Combining Thermal Treatment with MNA at a Brownfield DNAPL Site

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ABSTRACT
A heavily contaminated Brownfields site in New York was remediated and redeveloped using a combination of In-Situ Thermal Desorption and Monitored Natural Attenuation. Four source areas were addressed by the thermal technology, and groundwater beneath the site is undergoing natural attenuation. Approximately 86,000 lbs of volatile organics were extracted and treated on-site. The performance of the thermal remedy was documented by the collection of soil samples from 51 locations. All areas met the negotiated cleanup standard after thermal treatment. Monitoring of redox-sensitive groundwater parameters and the concentration of VOCs in groundwater shows continued natural attenuation. Three of the seven monitoring wells at the site show concentrations below their respective NYSDEC Class GA groundwater standards. Based on current trends, it is anticipated that the remaining wells may meet these standards within 5 or 10 years. The site is now redeveloped and the location of a large home-improvement store and a federal credit union branch.

INTRODUCTION

Thermal remediation is being used for aggressive remediation of DNAPL source zones in urban areas, as exemplified by the fast-track clean-up at Point Richmond (LaChance et al. 2006). For such time-critical remedies, a high degree of confidence in the technology is needed, and robust thermal treatment must be applied to the DNAPL sources in order to meet the remedial standards (Heron et al. 2006). Therefore, sites with large contaminant mass (more than 5,000 lbs of CVOCs) have been treated using robust thermal technologies such as Thermal Conduction Heating, also called In-Situ Thermal Desorption (ISTD).

As compared to excavation and offsite disposal, the cost for thermal treatment for source zone remediation is considerably lower (cost have varied from $79 per cubic yard upward; Heron et al. 2009), it is however desirable to treat as small an area and volume as practical, while addressing the surrounding plume using other techniques such as monitored Natural Attenuation (MNA).

This paper presents a Brownfield Interim Remedial Measure where ISTD (first time ever deployed in New York State) was used to treat three separate CVOC source areas, followed by a site-wide groundwater remedy consisting of MNA.

SITE DESCRIPTION AND THERMAL DESIGN

A long standing dilapidated manufacturing complex situated on about 26 acres of land was thought to be the only obstacle preventing redevelopment of the site. The building had been occupied by a major manufacturer of industrial dry cleaning equipment. Early investigative work suggested that the site posed little evidence of extensive subsurface contamination. However, all that changed when samples of the underlying peat, which exhibited pronounced "rotten egg odor" were analyzed. Those analyses disclosed PCE and TCE exceeding several hundred mg/kg.

Subsurface strata beneath a veneer of urban fill including foundry sand and other inorganic debris consisting of:

- Peat or peat/marl which extended to depths ranging from 14 to 30 feet below ground surface. The depth of this deposit was found to generally increase in the southern part of the site, except along the western boundary.
- Soft clay was found below the peat or peat/marl layer. The clay layer was of variable thickness, sometimes observed for thirty or more feet uninterrupted. In some explorations the clay was integrated with silt or peat.
- Mixed sand, gravel, and silt layers of varying thicknesses were observed below the clay layer at most locations, underlain by a glacial till. The depth to till generally increased to the south, ranging from as shallow as 15 feet along the northern site boundary to more than 51 feet along the southern boundary. At most locations, a discernible sand unit was found just above the glacial till.

The RI also revealed that top of groundwater was generally found at 2 to 4 feet below grade (C&S Engineers, Inc. 2007b). This condition compounded the geotechnical concerns associated with soft ground, and posed a challenge for the implementation of traditional source removal technologies.

Soil quality data from over 300 sampling points performed during the RI indicated the average concentration of chlorinated VOCs (CVOCs) in three of the four primary source areas ranging from 57 mg/kg to over 4,400 mg/kg. In the fourth source area free product was detected. However, groundwater quality down gradient of those source areas at the property line, revealed minimal CVOC impact, which in-part was attributed to the high carbon content of the peat and the resultant inhibitory affect on the partitioning of CVOCs to groundwater. RI sampling also found that *Dehalococcoides* (Dhc) and the Dhc functional gene vinyl chloride reductase (*vcrA*) was present in groundwater. Extensive peat, 40 years of site inactivity, low level groundwater CVOC concentrations relative to CVOCs in soil, and evidence of Dhc laid the groundwork for MNA to be the final site remedy.

The primary objective of this ISTD remediation project was to reduce the mass and concentration of COCs within the three major source areas to make way for redevelopment of the site. Given the high concentration of total organic carbon, which ranged from 3.5 % to 19.6 % and averaged 8%, Specific Soil Cleanup Objectives (SSCOs) as shown in Table 1 below were developed and eventually accepted by NYSDEC (C&S Engineers, Inc. 2006).

Table 1. Remedial Standards for Soil Samples.

Contaminant	Concentration (mg/kg)
PCE	5.6
TCE	2.8
Vinyl chloride	0.8
Trans-1,2-DCE	1.2
Total CVOCs	10.4

A detailed delineation was conducted to determine the foot-print of each source area that would require thermal treatment. The Interim Remedial Measure Work Plan presented the results and identified ISTD as the technology of choice (C&S Engineers, Inc. 2006).

The ISTD treatment program comprised three separate irregularly shaped areas. A total of 16,207 cubic yards of subsurface was treated thermally, to a maximum depth of 27 ft (Table 2). Based on the soil data, which contained very variable soil data, an initial mass of

146,000 lbs of CVOCs was calculated. The required reduction in mass (and soil concentration) was approximately 99.9%.

Table 2. Treatment Areas and Volumes.

Location	Surface area (ft^2)	Average depth (ft)	Volume (cy)	Comment
B-3	12,675	20	9,389	In-situ treatment
B-1	8,400	18	5,600	In-situ treatment
B-5	840	13	404	Excavated and placed in B-1 area
MW-3D	1,220	18	813	In-situ treatment
Total	22,295		16,207	

Figure 1 shows the site at different stages before, during and after the thermal remediation.

Figure 1. Site Features at Different Stages.

As noted above, four CVOC source areas were identified. However, one of the areas (B-5) was relatively small and shallow. Consistent with the IRM Work Plan (C&S Engineers, Inc. 2006), soil from this area was excavated and placed on the ground surface within the boundary of one of the other thermal treatment areas prior to installation of the ISTD system. The three thermal treatment areas were heated using 288 ISTD heater borings (Figure 2). Boring and well counts are listed in Table 3. Vapor was extracted from 25 vacuum extraction wells and treated on site in a thermal oxidizer. Interim soil sampling was used to track progress (51 sampling locations), until all three areas met the remedial goals, which were attained after approximately 11 months of operation.

Table 3. Heater and Well Counts.

Location	Heaters in original design	Final number of heaters	Vapor collectors	Temperature monitoring locations	Pressure monitoring locations
B-3	108	110	13	15	3
B-1	82	157	10	10	2
MW-3D	21	21	2	5	1
Total	211	288	25	30	6

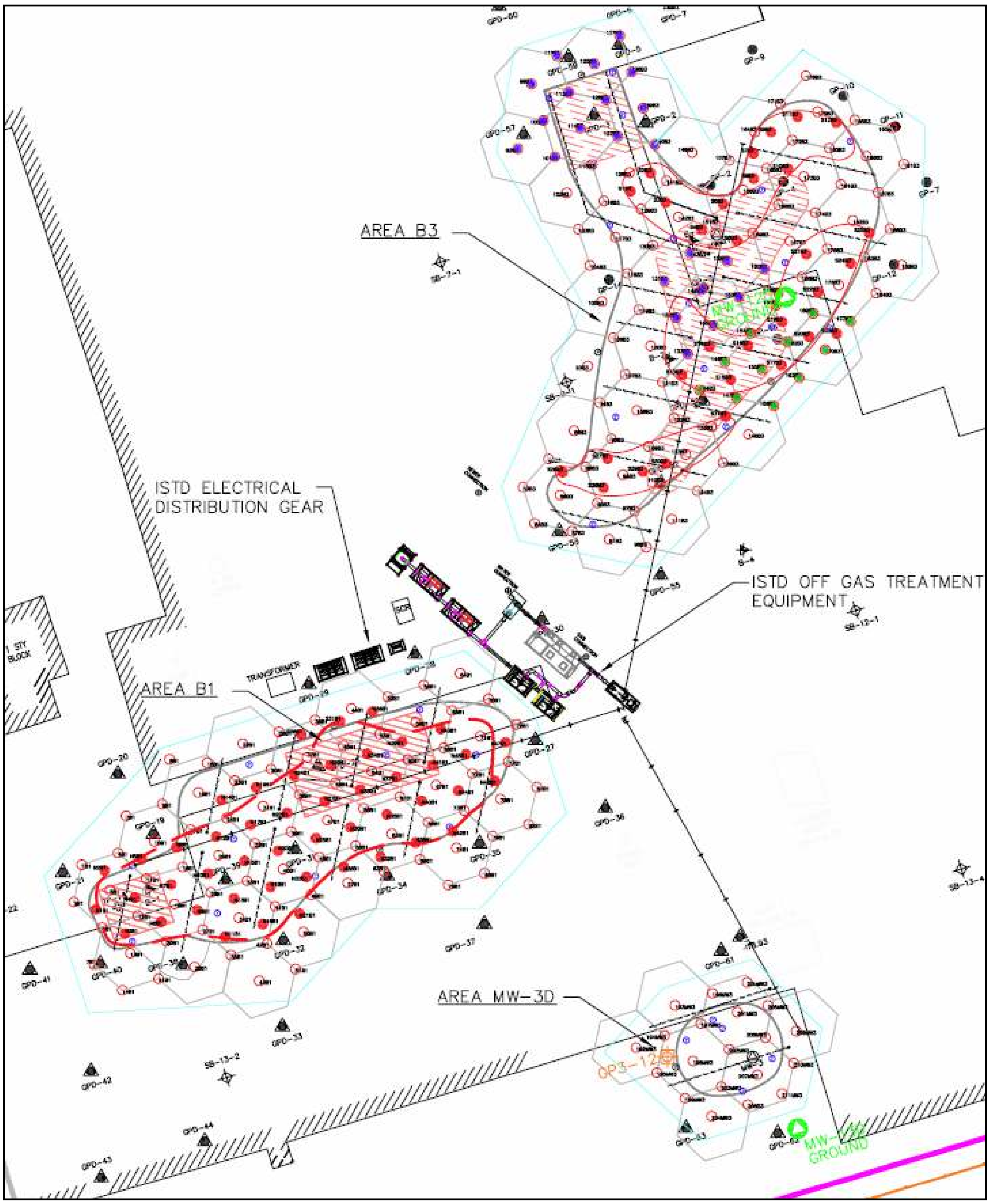

Figure 2. Boring and Well Layout for the ISTD Remedy. Red or open circles with red outline are heater borings. Heater spacing was 15 ft.

RESULTS

Figure 3 shows the energy balance for the three source zones over the 11 months of thermal treatment. Approximately 9.2 million kWh of electric power was delivered to the TCH heaters and turned into heating of the subsurface. In response, the three areas heated at different rates and reached temperatures near the boiling point of water after between 6 and 11 months of heating (Figure 4).

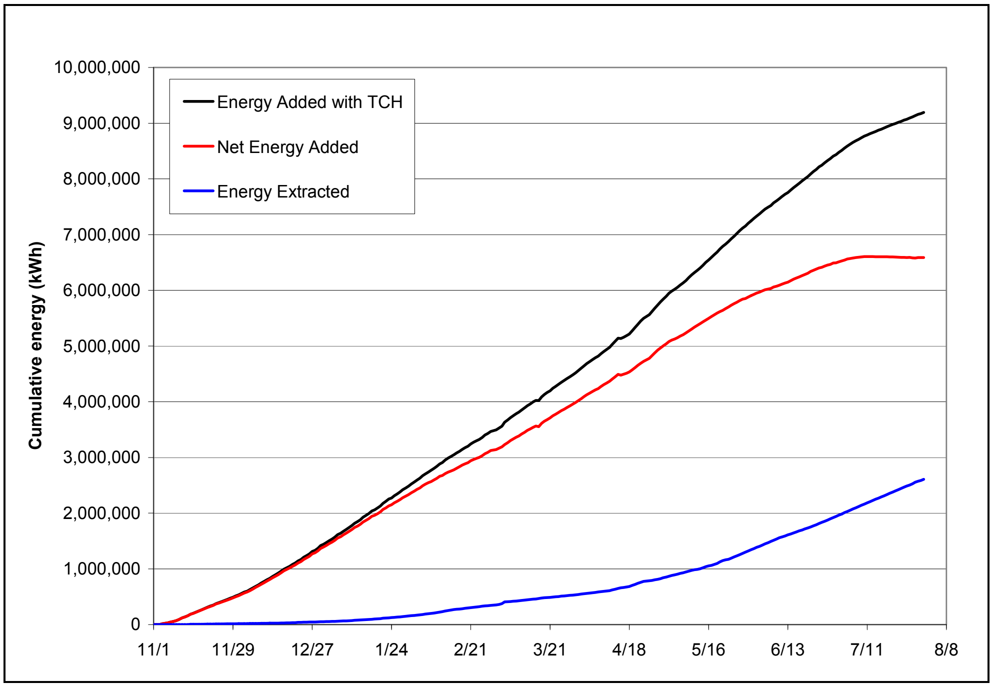

Figure 3. Energy Balance for the Thermal Remedy.

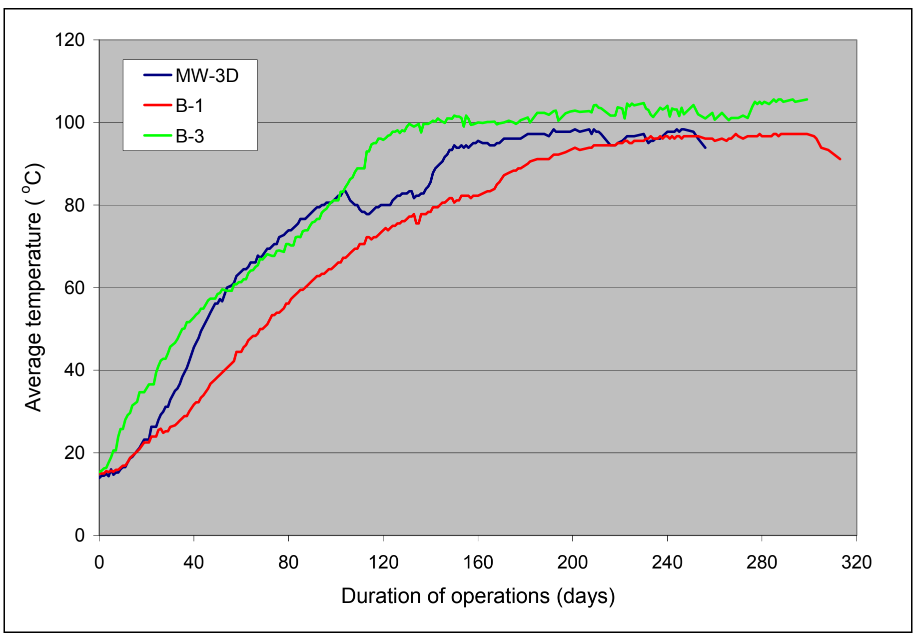

Figure 4. Temperatures Achieved in the Three Treatment Areas.

Area B1 showed signs of slow heating compared to the other areas. After a detailed investigation, groundwater flow into this area was minimized by the installation of a vertical sheet-pile wall on the north (up-gradient) side, and the heating was accelerated by the installation of an additional 75 heaters in this area. This lead to improved heating, and soil sampling after 11 months of operation confirmed that the remedial objectives had been met.

The extracted vapors were treated using thermal oxidation. All emissions were within acceptable limits set by NYSDEC. The total mass of CVOCs extracted and treated (Table 4) was estimated based on laboratory analysis of grab samples (EPA Method TO-15) and measured flow rates. Tetrachloroethylene (PCE) was the dominant contaminant, and a total of 86,205 lbs of CVOCs were removed (C&S Engineers, Inc. 2007a).

Table 4. Mass of CVOCs removed by the Thermal System.

Contaminant	Mass removed (lbs)
PCE	82,793
TCE	2,196
Cis-1,2-DCE	1,055
Trans-1,2-DCE	33
Vinyl chloride	128
Total CVOCs	86,205

In or near the IRM treatment areas, concentrations of several ketones (principally acetone and 2-butanone) in soil and groundwater were observed to increase during the IRM. The synthesis of these compounds during thermal treatment of soils has been documented at other sites and is apparently principally the result of physical/chemical reactions associated with humic acids present in the soils and the applied heat from the remedial system. The concentrations of these compounds declined relatively quickly after the ISTD system was decommissioned. The other observation was a dramatic increase of vinyl chloride (VC) in a monitoring well down gradient of the source area where free product was once evident. During the last month of heating (October 2007) VC was detected at a concentration of 21,000 ug/L. By February 2008, VC had declined to 3,100 μg/L and to 380 μg/L in June 2008 in that same well.

As previously noted, CVOC concentrations in groundwater were significantly lower than what was found in subsurface soils. This observation combined with the predominant CVOCs in groundwater being associated with daughter products of PCE/TCE as well as the general nature of subsurface soils led to the early identification of MNA to be the likely remedy for the groundwater beneath the site. As the IRM reached the late stages, additional groundwater quality data, including Gene-Trac® Dhc analysis, indicating a suitable dechlorinating microbial community was present, was used to establish multiple lines of evidence to support MNA. The Remedial Work Plan for the site documented those lines of evidence and proposed a MNA program consisting of quarterly groundwater sampling (C&S Engineers, Inc. 2007c).

The Remedial Work Plan also presented a discussion of rate constants using USEPA protocol. However, the Remedial Work Plan did include a cautionary note concerning rate constants, as typically three or more years of data would be needed to develop meaningful trends and that groundwater quality data collected during the cool down period after the ISTD system was decommissioned, would not be representative of "normal" ambient conditions.

Information obtained since the initiation of the MNA program in February 2008, has revealed several noteworthy conditions as documented in the most recent status report to NYSDEC (C&S Engineers, Inc. 2010):

- ORP- Generally remains at -300mV or greater.
- Dissolved Oxygen continues to be essentially non-existent and indicative of a reducing environment.
- Methane concentrations of 6.5 mg/l or less are present in MW-2D. MW-9D and MW-10D. Concentrations exceeding 11 mg/l are consistent in the remaining four wells.
- Sulfate concentrations exceeding 377 mg/l were recorded in four wells. Lower concentrations ranging from 3.2 mg/l to 155 mg/l were found in the remaining three wells. According to USEPA MNA guidance, sulfate in excess of 20mg/l may cause competitive exclusion of dechlorination. However, in many plumes with high concentrations of sulfate, reductive dechlorination still occurs. Based on CVOC data collected at the Midler Avenue site, it would appear the reductive dechlorination is occurring.
- The *Dehalococcoides* population has decreased with time as reductive chlorination occurred. However, a rebound appears to be taking place in three wells. Over the course of the remediation *Dehalococcoides* concentrations in a number of wells have been sufficiently high (greater than 1 x 10^7/L) for significant dechlorination rates to be expected (Lu et al., 2006).
- In concert with total Dhc, vinyl chloride reductase (vcrA) has decreased, however, data suggest a possible increase in two wells.

Generally, groundwater VOC concentrations at the site have been declining since the thermal remedy: Three of the seven monitoring wells have met NYSDEC Class GA standards for CVOCs. Three other wells have exhibited a continued decline of CVOCs, with trends indicating that Class GA standards may be achieved within the next five to ten years. One of the seven monitoring wells exhibit declining concentrations of higher order CVOCs, along with increasing levels of VC. This condition indicates that additional data are needed to ascertain that a complete degradation pathway is present at this location.

CONCLUSIONS

Subsurface conditions, the nature of deposits and contaminants combined with the need to ready the site for redevelopment were instrumental in selecting ISTD as the Interim Remedial Measure to attack the significant sources of CVOC. Furthermore, the presence of peat and, recognition of evidence that the high organic content of these deposits not only retarded the ability of CVOCs to partition into groundwater, but also created an environment where Dhc could be established due to the presence of naturally occurring electron donor. Although the ISTD process heated the ground to temperatures above that which can be typically tolerated by Dhc (above 40 °C, Friis et al., 2007), the increase in temperature resulted in the production of acetone. The increased concentration of acetone and the thermal "halo effect" around each ISTD zone, appears to have created an environment that allowed Dhc to flourish and readily dechlorinate the residual CVOCs in groundwater.

The site now known as Midler Crossings, which is currently the location of a major home improvement center and local federal credit union, is a prime example of Brownfield redevelopment and selection of "best fit" alternative remedial technologies.

REFERENCES

C&S Engineers, Inc. 2006. Interim Remedial Measure Work Plan. Midler City Industrial Park Site Brownfield Cleanup. City of Syracuse, Onondaga County, New York. Prepared for Pioneer Midler Avenue, LLC, July 2006.

C&S Engineers, Inc. 2007a. Interim Remedial Measures Report Midler City Industrial Park Site Brownfield Cleanup. City of Syracuse, Onondaga County, New York. Prepared for Pioneer Midler Avenue, LLC, December 2007.

C&S Engineers, Inc. 2007b. Remedial Investigation and Remedial Alternatives Analysis Report Midler City Industrial Park Site Brownfield Cleanup. City of Syracuse, Onondaga County, New York. Prepared for Pioneer Midler Avenue, LLC, December 2007.

C&S Engineers, Inc. 2007c. Remedial Work Plan Midler City Industrial Park Site Brownfield Cleanup. City of Syracuse, Onondaga County, New York. Prepared for Pioneer Midler Avenue, LLC, December 2007.

C&S Engineers, Inc. 2010. Periodic Review Report Midler City Industrial Park Site Brownfield Cleanup. City of Syracuse, Onondaga County, New York. Prepared for Pioneer Midler Avenue, LLC, March 2010.

Friis A.K., A.C. Heimann, R. Jakobsen, H.-J. Albrechtsen, E. Cox, P.L. Bjerg. 2007. "Temperature dependence of anaerobic TCE-dechlorination in a highly enriched *Dehalococcoides*-containing culture". *Water Res.* 41:355 – 364.

Heron, G., R.S. Baker, J.M. Bierschenk and J.C. LaChance. 2006. "Heat it All the Way - Mechanisms and Results Achieved using In-Situ Thermal Remediation." Paper F-13, in: Bruce M. Sass (Conference Chair), Remediation of Chlorinated and Recalcitrant Compounds—2006. Proceedings of the Fifth International Conference on Remediation of Chlorinated and Recalcitrant Compounds (Monterey, CA; May 2006). ISBN 1-57477-157-4, published by Battelle Press, Columbus, OH, www.battelle.org/bookstore.

LaChance, J., G. Heron and R. Baker. 2006. "Verification of an Improved Approach for Implementing In-Situ Thermal Desorption for the Remediation of Chlorinated Solvents." Paper F-32, in: Bruce M. Sass (Conference Chair), Remediation of Chlorinated and Recalcitrant Compounds—2006. Proceedings of the Fifth International Conference on Remediation of Chlorinated and Recalcitrant Compounds (Monterey, CA; May 2006). ISBN 1-57477-157-4, published by Battelle Press, Columbus, OH, www.battelle.org/bookstore.

Lu, X., J. T. Wilson, D. H. Kampbell. 2006. "Relationship between *Dehalococcoides* DNA in ground water and rates of reductive dechlorination at field scale". *Water Res.* 40: 3131- 3140.