Thermally Stimulated Degradation of Contaminants as an Emerging Application for Six-Phase Heating

William Heath, Chief Operating Officer
Current Environmental Solutions
www.cesiweb.com

Six Phase Heating is a thermally enhanced soil vapor extraction (SVE) technique that targets both contaminated soil and groundwater. It delivers conventional three-phase electricity to the subsurface through metal electrodes. Once in the subsurface, the electrical energy resistively heats soil and groundwater to generate steam. Contaminants are mobilized by direct volatilization and in situ steam stripping, removed by SVE, and treated before venting to the atmosphere. In parallel with steam assisted removal, subsurface heating has also proven effective in stimulating rapid in situ degradation.

Current Environmental Solutions (CES) is actively researching techniques for accomplishing in situ degradation of soil and groundwater contaminants, as a both a primary thermal treatment technique, and as a polishing step following steam induced separation. The potential for rapid in situ degradation of contaminants as observed at prior CES treatment operations and in the laboratory suggests a less energy and capital intensive method for treating contaminated sites at temperatures below boiling and the possibility of extending treatment to low-volatility contaminants.

In particular, low-temperature heating in the range of 50 to 80˚C has been shown effective in degrading a variety of dissolved-phase compounds. At these low temperatures, the need and costs for significant venting operations and above-surface treatment of soil off-gases can be avoided, and steam condensate requiring secondary treatment is not generated. Furthermore, significantly less electrical power and energy is required, enabling larger volumes to be treated with the same Six-Phase Heating™ equipment, using fewer electrodes at larger inter-electrode spacing, and a presenting a much smaller electricity bill on a per volume basis.

Contaminants that have been thermally degraded during Six Phase Heating operations include trichloroethylene (TCE), methylene chloride, cis 1,2 dichloroethane, 1,2 ethylene dibromide, 1,1,2,2 tetrachloroethane, and diesel range organics. We believe in situ degradation occurs as a result of the following mechanisms:

- thermally accelerated hydrolysis reactions,
- biodegradation by thermophilic consortia that are stimulated by heating,
- oxidation-reduction (redox) reactions driven by a shift in the thermo-chemical groundwater equilibrium,
- hydrous pyrolysis (under aerobic conditions) as reported by Knauss et al (1998).

Degradation of TCE during Pilot-Test at Cape Canaveral

During late 1999 through mid 2000, Six-Phase Heating was demonstrated at Launch Complex 34 at Cape Canaveral, Florida, as part of a multiple technology demonstration for the in situ remediation of dense DNAPL. The contaminant of concern was TCE, residing as a separate phase along the surface of a clay aquitard at a depth of 45 ft. A total of 6,250 yd^3 (4780 m^3) was treated at relatively low electrical power levels.

The contaminant impact at Launch Complex 34 was limited to a surficial aquifer overlying a confining clay unit located about 45 ft bgs. Across most of the site, groundwater was encountered at 4 to 7 ft bgs, with a typically flat groundwater gradient. The subsurface was divided into the following four distinct geologic units:

- The upper sand unit (USU)
- The middle fine-grained unit (MFGU)
- The lower sand unit (LSU)
- The lower clay unit (LCU)

The USU is a lens of uniform fine sand extending from grade surface to the top of the MFGU, which is at 20 to 23 ft bgs. The MFGU consists of silty and clayey fine–sands, with occasional thin sand lenses filled with shell fragments. The thickness and depth of the MFGU unit is irregular across the test site. Located beneath the MFGU, the LSU is a silty, fine sand lens that extends to the top of the LCU. The LSU typically extends from 30 to 45 ft bgs. The LCU is located at approximately 45 ft bgs, and acts as an aquitard.

Pre-demonstration sampling and monitoring within and adjacent to the test cells determined that the SPH test cell contained approximately 11,313 kg of TCE. Of this, 93 % was designated as a separate-phase DNAPL, based on the previously calculated maximum theoretical soil saturation concentrations equal to or greater than 300 mg/kg of TCE. Most of the DNAPL was located within the LSU above the LCU. As expected, the highest TCE soil concentrations were measured along the LCU aquitard at 45 ft bgs, ranging up to 42,405 mg/kg.

The Six Phase Heating demonstration system used 13 electrodes, each with two conductive intervals located at 23 to 30 ft bgs and 38 to 45 ft bgs. The lower heating interval was selected so that extra power could be directed into the most heavily impacted DNAPL region, within the LSU. To protect the thin aquitard, the electrodes were terminated at, or slightly above, the surface of the LCU. The upper heating zone was selected to decontaminate the lower-permeability MFGU formation, and to promote buoyant steam flow through that layer to the vadose zone above. In response to a rise in the water table caused by tropical storms that occurred during the demonstration, ground rods were inserted to extend the electrode heating to the 3 to 10 ft bgs interval.

The Six Phase Heating system was operated intermittently over an 11-month period, from August 18, 1999 through July 12, 2000. Subsurface temperatures ranged from 120˚C at the bottom of the treatment zone (45 ft bgs) to 100˚C in the vadose zone while power was applied.

However, the intermittent nature of the operation caused temperatures within the uppermost 10 ft of the treatment zone to average about 80˚C.

The demonstration was successful in that 97 % of the DNAPL mass was removed, based on analysis of soil cores taken before and after the demonstration. From data on the production of elevated levels of chloride ion and other degradation byproducts throughout the demonstration, it appeared that the majority of the TCE mass removal was via in situ degradation. **Figure 1** illustrates the production of organic daughter products at Cape Canaveral during the progressive reductive dechlorination of TCE. While the mechanism for the in situ degradation could not be identified, microbiological analysis of soil core samples showing not only viable but elevated microbial activity following heating.

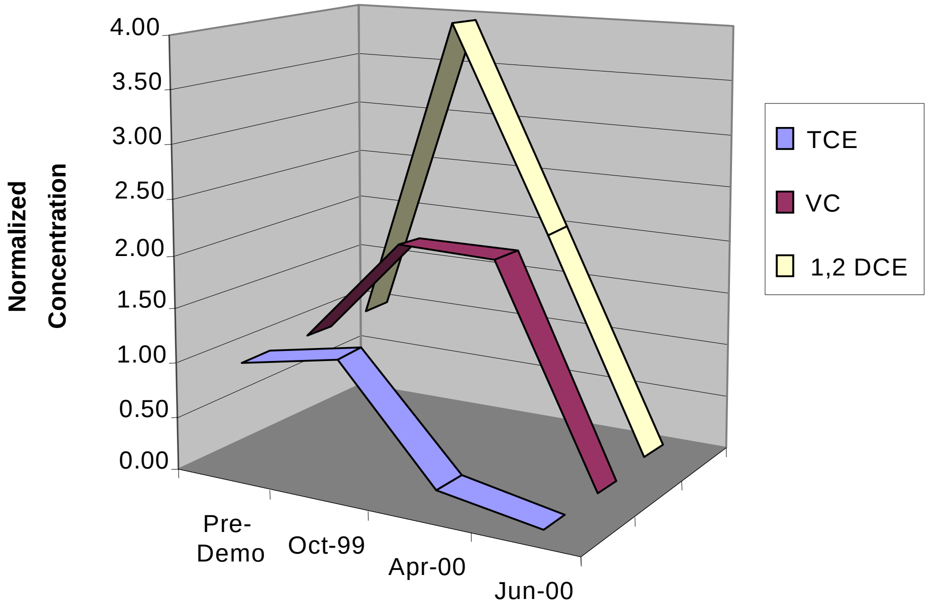

Figure 1. Normalized Concentration of TCE Daughter Products (Well PA-13S)

Figure 2 shows levels of chloride ion produced within and near the test volume. Based on the available characterization data, decontamination took place as follows:

- At least 44 % was removed via the primary route, an in situ degradation pathway
- 19 % was removed in the vapor phase by steam stripping
- Approximately 2 % was mobilized to the surrounding aquifer during a single flooding event, caused by a tropical storm that occurred early in the demonstration
- The remaining 33 % could not be accounted for, but is likely to have been degraded in place
- Sampling wells and soil borings beyond the perimeter of the treatment area revealed a net decrease in contaminant levels, indicating that treatment extended beyond the boundaries of the test cell

Data recently released by the demonstration program team appears to show the presence of an elevated concentration of chloride ions down-gradient of the Six Phase Heating test volume that may account for most of the missing 33% of TCE, suggesting it was indeed degraded in place. This data is, shown in **Figure 3**, is being further evaluated.

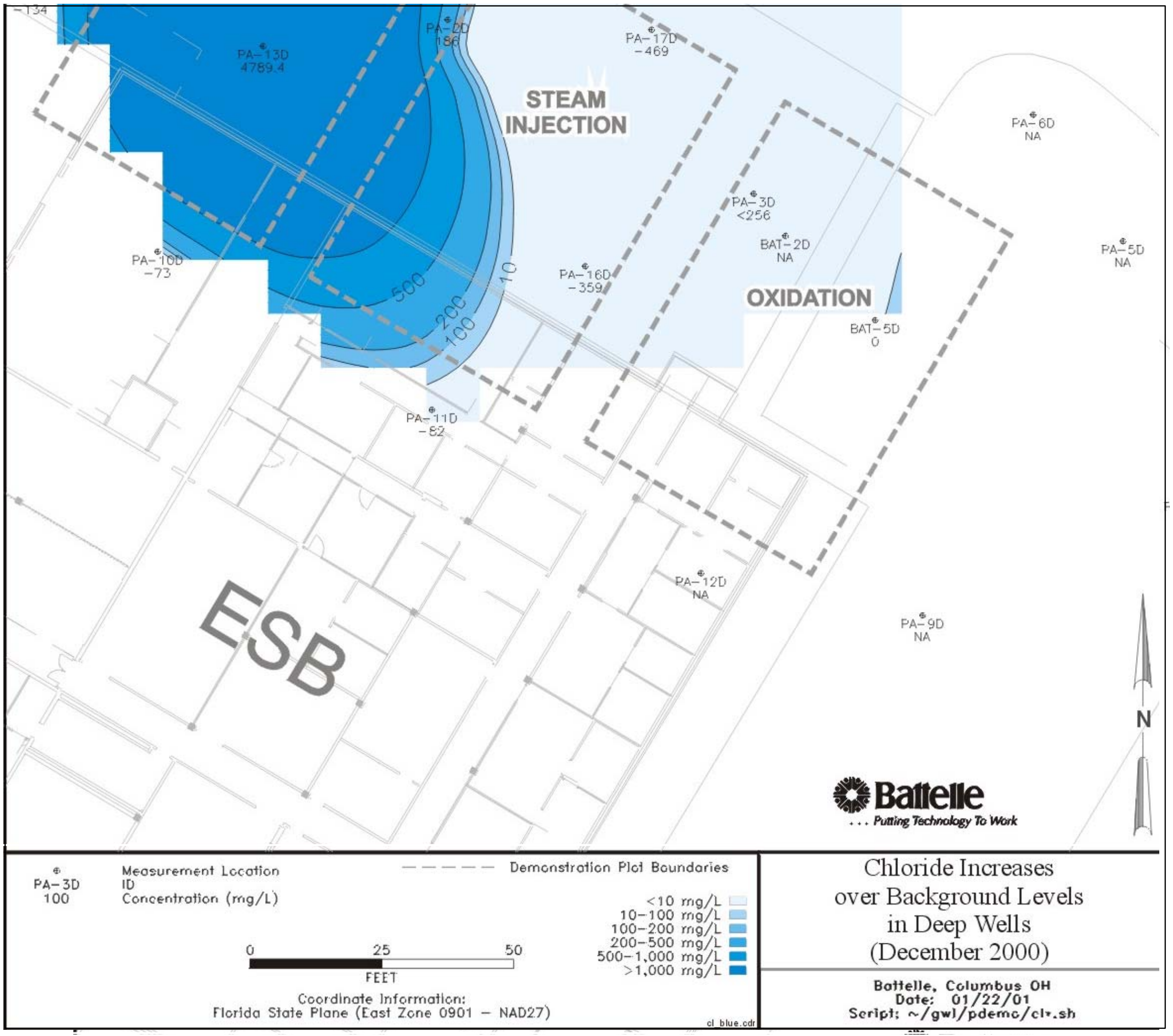

Figure 2. Deep Wells Chloride Concentrations (December 2000)

Subsequent laboratory experiments performed by Pacific Northwest National Laboratories (PNNL) confirmed the ability of indigenous microbial populations to degrade TCE at elevated temperatures (70˚C) and under anaerobic conditions similar to those during Six Phase Heating operations. Ongoing treatability tests initiated in November 2001 by CES for a commercial client are further demonstrating the ability of elevated temperatures (75˚C) to promote rapid in situ degradation of TCE, cis 1,2 DCE and vinyl chloride.

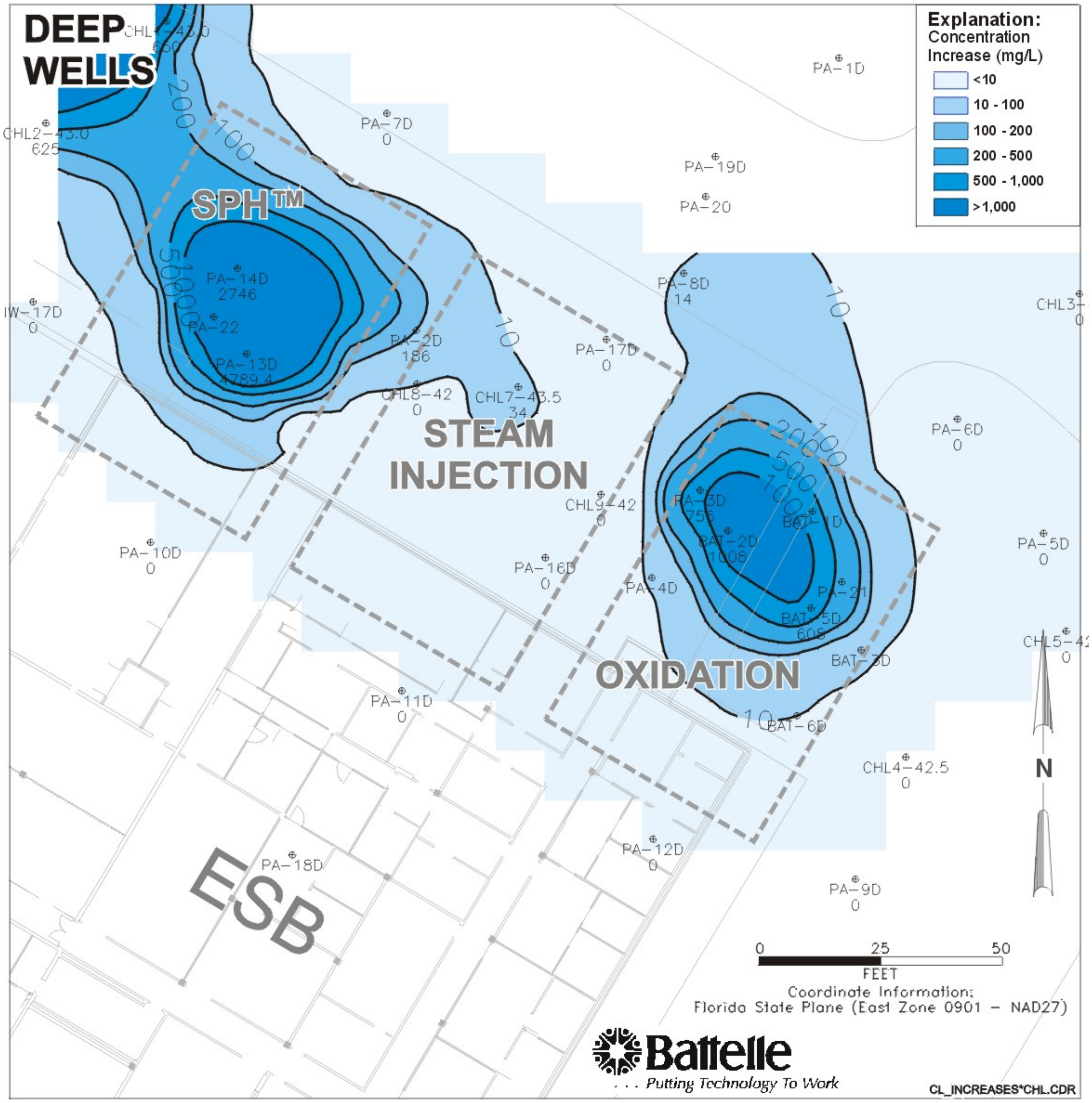

Figure 3. Deep Wells Chloride Concentrations (August 2001)

Degradation of TCE and 1,1,1 TCA at Manufacturing Plant

Six Phase Heating was applied at a former telecommunications manufacturing facility in Skokie, IL using a large-scale network of 107 electrodes to remediate DNAPL pools under a large building. The contaminants of concern were cis 1,2-DCE, TCE, and 1,1,1-trichloroethane (TCA). Initial concentrations in groundwater for cis 1,2-DCE were as high as 160,000 micrograms per liter (ug/L), for TCE up to 130,000 ug/L, and for TCA as high as 150,000 ug/L. The site lithology consisted of heterogeneous sandy silts to 18 feet below ground (bg) and a dense silty clay till from 18-25 feet bg. A shallow groundwater table was encountered at 7 feet bg and hydraulic conductivity through the remediation zone ranges from10^{-4} to 10^{-8} cm/sec. Most of the solvent mass was pooled on top of the clay till at 18-20 feet bg. Treatment was initiated in early June, 1998 and completed in April 1999. Temperatures averaged between 98 and 105˚C

Average groundwater concentration before, during and after remediation are summarized in **Figure 4**. Sampling results showed that all of the DNAPL had been removed and that groundwater concentrations were reduced by 97.9% DCE, 99.1 % for TCE, and 99.9% for TCA. The final groundwater concentrations were well below target cleanup levels given by the State of Illinois TIER III requirements. In fact, groundwater concentrations were approaching TIER I levels throughout the site at the end of treatment operations (< 350 ppb DCE, <25 ppb for TCE, and <1000 ppb for TCA.)

Two striking observations can be made from the data in **Figure 4**. First, increases in the concentration of cis-1,2 DCE during the later stages of treatment (shown in the data on DEC-'98) suggest its production as a result of TCE degradation. Second, the rapid decrease in 1,1,1 TCA is consistent with rapid hydrolysis. The hydrolysis half life of 1,1,1 TCA is 0.03 days at 100˚C.

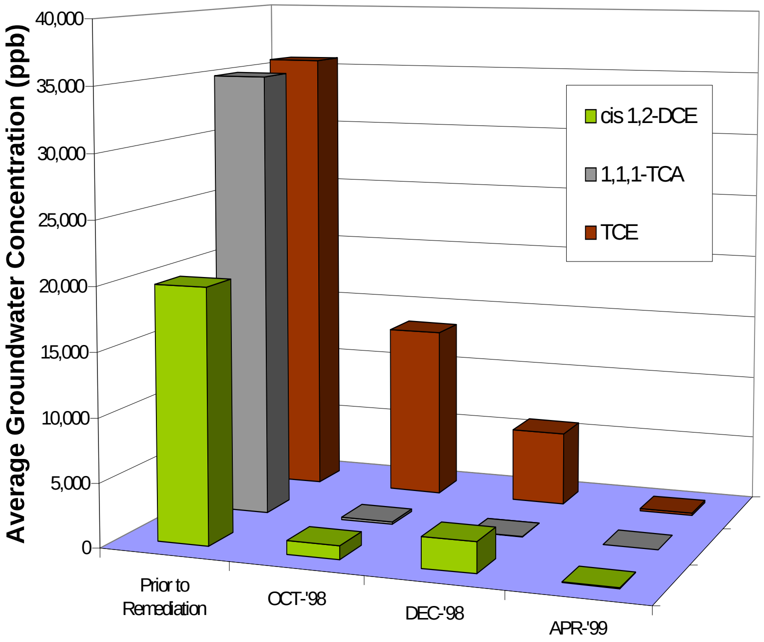

Figure 4. Contaminant Levels before, During and After DNAPL Remediation

Following treatment, groundwater sampling was continued for 12 months with no contaminant rebound. The site was then delisted by the State of Illinois EPA, and represents the first successful DNAPL remediation in U.S. history.

Degradation of Methylene Chloride at Plastics Manufacturing Plant

Six Phase Heating was deployed in 1999 and 2000 to treat a vadose zone contaminated with methylene chloride at the Avery Dennison commercial property located in Waukegan, Illinois.

A 3-D visualization of the extent of methylene chloride impacted soils is shown in **Figure 5**. Methylene chloride levels in the soil beneath the property were in excess of 40,000 mg/kg, with an average concentration of 1,389 mg/kg. The cleanup was conducted under the Illinois EPA Site Remediation Program, with a soil remediation objective of 24 mg/kg.

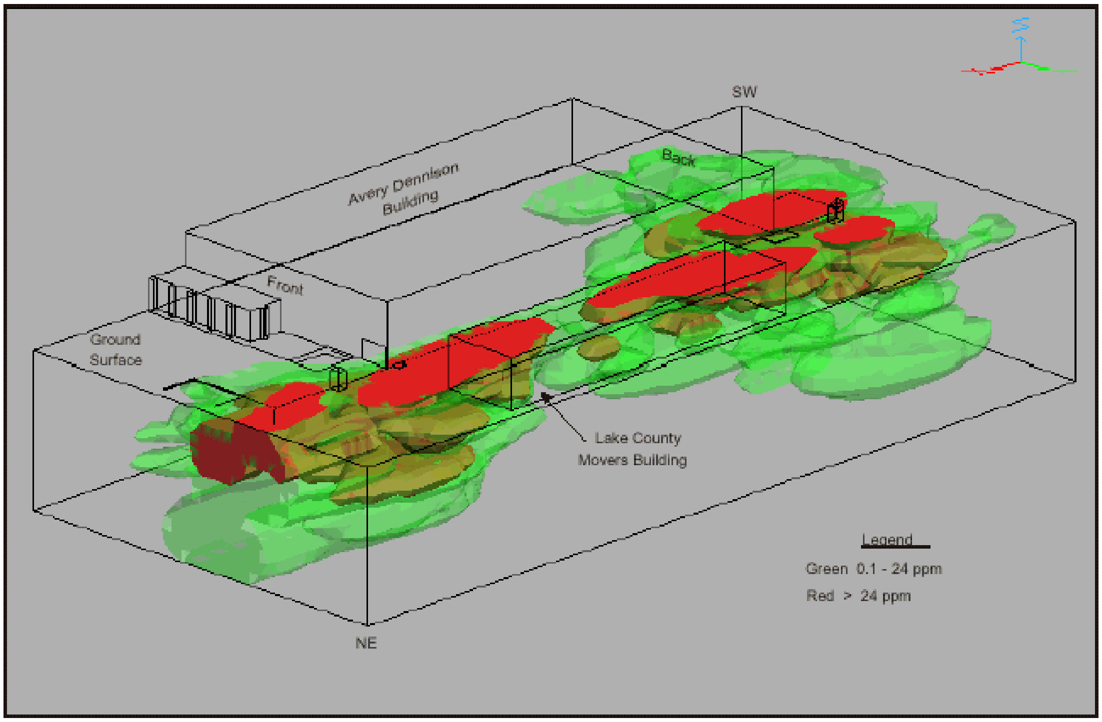

Figure 5. Methylene Chloride Impacted Soils at Avery Dennison Site

Roughly halfway through the 47-week treatment operation, the average temperature was 72°C, but the VOC extraction rates had declined to much lower than expected levels and the total mass extracted was a small fraction of the initial subsurface mass. Extraction rates were likewise lower than expected in the most heavily contaminated regions where subsurface temperatures were at or near 100°C. A decision was made to collect soil samples to determine the remaining methylene chloride concentrations, measure soluble chloride levels, and measure levels of any microbiological activity that may have been stimulating the in situ degradation of methylene chloride degradation. Samples were collected at the most heavily contaminated locations, where subsurface temperatures had reached 100°C, 70°C, and 30°C, along with background samples from untreated locations. Test results are summarized in **Table 1**.

At the 100°C location, the methylene chloride levels were well below the closure objective and six orders of a magnitude less than the original concentration. The samples at 70°C showed a 60% decreases in methylene chloride, and a 30% decrease at 30°C. Soluble chloride levels were found to be elevated by an order of magnitude or more in areas where treatment had occurred. These results suggested to CES that thermally enhanced degradation may be occurring, and may in fact be serving as the primary treatment pathway at the site. A cursory literature review identified the most likely pathways to be microbiological degradation, hydrous/pyrolysis oxidation (HPO), and reductive hydrolysis. However, biological testing on samples removed from the site indicated the biological activity was minimal at optimum temperatures (30°C) and nonexistent at greater than 70°C. Since degradation appeared to be active at temperatures in the 70-80°C range, CES tentatively concluded that either reductive hydrolysis or HPO was occurring at the elevated subsurface temperatures and apparently at sufficiently high rates that heating the subsurface to 100°C was not required to affect treatment.

Table 1. Interim Sampling Results

Sample Location	Initial [MeCl] mg/kg	May [MeCl] mg/kg	Temperature °C	Biological Activity	HPO/Hydrolysis Indicator as Cl-
Background	BDL	BDL	10	moderate	<50 mg/L
TMP 17	3,000	1,000	30	moderate	240
TMP2	40,000	0.07	100	none	445
TMP6	1100	450	70	none	340
EL2	~1,500	0.1	100	none	230

Additional research was performed by CES to determine whether HPO or hydrolysis was the most likely mechanism responsible for the in situ degradation of the methylene chloride. Vapor sampling was performed for methane and carbon dioxide to help differentiate which process was predominant. HPO typically produces carbon dioxide as an end product and hydrolysis liberates methane. The vapor samples indicated that there was a miniscule amount of methane, while carbon dioxide was at four times that of the background level. While hydrolysis and HPO may have been occurring simultaneously, the results were consistent with HPO as the primary thermal degradation mechanism. Further sampling during the remainder of the remedial operation confirmed that treatment to well below target cleanup levels occurred despite boiling conditions.

At the conclusion of treatment operations, the average concentration of methylene chloride remaining in the soil was 2.51 mg/kg, well below the treatment objective of 24 mg/kg. In fact, this is below Illinois EPA’s most stringent ingestion/inhalation Tier 1 Soil Remediation Objective for Residential Properties (13 mg/kg). The success of the remediation was confirmed with the collection and analysis of one hundred and twenty-five (125) soil samples. Based on the results of the confirmatory samples, the remediation of the Avery Dennison property was complete and the Illinois EPA determined that no future remediation would be required.

Degradation of Ethylene Dibromide and DCA at Specialty Chemicals Manufacturing Plant

The Six Phase Heating technology was pilot tested at a former chemical manufacturing site in Newark, California from May through July, 2000. The subsurface was heated to between 70˚C and 90˚C over a 2-month period. Following heating operations, subsurface core samples showed high levels of EDB removal while the co-contaminant, DCA, was not removed to any extent. The mass of EDB recovered in soil off-gases and steam vented during the pilot test was insufficient to account for the apparent mass loss. The analytical results are summarized in **Table 2**.

Table 2. Contamination Levels in Soil Cores Before and After Pilot Test

sample depth (feet)	Pre-SPH EDB (mg/kg)	Post-SPH EDB (mg/kg)	Pre-SPH DCA (mg/kg)	Post-SPH DCA (mg/kg)
Boring:	**SPH-7**	**PSB-1**	**SPH-7**	**PSB-1**
3	210	1.9	0	2.4
7	15	1.3	14	2.9
13	180	47	0	99
18	53	180	45	93
Boring:	**SPH-4**	**PSB-2**	**SPH-4**	**PSB-2**
3	0	44	2	49
7	220	120	10	84
13	2,900	560	0	130
18	50,000	4.9	0	54

Immediately following the pilot test, the CES laboratory facility in Richland, Washington initiated a series of exploratory tests using samples of contaminated soil cores and groundwater obtained from the Newark subsurface. These included tests to evaluate the effect of elevated groundwater temperatures on degradation of dissolved contaminants.

Small (50 ml) samples of soil and groundwater obtained from the FMC Site were deoxygenated, and subjected to heating at controlled temperatures of 25˚C (baseline), 50˚C and 70˚C. After two weeks, the samples were analyzed to assess whether exposure to elevated temperatures alone could affect contaminant degradation. The primary contaminants of interest were ethylene dibromide (EDB) and 1,2 dichloroethane (DCA). Samples were analyzed by an independent testing laboratory using EPA Method 8260 for volatile organic compounds at an exposure duration of 2 weeks. The results are summarized in Table 3. Concentrations labeled ND refer to levels below the analytical detection limit. Further analysis of the laboratory samples is underway to detect changes in inorganic daughter products (bromide and chloride ions).

The results in **Table 3** indicate significant reduction in EDB and DCA concentrations in the heated samples compared to baseline. In particular, EDB was reduced by 28% and 99.9% in the samples held at 50˚C and 70˚C, respectively. Reduction of DCA was 0% and 54% over the same temperatures. The presence of known daughter products 1,2 dibromoethane, dibromomethane and vinyl chloride suggests that disappearance was caused by an in situ degradation pathway rather than by fugitive losses during sample handling. Fugitive losses were mitigated by carefully cooling the samples prior to opening the containers, and maintaining zero vapor headspace during heating. The results of the laboratory tests summarized in **Table 3** also tend to corroborate the dramatic decrease in EDB concentrations observed in soil cores obtained before and after the initial SPH pilot test at Newark. The most likely anaerobic degradation mechanisms active at Newark are hydrolysis, and abiotic reductive dehalogenation.

Table 3. Volatile Organic Compound Levels (in ppb) After Two Weeks

Analyte	Baseline	50 ˚C	70 ˚C
1,2 dibromoethane (EDB)	220,000	160,000	190
1,2 dichloroethane (DCA)	19,000	21,000	8,700
bromoform	75	ND	ND
dibromochloromethane	120	ND	ND
dibromomethane	ND	23	ND
Methylene chloride	160	140	270
Benzene	61	64	45
Vinyl chloride	ND	ND	93

Hydrocarbon Degradation at Commercial Fuel Storage Yard

In late 1998, CES performed a pilot treatment of a gasoline spill associated with a fuel storage facility for a major U.S. oil company. The remediation was conducted over the brief period of October 19, 1998 through November 30, 1998. During this time, the treatment was successful in that a targeted 98% removal of benzene was achieved, with post-treatment groundwater concentrations reduced to below a target level of 50 ppb. Surprisingly, the site was also found to be contaminated with kerosene although the source could not be identified. Dual-vapor extraction wells installed by CES to control the water table removed 51,000 gallons of groundwater and 4000 lb of free product. Even more surprisingly, post-test sampling indicated that total petroleum hydrocarbons, specifically diesel-range organics (TPH-DRO) were also reduced. The average reduction in TPH-DRO concentrations was only 7% in soil but 80% in groundwater. Further analysis of core samples was performed to assess whether biodegradation could have occurred as a cleanup mechanism. The results are summarized in **Figure 6**.

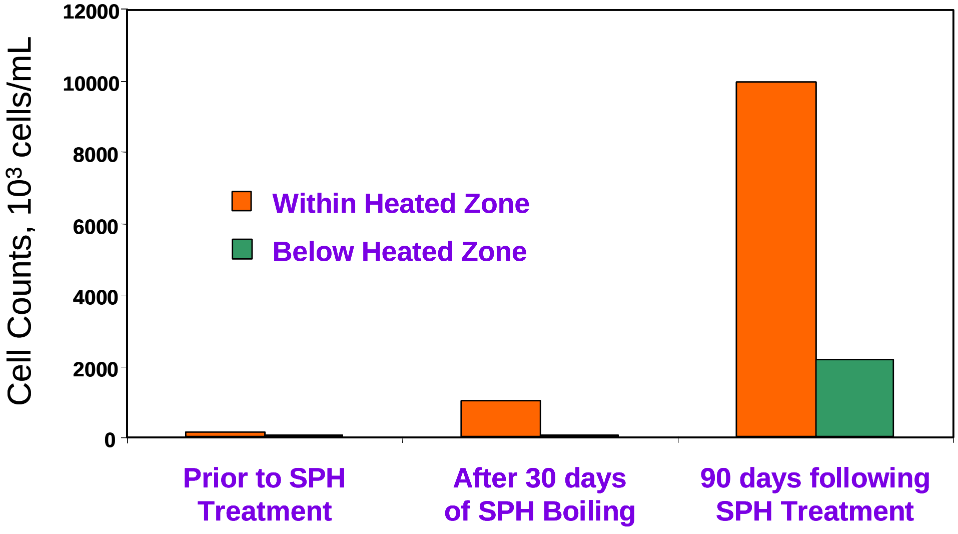

Figure 6. Petrophilic Microbial Activity Before, During and After Treatment

As shown, cell counts for microbes adapted to petroleum metabolism were found to increase dramatically during and following the treatment period even though the site was held at boiling conditions for 4 weeks. In fact, the largest increase was found within the heated area in comparison with samples taken in the cooler region directly below the electrode arrays.

Research and Laboratory Testing Capabilities

Further work is underway to assess which mechanisms are most important depending on the type of contaminants involved and depending on site conditions. To better understand and predict in situ degradation pathways, CES has teamed with Pacific Northwest National Laboratories (PNNL) and Portland State University (PSU). Researchers at PNNL are engaged in studies with the U.S. Department of Energy to measure byproduct distributions and mechanisms for thermally accelerated TCE degradation, degradation of low volatility diesel components, and phenanthrene and crysene, which are components of manufactured gas plant (MGP) sites. Portland State University is performing work to identify through DNA fingerprinting the thermophilic bacteria responsible for contaminant degradation at Six Phase Heating operations as an adjunct to their research on extremophilic biology at undersea thermal vents and hot springs.

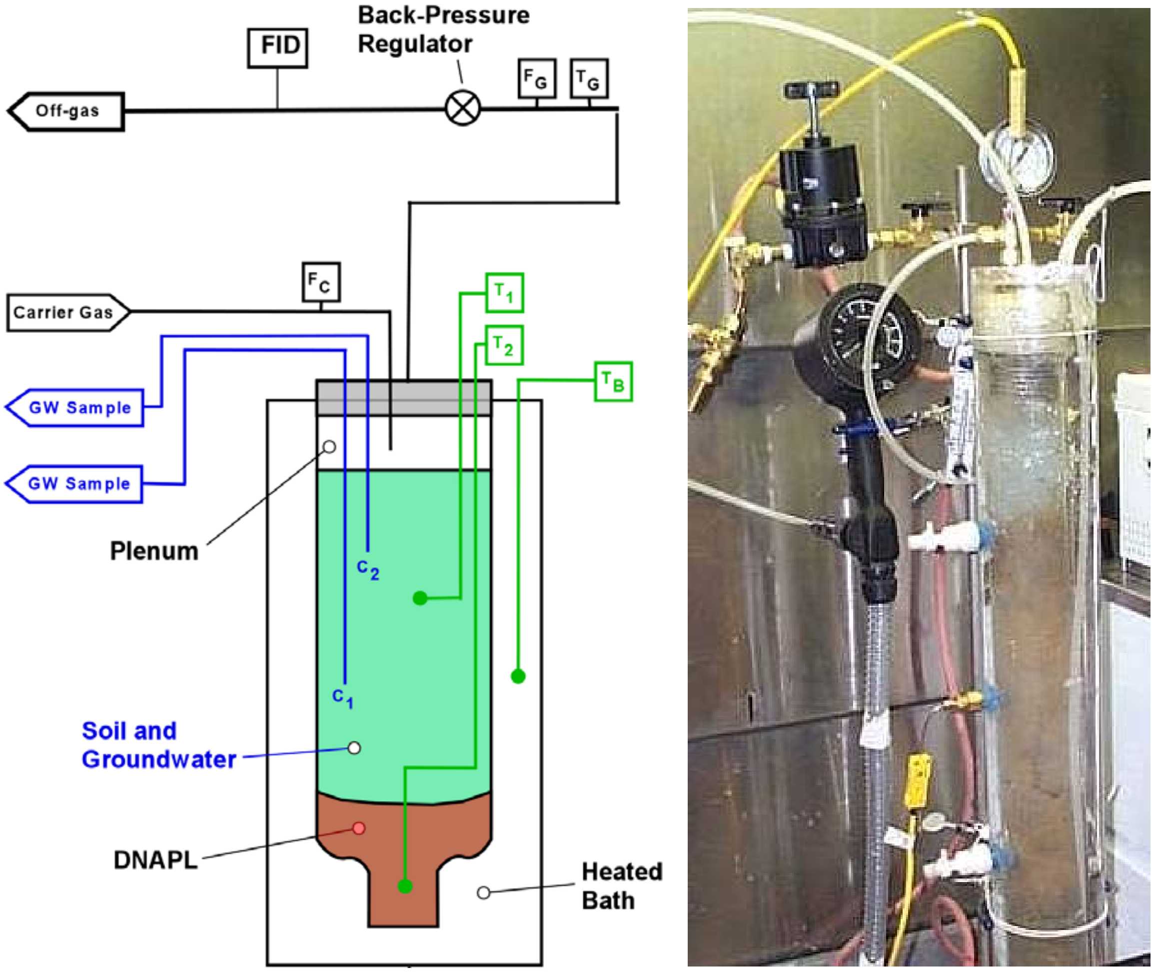

Figure 7. Bench-Scale Treatability Test System

To provide engineering data for Six Phase Heating applications, CES has developed its own laboratory capabilities to enable cost effective determination of degradation rates, byproducts, and achievable endpoints using field samples of contaminated soil and groundwater. Tests are now being performed to measure degradation rates of TCE, cis 1,2 DCE and vinyl chloride for a pharmaceutical site in Portland, OR where low-temperature heating will be used to attempt to reduce dissolved-phase concentrations to MCLs.

We have also developed laboratory techniques and apparatus for assessing the combined effects of multiphase transport with in situ degradation to track volatilization of pure-phase components, their dissolution, and degradation in a sediment column. This apparatus is depicted in **Figure 7**. It is being used to develop engineering design data for applying Six Phase Heating for treating a DNAPL at a former chemical manufacturing plant in the Bay Area of Northern California. Further tests are planned for an EPA Superfund site contaminated with chlorobenzene and DDT present as a DNAPL.