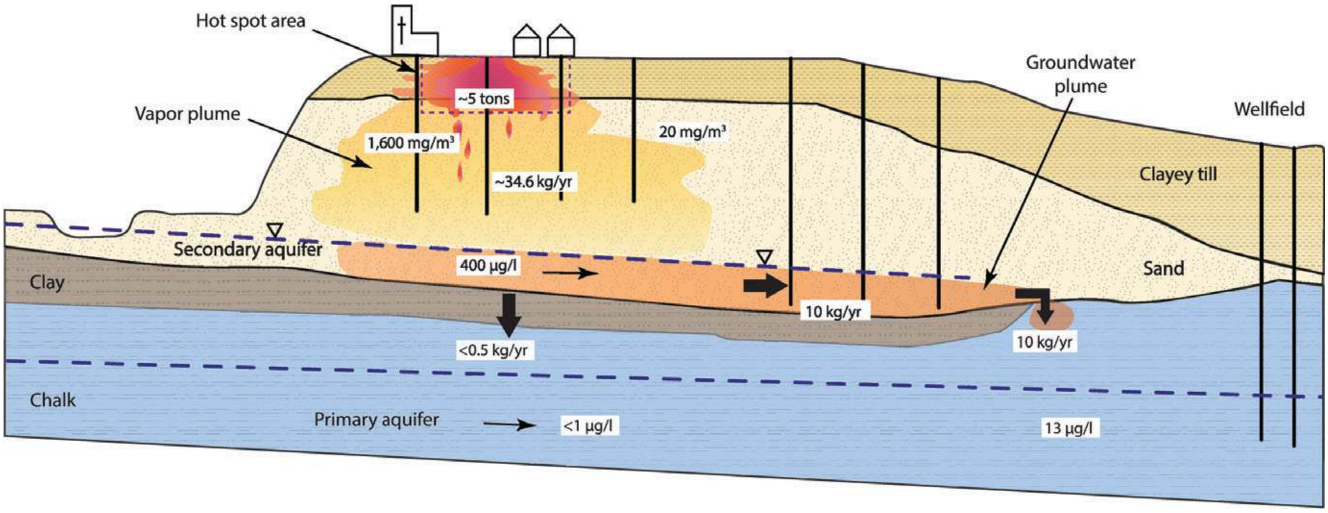


Figure 8. Reerslev, Denmark conceptual site model. Indicated contaminant mass in source (tons), concentrations (µg/l, mg/m^3) and estimated mass fluxes (kg/yr) were prior to thermal remediation. Following thermal remediation, mass flux from source was estimated to have been reduced to <<0.7 kg/yr.

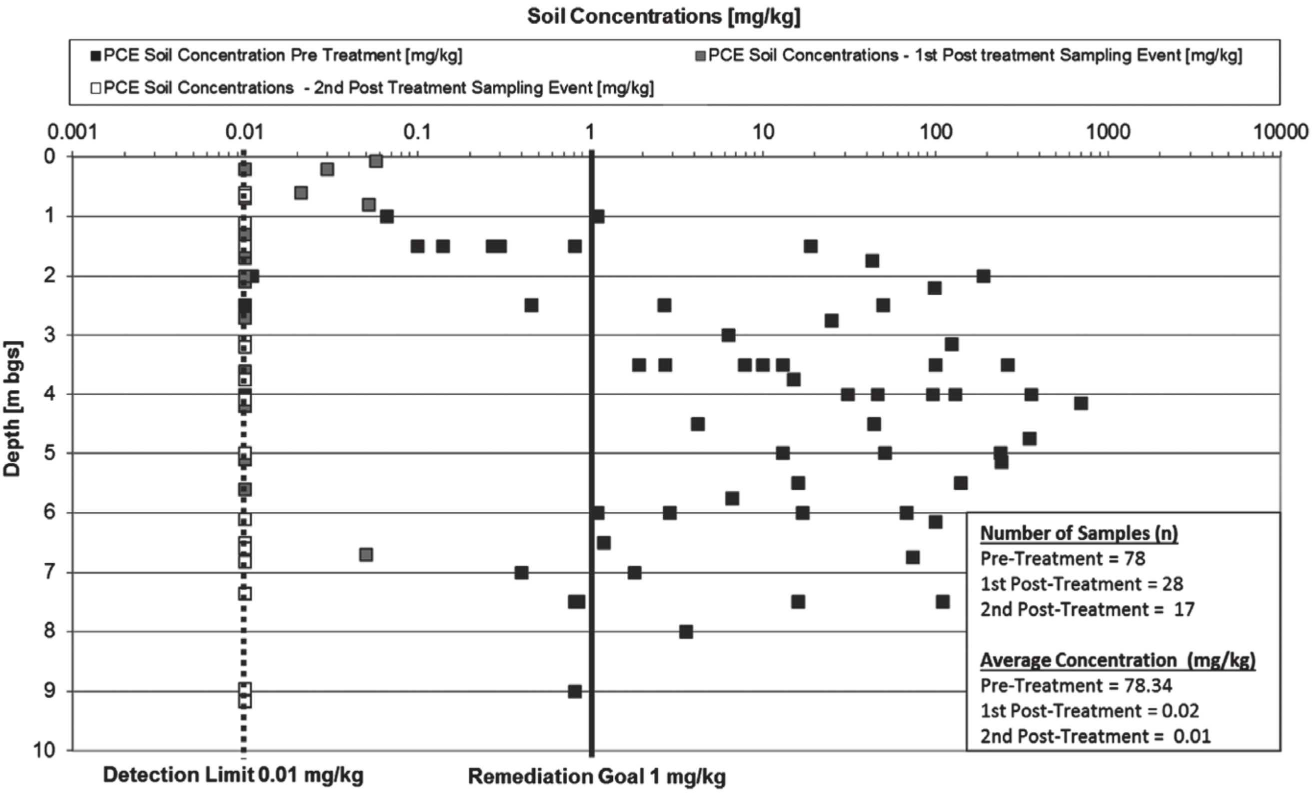


Figure 9. Reerslev, Denmark: Source areas soil concentrations pre- and post-thermal remediation.

the operation of SVE and P&T for protecting the municipal wellfield would have needed to continue indefinitely, and the source zone thus had to be removed.

The selected technology was thermal remediation by ISTD. A soil volume of 11,500 m^3 was treated with 147 heater wells, located in two separate but side-by-side TTZs. The heating period was 169 days, from May until November 2009. Over 2,400 kg of PCE were recovered. Pre- versus post-treatment soil concentrations within the TTZs are presented in Figure 9 and summarized in Table 1. The data indicate >99.98% removal of PCE, with post-treatment soil concentrations <0.05 mg/kg PCE relative to the treatment goal of 1.0 mg/kg PCE (Baker et al. 2010). Results of a second post-treatment sampling round completed 22 months after shutdown of the thermal system (when soil temperatures were close to ambient) documented maximum and average PCE concentrations below the laboratory detection limit of 0.01 mg/kg (Nielsen et al. 2012). Thus, it is expected that the mass discharge following thermal remediation was reduced to much less than 0.7 kg/year.

Measurements of post-thermal remediation of low and stable cVOC concentrations in the unsaturated zone led to

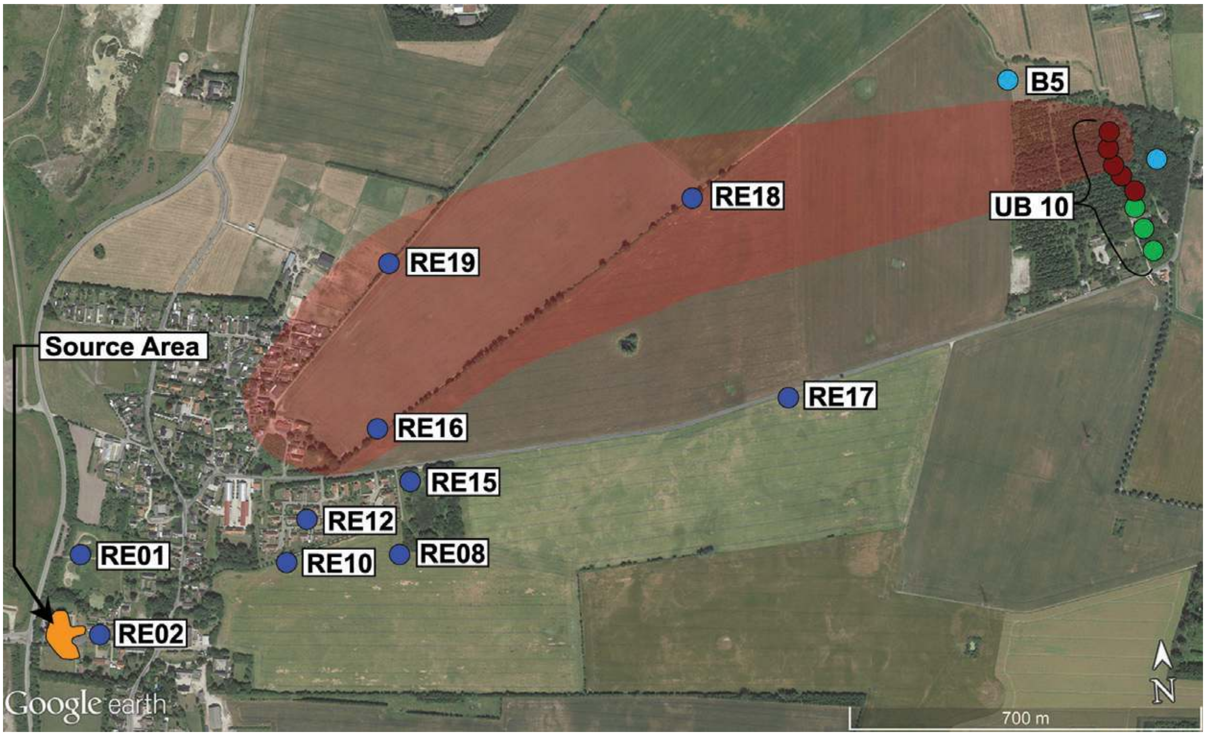


Figure 10. Reerslev, Denmark: Source and plume monitoring well and production well locations.

the shutdown of the SVE system in March 2012 following agency approval. Evaluations had determined that passive ventilation beneath the homes is sufficient. Additionally, the P&T system in the secondary aquifer was shut off with agency approval in April 2012 (NIRAS 2014) .

Figure 10 shows the locations of the source (at RE02) and the monitoring wells within the plume (RE12, RE16, RE19, and RE18). The monitoring well at the municipal production wellfield is designated UB10. As the data indicate in Figure 11, concentrations at RE12, in the nearfield portion of the plume, had begun declining after implementation of SVE and P&T and approached drinking water standards of < 1 μg-PCE/L within the plume. Further downfield, at RE16, RE19, and RE18, a similar pattern is observed. Groundwater data collected at UB10, which had been as high as 3.1 μg/L PCE and 3.19 μg/L sum chlorides in 2009, dropped below the drinking water standard of 1.0 μg/L after thermal and have remained below the standard ever since. Note that concentration plots for the other wells shown in Figure 10 are not provided because they remained below the 1.0 μg/L standard prior to and following thermal. Both the P&T and SVE wells were shut off in 2012 (NIRAS 2014).

Case 4: Knullen, Denmark

At a site in Odense, Denmark, a similar story unfolded following the ISTR treatment of a PCE source area. There, the source area resided beneath an operating dry cleaner facility, which had to remain in operation throughout the implementation of ISTR. All treatment was conducted under the dry cleaner building with extremely limited access for drilling. The DNAPL TTZ extended through fill and clay till to a depth of 11 m bgs, where the clay till was underlain by a high-yielding sandy aquifer. The source zone contained an estimated 3,500 kg of PCE. The contaminants had migrated from the bottom of a leaking separation tank located 4 m bgs through 7 m of till clay down into a high-yielding sandy groundwater aquifer (Figure 12). The site was remediated by a combination of ISTD to address the low-permeability clay till and steam-enhanced extraction (SEE) for the underlying aquifer. A critical groundwater production field supplying more than 100,000 citizens is located 1 km from the site in a downgradient direction. The PCE plume from the site reaches almost to this field. The goal of the thermal remediation was the removal of the DNAPL hot spot to save the local groundwater resource (Region Syddanmark 2012).

The area of the source zone was 250 m^2, with a total remediated TTZ volume of 2,500 m^3. Heat was supplied by 45 ISTD borings and nine steam injection wells. The mobilized contamination was captured by more than 60 vacuum borings in the fill and clay and three multiphase extraction wells in the aquifer.

Pre- versus post-treatment soil concentrations within the TTZ are presented in Figure 13 and summarized in Table 1. While the average pre-treatment soil concentration in the source zone was 337 mg PCE/kg, the average post-treatment concentration was 0.55 mg PCE/kg. Thus, the overall remediation efficiency within the TTZ was 99.8%.

Locations of the monitoring wells relative to the plume are depicted in Figure 14. Three months prior to the onset of thermal remediation (March 2008), PCE concentrations in groundwater at E-1/E-4/I-5/B-402 within the source area were as high as 43,000 μg/L. By October 2014, 6 years after heating, PCE concentrations there had declined to 120 μg/L (maximum concentration in source zone borings) (Figure 15). At B405, 50 m (165 ft) downgradient of the source, PCE concentrations had declined from 15,000 μg/L prior to heating to 150 μg/L in October 2014, while at B409-4, 100 m (330 ft) downgradient of the source, they had

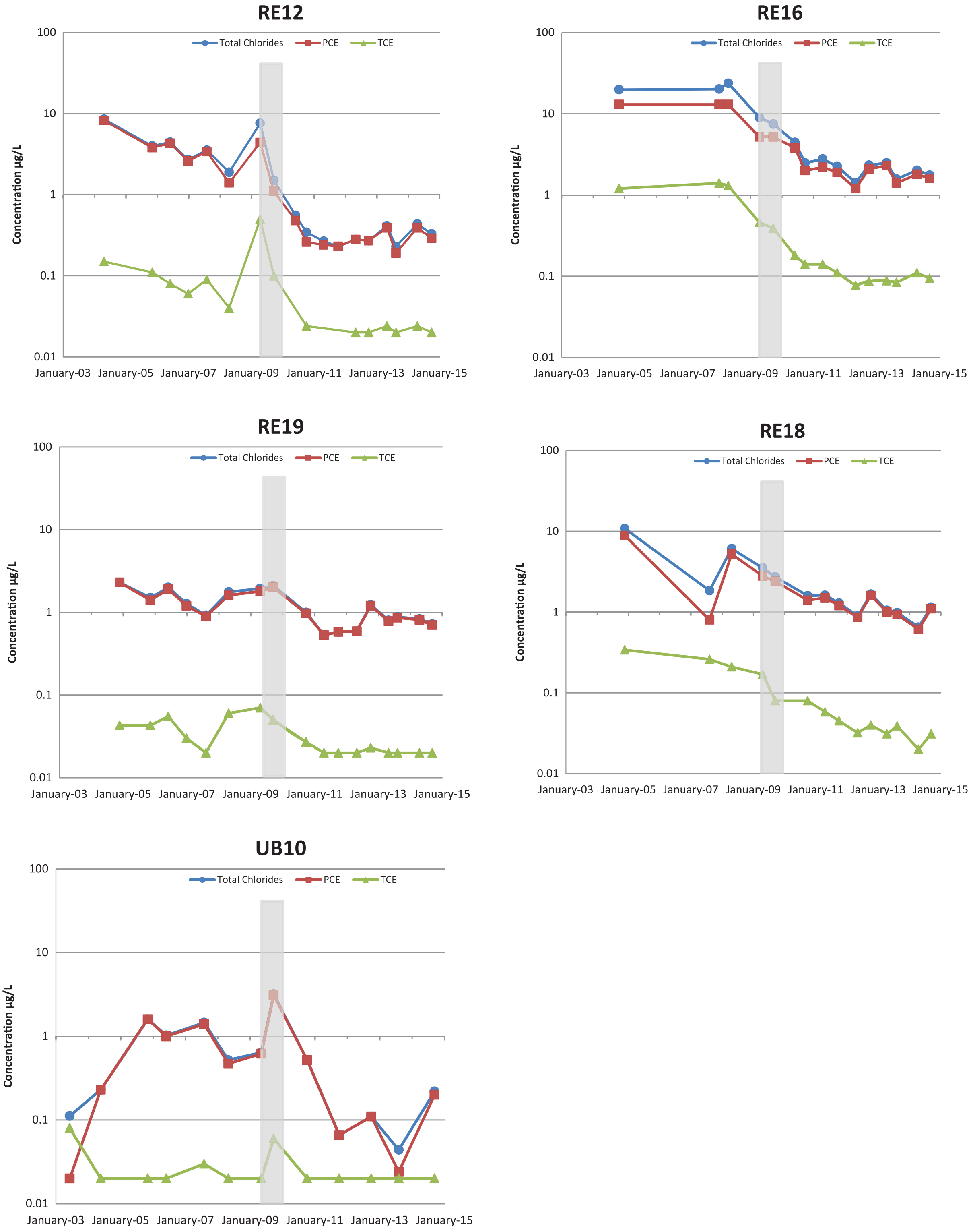


Figure 11. cVOC concentrations in the Reerslev, Denmark plume, pre- versus post-thermal. SVE and P&T systems started up in 2005. Shaded bar indicates period of thermal remediation.

declined only slightly. The effect of source remediation on groundwater concentrations is clearly more apparent closer to the source. Given the very slow groundwater flux (~5–10 m/year), not enough time has passed for the full effect of source remediation to become evident at B409, B411, B414, and locations farther downgradient of the source (Region Syddanmark 2012). While the source was effectively removed, there may still be some mass in the plume, which may also help explain why strong reductions have not yet been observed in the downgradient plume wells.

Case 5: Endicott, New York

Note: As this site is the subject of a separate paper in this issue (Heron et al. 2016), only a brief synopsis will be provided here. At a site in Upstate New York, dissolved plumes of PCE and daughter products TCE, *cis*-1,2-Dichloroethene

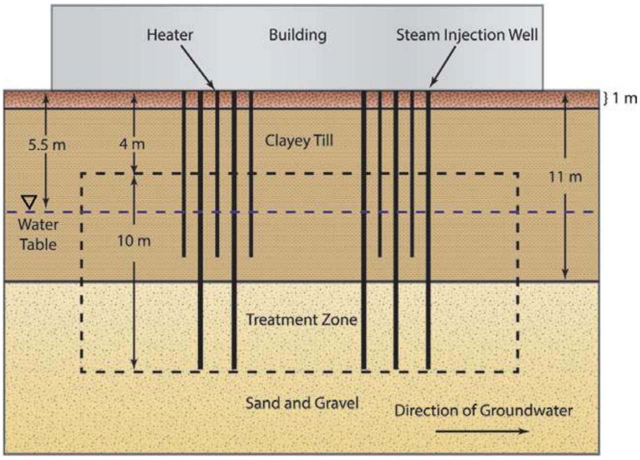


Figure 12. Knullen, Denmark source area cross section.

(*cis*-1,2-DCE), and VC emanated from the DNAPL source area and extended ~1 km downgradient beneath a residential neighborhood. A source treatment using ISTD resulted in >99.9% reductions in soil cVOC concentrations, as summarized in Table 1. Four years following the completion of source treatment using ISTD conducted by TerraTherm, the dissolved plume concentrations had diminished by 3 to 4 orders of magnitude and achieved drinking water standards at the property line, such that the regulatory agency NYSDEC gave permission for all three of the pumping wells that had operated there for decades to be shut off, with MNA now being the accepted remedial alternative. Based on the post-thermal treatment groundwater monitoring data collected at six monitoring wells, the hydraulic containment system was reduced in 2014 and discontinued altogether in early 2015 (Heron et al. 2016).

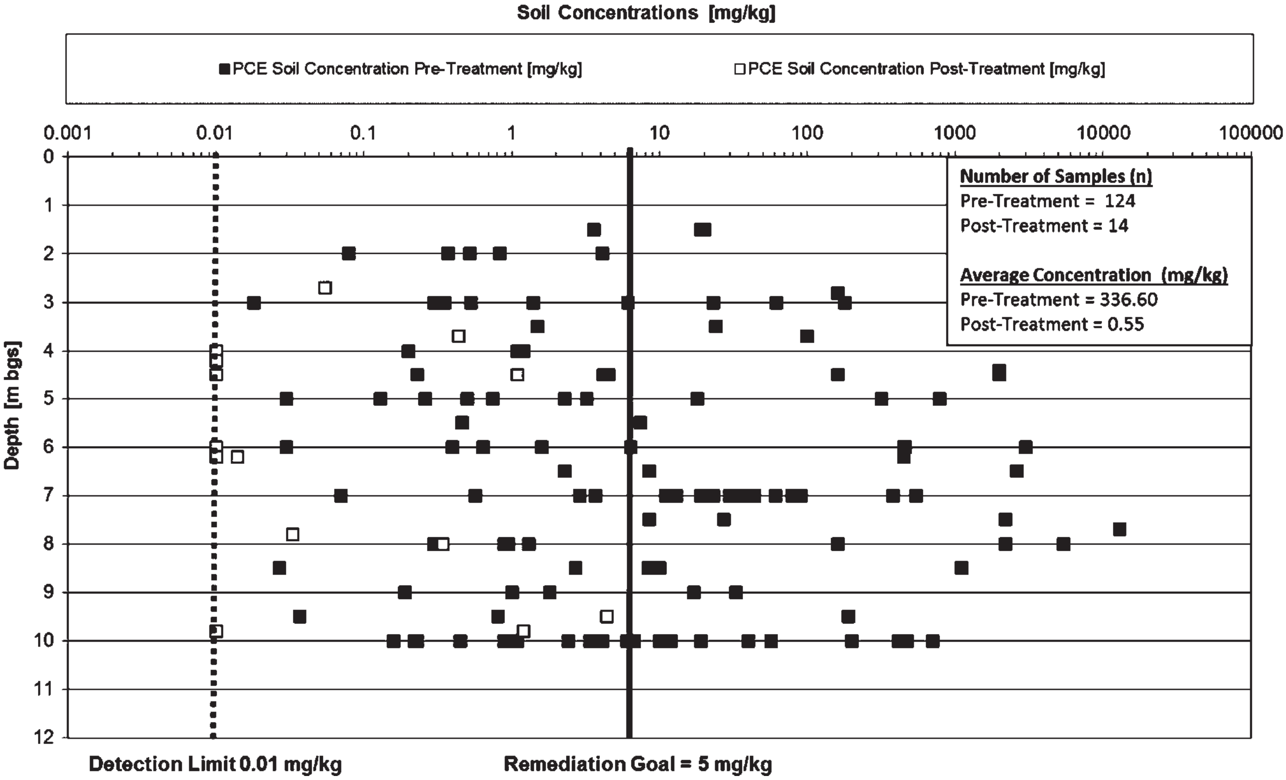


Figure 13. Knullen, Denmark: Source area concentrations pre- and post- thermal remediation.

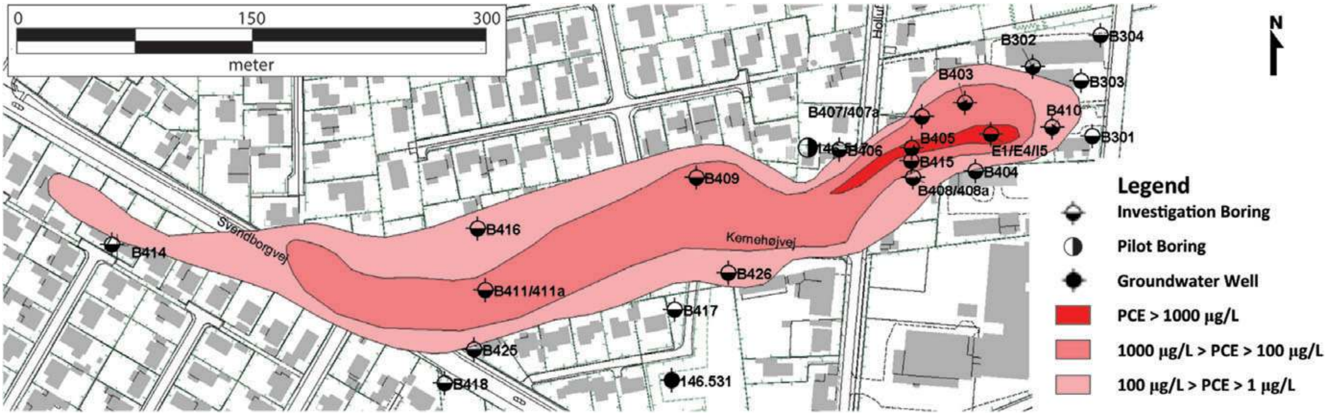


Figure 14. Knullen, Denmark source and plume monitoring well locations.

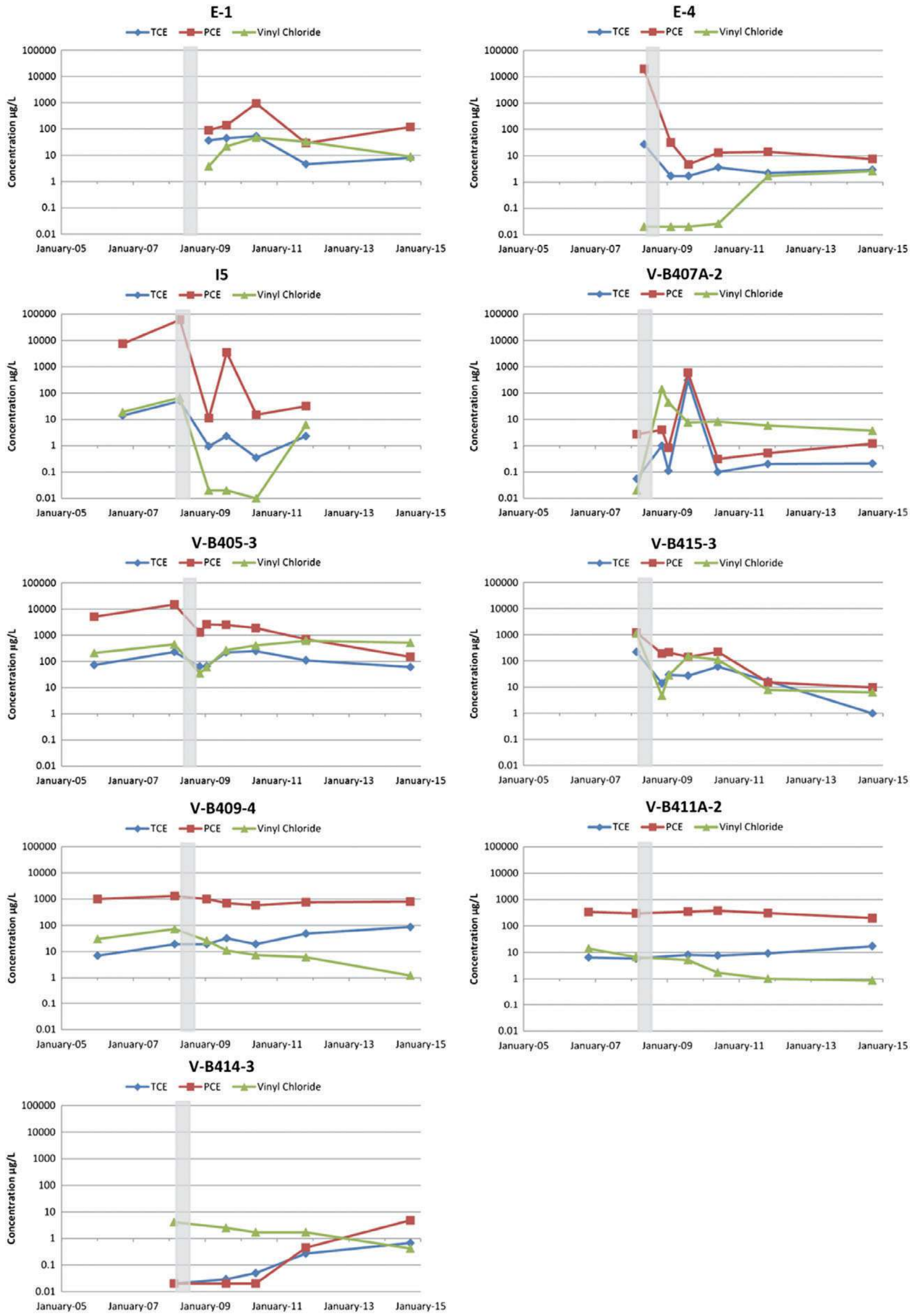


Figure 15. cVOC concentrations in the Knullen, Denmark plume pre- versus post-thermal. Shaded bar indicates period of thermal remediation.

Discussion

Our cases indicate that by removing more than 99% of the source CVOC mass, the mass discharge into the plumes is reduced substantially. This, in turn, leads to much less input of CVOCs to the core of the plume and the zones where MNA is occurring and, therefore, a rapid consumption of the parent compound by the mechanisms that previously kept the plumes near steady-state conditions. Thus, the result is rapid plume shrinkage and lowering of aqueous cVOC concentrations over a period similar to the time it takes water to flow downgradient into the plume. This rapid decrease in plume strength and size following ISTR in the source can lead to the attainment of drinking water standards in a matter of years.

After considering the geological and hydrogeological conditions at the five sites (Tables 1 and 2), a few observations can be made. First, all five sites are in the same general geological domain, that is, glacial and glaciofluvial deposits. To varying degrees, the sites contain fine-textured glacial till, sand and gravel, and/or lacustrine sediments. While the source zones presented here embody a considerable range of conditions within type categories III and V (NRC 2005, Sale and Newell 2011), they have in common the fact that the contaminants were released into low-permeability materials with inherent heterogeneity—ideal candidates for ISTR. Further, the dissolved contaminant plumes emanating from the sources are mostly in sand and gravel (glaciofluvial) materials. The rates of groundwater flow range over three orders of magnitude, from a low of 0.01 m/d at Knullen (slow moving) to a high of 9.0 m/d in Ohio (fast flowing). Thus, while at the Ohio site, the upper and middle portions of the plume were able to be flushed by clean water post-source removal, at the Knullen site, where the flow is many times slower, there has not been enough time for the effects of source removal to be felt at the middle portion of the plume. Some of the plumes were identified as having oxidizing conditions, others reducing or oxidizing/reducing. They, therefore, are not that similar in their susceptibility to MNA. In summary, this population of five sites is judged to be too small to lead to broad generalizations as to what sites are likely to experience similar results.

Remediation of source areas by ISTR is a feasible way to address the associated dissolved plumes, at least in most of these cases and likely many others. The conventional wisdom about secondary sources and back diffusion making aggressive source remediation of CVOCs unjustifiable may be an overgeneralization.

Restoration of DNAPL-contaminated groundwater to drinking water standards has long been considered one of the greatest challenges faced by the remediation community. Evidence that restoration can occur within a decade or so of source treatment shows that this formidable challenge can be overcome in some cases.

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Supporting Information

The following supporting information is available for this article:

Figures S1 to S20. cVOC concentrations in the Ohio plume pre- versus post-thermal, at each of the designated monitoring wells. Shaded bar indicates period of thermal remediation.

Table S1. Monitoring Well Screen Depths

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