

Former Metals Manufacturing Site

Soil Vapor Extraction—Hydrolysis—In Situ Chemical Oxidation—Heat—Chemical Reduction—Bio Reduction

Site Name: Former Industrial Site

Site Location: Southeast Wisconsin near Lake Michigan

Technology Used:

Vapor Intrusion Mitigation

- Soil Vapor Extraction (SVE)
- Hydrolysis by application of base
- In Situ Chemical Oxidation (ISCO)
- Steam (to Activate Sodium Persulfate)

Groundwater Mitigation

- Chemical Reduction and Biological Reduction (ABC+®)

Regulatory Program: Voluntary Cleanup

Project Duration: April 2010 to June 2010 for soil treatment; January 2011 to February 2011 for groundwater treatment.

Site Information: The site is a 325,000 square foot (ft²) industrial facility, currently used as a warehouse and for manufacturing. Past industrial activities that included degreasing handling resulted in contamination of soil and groundwater with chlorinated solvents—primarily 1,1,1-trichloroethane (TCA) and trichloroethene (TCE).

Contaminants: Site investigations indicated that soil and soil gas below the building slab were contaminated with chlorinated volatile organic compounds, primarily 1,1,1-TCA and degradation products 1,1-dichloroethene (1,1-DCE) and 1,1-dichloroethane (1,1-DCA). A 15,000 ft² hot spot causing vapor intrusion into the building was identified. Soil vapor concentrations of 1,1,1-TCA were found up to 4020 parts per million by volume (ppmv). Soil vapor concentrations of 1,1-DCE were found up to 753 ppmv. Concentrations of 1,1-DCA were as high as 68.4 ppmv.

Three persistent contaminated groundwater areas were present outside the building and in proximity to the area posing TCA vapor intru-

sion risk. The contaminants in groundwater in these areas was predominately TCE at a maximum concentration of 4380 micrograms per liter (µg/L) and reductive dechlorination daughter product, *cis*-1,2-DCE (cDCE) at concentrations up to 756 µg/L. Small amounts of vinyl chloride (VC), and TCA and its daughter products were also identified.

Hydrogeology: The upper soil layer consists of 3-4 feet of sand and gravel fill on top of low permeability clay several feet thick. Depth to groundwater varies between 10 and 13 feet below ground surface (bgs) at the interface between the clay and an underlying sand layer. Bedrock occurs at approximately 25 feet bgs.

Project Goals: The goal of the project was to rapidly mitigate any contamination source posing potential indoor air intrusion risk. The primary objective was to facilitate transfer and resumption of commercial activity in the building.

Cleanup Approach: The focus of remediation was soil and groundwater contamination underneath a portion of a large manufacturing/warehouse building.

Soil

Limited time to remediate, limited access to the contaminated area, and a shallow confining unit, led to the selection of SVE for removing mass in the vapor phase from the sand and gravel fill and subsequent aggressive treatment of residual contamination using hydrolysis, oxidation, and steam.

SVE was expected to have a significant and immediate impact due to high vapor pressures and Henry's law coefficients of TCA, DCE, and DCA. The target volume of SVE was 15,000 ft² by 4 feet thick (60,000 cubic feet) with an effective porosity of 0.25 inches in the unsaturated sub-slab of the building. The SVE system was operated for 48 hours at eight extraction points. Total flow rate was approximately 125 standard

cubic feet per minute (scfm) (~3540 L per minute).

Following SVE, the contaminated area was treated using sodium hydroxide, followed by sodium persulfate and steam injection to help degrade 1,1,1-TCA, which is recalcitrant to most oxidants. All amendments were injected into a grid of 100 shallow injection points drilled to a depth of approximately 4 feet bgs just above the clay/fill interface in the 15,000 ft² contaminated zone. The injection points were installed by direct push and constructed of black iron pipe covered by a well sock and carefully sealed at the concrete slab to minimize leaks. Each set of injections was conducted one to four weeks apart to allow the chemicals to disperse and react.

Sodium hydroxide was injected over a 4-day period between May 3 and May 10, 2010 to help hydrolyze DCA and DCE and to potentially enhance the effectiveness of the subsequent sodium persulfate injections. At each of the 100 injection points, approximately 30 gallons (113.6 L) of 25 percent by mass (wt%) sodium hydroxide and 45 gallons (170 L) of water were injected. A total of 7,500 gallons (28,391 L) of solution was used. The coarse materials above the clay were expected to act as an infiltration gallery while the clay absorbed the base solution.

Sodium persulfate was injected June 1 – June 4, 2010, four weeks after the sodium hydroxide injection, to oxidize the DCE and portions of the TCA and its daughter products. Approximately 254 pounds of persulfate in 100 gallons (379 L) of water (approximately 25 wt%) were injected at each point for a total of 10,000 gallons (37,854 L) of persulfate solution.

Steam injection was performed approximately two weeks later (June 14 – June 18, 2010) to catalyze the remaining persulfate into sulfate radicals. The sulfate radicals produced by the heat increase the kinetics of all chemical and biological processes occurring in the subsurface. Approximately 75 gallons (284 L) of superheated water was injected (165,000 British thermal units [BTU]) into each injection point for a total of 16,500,000 BTU (17,408,422 kilojoules). Three brief instances of steam escape

occurred and were quickly contained. Heat also increases the rate of hydrolysis of TCA to the more easily oxidized DCE.

Groundwater

Presence of TCE daughter products indicated that biodegradation was occurring naturally in the groundwater. Historic water quality data indicated neutral pH, low dissolved oxygen, and moderately positive (142 millivolts [mV]) to moderately negative (-186 mV) oxidation-reduction potential values, which are conditions where anaerobic degradation of these chemicals is possible.

To increase the rate of biodegradation and reduce the number of intermediate daughter products, a combined chemical (via beta elimination) and biological reductive dechlorination (via hydrogenolysis) strategy was used. Anaerobic Biochem+ (ABC+), which consists of carbon substrate, nutrients, and pH buffer, as well as microscale zero-valent iron (ZVI) was selected as the combined chemical and biological reductive dechlorination strategy.

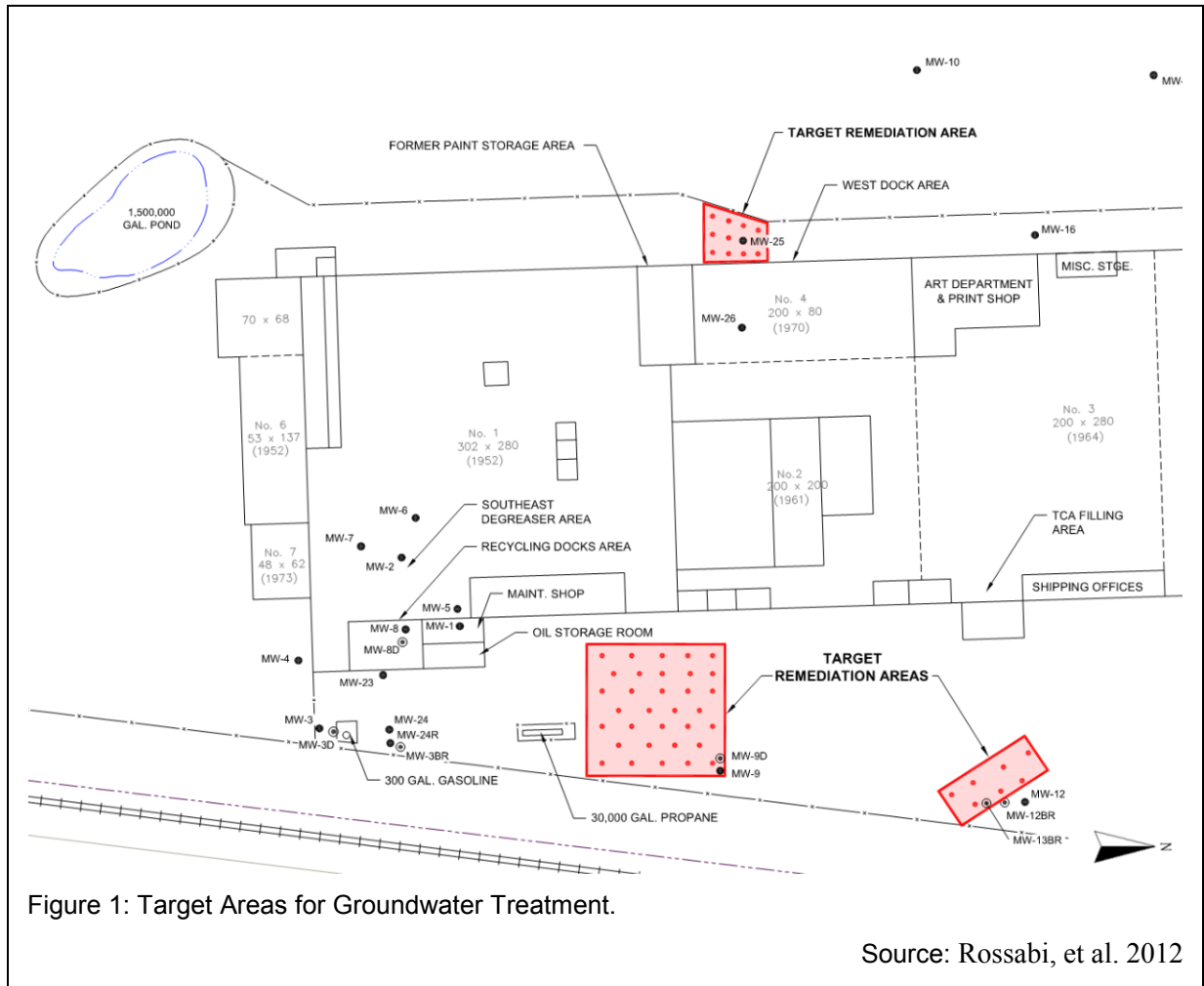
The carbon substrate, nutrients, and buffer encourage growth of microorganisms that reductively degrade chlorinated solvents. ZVI enables direct chemical reduction of chlorinated contaminants on the surface of the iron and produces hydrogen and lower oxidation-reduction potentials to encourage biological reduction.

Three areas totaling approximately 12,000 ft² were selected for amendment application (Figure 1). An 8000 ft² rectangular area in the eastern portion of the site received an injection of ABC+ slurry through 33 direct push rods at multiple depths (10 to 30 feet bgs). ABC+ also was injected in seven locations at depths between 10 and 25 feet bgs in the northeastern area of the site. Finally, ABC+ was injected in 10 locations at depths between 12.5 and 22 feet bgs in a 2400 ft² area in the western portion of the site. A total of 24,925 pounds of ABC+ in 22,205 gallons water was injected at the site between January 24, 2011 and January 31, 2011.

Project Results:

Soil

The SVE system removed approximately 360,000 cubic feet (10,195,200 L) of soil vapor. Assuming maximum contaminant concentrations



throughout the target area, SVE was estimated to have removed approximately 2.2 to 110 pounds (15,000 cubic feet) of TCA, DCE, and DCA.

Samples collected eight weeks after implementation of the full soil remedy indicated a reduction in concentration of TCA by 94%, DCE by 98%, and DCA by 89% (Table 1). All post-treatment sub-slab concentrations were well below the Permissible Exposure Limits prescribed by the Occupational Safety and Health Administration.

Groundwater

Samples collected approximately 10 weeks after the injections were completed indicated that both chemical and biological reduction occurred at the site (Table 2 provides results from several of wells sampled after injection).

Samples from two of the wells indicated little change in contaminant concentrations, which

was attributed to difficulty in obtaining access to those wells during the injection period. Additional injections in these areas are planned for the future to better distribute the amendments.

Sources:

Rossabi, J., Powers, G., Haselow, J., Stolzenburg, T., Sellwood, A., Rice, J. 2012. Combined Strategy for Remediating TCA and TCE at Former Manufacturing Site. Redox Tech, LLC and TRC, Inc. Remediation of Chlorinated and Recalcitrant Compounds—2012. Eighth International Conference on Remediation of Chlorinated and Recalcitrant Compounds (Monterey, CA; May 2012).

Project Contact:

Joe Rossabi
 Redox Tech, LLC
 Phone: 919-678-0140
 Email: rossabi@redox-tech.com

Table 1 – Contaminant Concentrations in Soil Before and After Treatment (ppmv)

Sampling Point	1,1 TCA	1,1 DCE	1,1 DCA
PL-1 <i>Before</i>	0.5	0.1	0.01
<i>After</i>	ND*	ND	ND
PL-2 <i>Before</i>	20.1	10.5	33.6
<i>After</i>	4.1	0.4	7.9
PL-3 <i>Before</i>	1.7	0.3	0.5
<i>After</i>	ND	ND	ND
PL-4 <i>Before</i>	4,020.0	753.0	68.4
<i>After</i>	103.0	2.3	5.4
PL-5 <i>Before</i>	0.460	0.1	0.01
<i>After</i>	ND	ND	ND
PL-6 <i>Before</i>	18.4	5.9	0.5
<i>After</i>	0.3	0.2	0.05
PL-7 <i>Before</i>	74.3	25.8	9.0
<i>After</i>	18.7	0.1	0.02
PL-8 <i>Before</i>	0.1	0.1	0.04
<i>After</i>	ND	ND	ND
PL-9 <i>Before</i>	11.6	8.0	13.3
<i>After</i>	1.0	0.3	1.4
OSHA PEL**	350	100	100

* ND=not detected

**OSHA PEL=Occupational Safety and Health Administration's Permissible Exposure Level

Table 2 - Contaminant Concentrations in Groundwater Before and After Injection of Amendments (µg/L)

Well	TCE	cDCE	VC	TCA	1,1-DCA
MW 9 <i>Before</i>	881	370	1.8	82.2	19.7
<i>After</i>	31	2.4	<0.18	14.3	2.0
MW 9D <i>Before</i>	766	137	10.3	116	5.9
<i>After</i>	76.1	430	4.5	90	7.7
MW 12 <i>Before</i>	354	6.5	1.5	16.6	2.4
<i>After</i>	186	4.2	<0.45	5.7	<1.9
MW 12BR <i>Before</i>	10.8	168	2.2	62.2	66.2
<i>After</i>	0.61	171	<0.18	46.6	61.8
MW 13BR2 <i>Before</i>	269	21.8	1.8	105	128
<i>After</i>	258	29.1	2.3	105	177
MW 13BR3 <i>Before</i>	124	13.4	0.64	30.7	39.2
<i>After</i>	121	14.7	0.71	27.9	41.4
MW 25 <i>Before</i>	4380	612	54.3	<45	<37.5
<i>After</i>	125	587	17.3	<4.5	<3.8
MW 26 <i>Before</i>	32.8	756	144	6.4	24.3
<i>After</i>	5.1	1130	401	<4.5	24.7