Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

Disclaimer:

This work was prepared under an agreement with and funded by the U.S. Government. Neither the U.S. Government or its employees, nor any of its contractors, subcontractors or their employees, makes any express or implied:

- warranty or assumes any legal liability for the accuracy, completeness, or for the use or results of such use of any information, product, or process disclosed; or
- 2) representation that such use or results of such use would not infringe privately owned rights; or
- 3) endorsement or recommendation of any specifically identified commercial product, process, or service.

Any views and opinions of authors expressed in this work do not necessarily state or reflect those of the United States Government, or its contractors, or subcontractors.

Concluding A Steam Injection Remediation Project At A Dense Non-Aqueous Phase Liquid Source Zone At The Savannah River Site – 15303

Branden J. Kramer*, James Kupar*, Jeffery Ross*, Joao Cardoso-Neto*, Dennis G. Jackson**, Brian B. Looney**, and Karen M. Adams***

- Savannah River Nuclear Solutions, LLC
- ** Savannah River National Laboratory
- *** United States Department of Energy

ABSTRACT

Multiple subsurface dense non-aqueous phase liquid (DNAPL) source zones served as latent sources for the extensive groundwater plume within the A/M Area of the SRS. Between 1952 and 1985 over 3.53 million pounds of trichloroethylene (TCE), tetrachloroethylene (PCE) and 1,1,1-trichloroethane were released to the environment at multiple use and discharge locations. While the use and discharge locations are well defined and small, the releases have resulted in a dissolved phase plume that extends over 647.5 hetare (1,600 acres). The M-Area Settling Basin (MASB) received over half of the solvent discharges, and was emptied and closed in 1991 with a Resource Conservation and Recovery Act (RCRA) cap. In 1991, DNAPL was found in an adjacent water table well 140 feet below ground. A successful demonstration of steam injection at a nearby site removed 31,751 kg (70,000 lb) of solvent. This technology was selected to remediate the DNAPL source zone at the MASB.

Based on comprehensive characterization data, the identified treatment area was a 1.21 hectare (3 acre) footprint with target depths of 13.7 to 50.3 m (45 to 165 ft). The site is unconsolidated sand, silt, and clay typical of shallow marine depositional environments. The remediation system included 96 vertical, horizontal, and angled steam injection and soil vapor extraction wells and a thermal monitoring system. Construction of the system began in early 2004 and operation began in August 2005. Steam was applied to the deep vadose zone first, then progressed to the aquifer zone, and followed with the mid-vadose zone. Multiple steam strategies were utilized to enhance mass removal. Steaming was concluded in 2009. Soil vapor extraction is ongoing, with residual temperatures in the deep low permeability zones still exceeding 65.6°C (150°F). To date over 204 metric tons (450,000 lb) of VOCs has been removed.

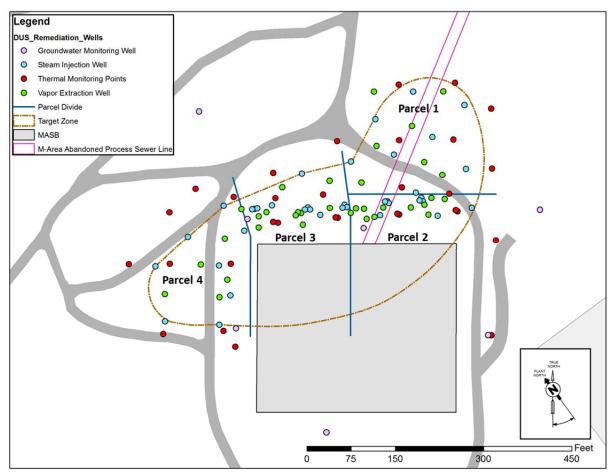
In the summer of 2013, post-remediation soil, vapor, temperature, and groundwater data were used to evaluate the effectiveness of steam injection at the MASB. The collection of post-treatment soil data demonstrated significant reduction in soil concentration, including removal of DNAPL that was present in several soil cores prior to treatment. Assessment of vapor concentrations in the target zone has allowed for abandonment of one-third of the extraction wells and conversion of another third of the extraction wells to passive solar operated vapor extraction equipment. Heating the subsurface increased the solubility of VOCs in groundwater, which increased mass removal rates at two extraction wells (EW) outside the target zone in both the water table aquifer and the underlying aquifer.

INTRODUCTION

The MASB is managed under the RCRA Permit for SRS (Module IV-A for M-Area and Metallurgical Laboratory Hazardous Waste Management Facilities). It received an estimated

900,metric tons (2 million lb) of waste volatile organic compounds (VOCs) from 1958 to 1985. The MASB was emptied and closed with a RCRA cover in 1991. In the early 1990s, DNAPLs containing primarily PCE and TCE were detected in the water table aquifer north of the basin. Under the RCRA Permit, groundwater corrective action consisted of groundwater extraction and treatment and soil vapor extraction. In an effort to aggressively remediate the vadose zone and shallow groundwater contamination at the MASB, a RCRA project, the Western Sector Dynamic Underground Stripping (DUS) project was initiated in August 2005. DUS is a patented process developed after the oil industry standard of injecting steam into the subsurface to enhance removal performance.

The target zone (TZ) was a 1.2 hectare (3 acre) footprint with target depths of 13.7 to 50.3 m (45 to 165 ft) and an estimated 340,000 cubic meters (12 million cubic feet) of soil to remediate. A calculation of mass in the DUS TZ estimated a maximum of 317.5 metric tons (700,000 lb) of total VOCs. There were 33 vapor extraction wells (VEW) fully screened across the TZ, including four with groundwater pumps, and a horizontal vapor extraction well that stretched over 91.4 m (300 ft) underneath the footprint of the closed settling basin. Sixty three steam injection wells (SIW) were strategically placed throughout the TZ and thermal monitoring points (TMP) were installed to measure subsurface temperature. Figure 1 shows the location of the treatment area relative to the settling basin and the location of the SIWs and VEWs. The TZ was divided into four parcels to manage the input of steam and rate of extract to comply with permit requirements.



2

Figure 1. The MASB and location of the DUS remediation sytem.

During the first three years (2005 to 2008) of full-scale operation, the DUS system removed almost 181.4 metric tons (400,000 lb) of solvents from the target area. Heating criteria (110°C [230°F] soil temperature) was met by the summer of 2006, but additional heating strategies were performed for the next three years to enhance extraction of contaminant mass. With diminishing returns after several different heating strategies, injection steaming ceased in September 2009. At that time, total VOC removal in the area was estimated at over 195 metric tons (434,000 lb) of solvent.

As part of the completion of the DUS project, a post remediation characterization effort was initiated in the summer of 2013. The characterization was performed to evaluate the effectiveness of the DUS treatment system and determine the remaining source zone contamination architecture. Comparative information from pre- and post-remediation will be used to plan future remediation decisions based on the evaluation of this characterization data.

Pre-Remediation Characterization

Prior to the design and construction of the DUS system at the MASB, historic characterization data from the MASB area was compiled and evaluated. Based on the evaluation possible source zone architecture depictions were constructed and the 50.3 m (165 ft) deep TZ of the DUS remediation project was identified to include the mid to lower vadose zone, water table aquifer, and the underlying confining unit.

While drilling the SIW and VEWs for the DUS project, core was analyzed for VOC contamination at selected locations. These cores confirmed that the target area was a DNAPL rich environment that showed discontinuous areas of highly concentrated DNAPL. The pre-remediation cores were used as comparative analysis for the soil borings that were completed during the post remediation characterization.

Post-Remediation Characterization

The post-remediation characterization effort was designed to evaluate contamination remaining in the TZ with respect to soil, groundwater, and vapor. The post-remediation activities in the TZ included the collection of depth-discrete soil samples throughout the TZ at depth, vapor assessment of existing VEWs and some SIWs, and groundwater assessment from groundwater monitoring wells.

Depth discrete soil sampling was coordinated to mimic sampling performed during the preremediation characterization for comparison purposes. Soil borings were drilled in all parcels in vertical and angled orientations, but focused on areas that exhibited the highest concentrations measured from pre-remediation characterization effort (Figure 2). These locations were drilled when the localized subsurface temperature was measured at less than 70°C (158°F).

Soil vapor was collected from the individual VEWs to assess the performance of the soil vapor extraction system. The overall VOC vapor concentrations have declined since steaming ceased in 2009. The VEW with lower concentrations were transitioned from an active to passive system or abandoned.

Groundwater was also assessed from extraction wells (EW) and monitoring wells (MW) inside and outside of the TZ. A number of MWs located inside and outside of the TZ were abandoned

during construction of DUS to prevent them from being damaged during steaming and were replaced during the post-remediation characterization effort.

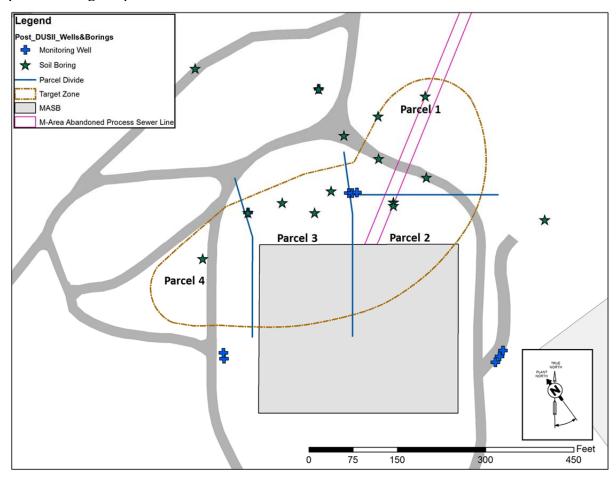


Figure 2. Location of post-remediation soil borings and replacement monitoring wells.

RESULTS

Thermal Monitoring Results

The TMPs were intermittently monitored since steam injection ceased in September 2009. Subsurface temperature data from May 2013 shows subsurface temperatures ranging from 33° to 79°C (91° to 174°F) with maximum temperatures, as expected, located within the TZ. At the end of the steaming campaigns, subsurface temperatures were over 105°C (221°F) throughout the TZ. The rate of temperature decline observed from the pilot DUS project was approximately 0.555°C every month after steam injection ceased. Using this cool down rate, a starting temperature of 105°C (221°F), and a cool-down period of 50 months (thru November 2013), it can be calculated that current subsurface temperatures should be around 77°C. Current maximum subsurface temperatures of 79°C (174°F) are slightly higher than the calculated temperature. At this rate, it is estimated that soil temperatures will return to background (~20°C [68°F]) in the year 2022.

Groundwater temperatures were monitored outside of the TZ in the surrounding area in MWs and EWs. Groundwater temperatures increased during operation of DUS and declined thereafter at MWs and EWs in the direct vicinity of the TZ. Although a decline in temperatures was observed, they remain above ambient groundwater temperatures measured at background wells located farther away from the MASB (Figure 3). Groundwater temperatures have not decreased significantly at the three wells (i.e., MW 2, MW 3, and EW 2) located west and downgradient of the MASB, while two wells (i.e., MW 1 and EW 1) located to the north and east have had groundwater temperatures decrease 5 – 10°C since steaming ceased

Since steam injection was stopped in 2009, the vapor extraction system has continuously operated. The extracted vapor temperatures have progressively dropped, which allowed the original vapor cooling system to be retired in 2012. The vapor temperatures recorded at the well heads in 2012 showed vapor temperatures that ranged between 32°C (90°F) and 74°C (165°F).

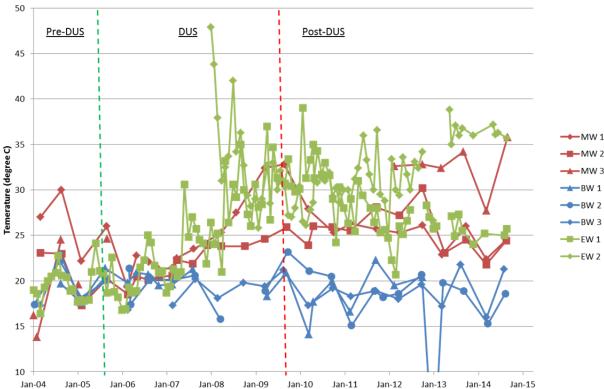


Figure 3. Groundwater temperatures from MWs and EWs near the MASB.

Soil Boring Sample Results

Post-remediation soil samples within the TZ had significantly lower contaminant concentrations than pre-remediation samples. Sample locations outside the TZ showed concentrations that were comparable or slightly higher than pre-remediation samples.

Figure 4 shows a representative soil profile from each parcel comparing pre- and post-remediation soil concentrations for PCE. In Parcel 1, PCE concentrations were reduced in the TZ while PCE was elevated in the upper 18.3 m (60 ft), above the TZ. Parcel 2 had some of the highest soil concentrations during pre-remediation sampling, while the post-remediation PCE concentrations have been significantly reduced. The soil concentration in Parcel 3 and 4 were low through the vadose zone and increased into the water table for pre- and post-remediation

samples. Similar to other post-remediation soil samples, PCE concentrations in Parcel 3 and 4 were less than the respective pre-remediation samples.

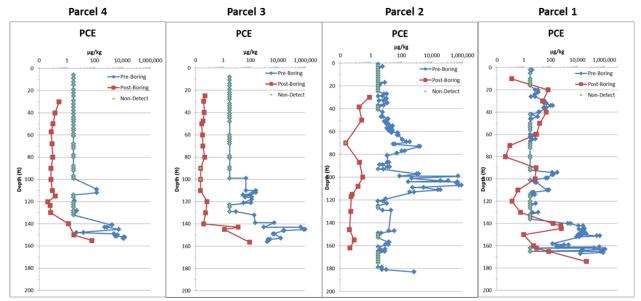


Figure 4. Representative soil profiles for each parcel comparing pre-remediation PCE concentrations to post-remediation concentrations.

Soil borings located outside of the TZ were collected to confirm contaminant mass was actually removed from the TZ rather than just redistributed in the subsurface. The post-remediation PCE concentrations at MW 1 are slightly higher than pre-remediation concentrations, while the pre- and post-remediation concentrations at MW 2 were very similar (Figure 5). The soil data from MW 1 and MW 2 also indicate that PCE concentrations are also prevalent in the aquifer underlying the water table aquifer.

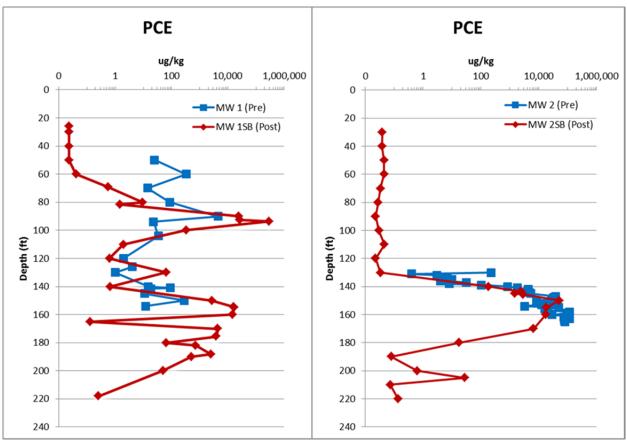


Figure 5. Soil profile comparing pre-remediation and post-remediation PCE concentrations at MW 1 and MW 2.

Soil Vapor Results

In 2012, the VEWs were sampled to determine individual output because the overall mass removal rates had fallen nearly 25% over three years (2010 thru 2012). Based on that assessment, it was determined that the wells could be grouped into three categories; active, passive, and abandon. The active group was determined to remove greater than 0.45 kg (1.0 lb) of solvent per day, while the passive group removed between 0.45 kg (1 lb) and 0.045 kg/day (0.1 lb/day), and the abandon group removed less than 0.045 kg/day (0.1 lb/day). The majority of the active group is in Parcel 1, the passive group in Parcel 2, and the abandon group were in Parcel 3 and 4 (Figure 6).

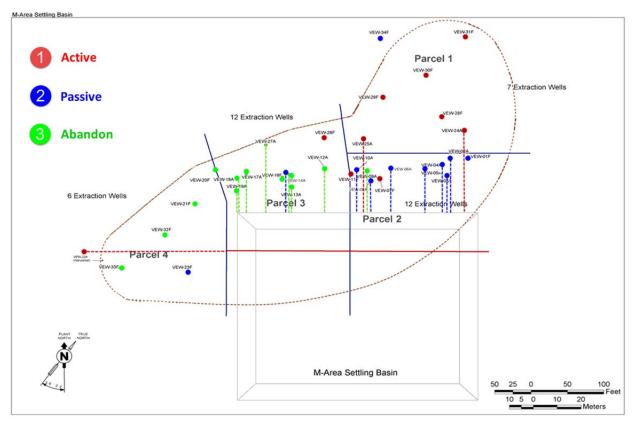


Figure 6. The VEWs separated into three groups based on vapor data collect post-remediation.

The VEWs in the passive group were converted to low-energy systems in 2014 and will be used as a polishing system to remove contaminant vapors that are outside the zone of influence of the active system. This combination will aid in the removal of contaminants in the TZ and keep the subsurface in an equilibrium state that does not allow contaminant to diffuse or transport to the groundwater.

Groundwater Results

The MWs and EWs surrounding the MASB are sampled at least semi-annually per the RCRA permit. During post-remediation, monitoring wells were installed to replace wells abandoned during the construction of the DUS remediation system.

The extraction wells (i.e., EW 1 and EW 2) had notable increases in total VOC concentrations during operation of DUS (Figrue 7). The most significant increase in concentration was observed at EW 1, which has since decreased but is still pulling higher concentrations than pre-DUS. The increase observed at EW-2 was gradual and lasted almost three years after steaming ceased.

In general, VOC concentrations in water table MWs near the MASB have declined with time. The decline appears to be independent of the DUS system. This trend was also observed at the replacement wells installed during post-characterization. Groundwater samples from the TZ have not yet been collected due to elevated groundwater temperatures (65°C [149°F]). The aquifer beneath the water table, however, has high VOC concentrations. The underlying aquifer is outside of the treatment zone.

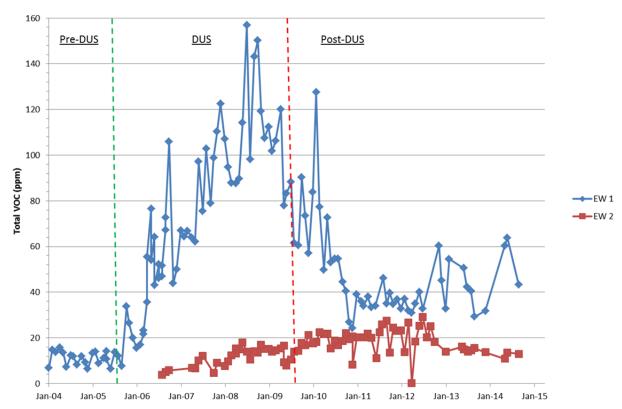


Figure 7. Time series trend of total VOC concentration at EW 1 and EW 2 before during and after operation of DUS.

DISCUSSION

All the data collected during the post-characterization at the MASB, suggest that the DUS remediation system was effective in hearting the subsurface and removing contaminant mass in the TZ. From 2005 to 2013, the DUS system was able to remove 207.5 metric tons (457,425 lb) of VOCs from the subsurface. This is more than 60% of the calculated mass within the TZ, preremediation.

The data also suggest that contaminant concentrations have increased outside of the TZ. This was evident in Parcel 1 in the shallow vadose zone (Figure 4) as well as at MW 1 (Figure 5). Since so much steam was used to heat the subsurface at MASB, the TZ reached its target temperatures and radiated outward into the area surrounding the TZ. Elevated groundwater temperatures were observed at distances of up to 122 m (400 ft) from the TZ in the water table and underlying aquifer. Data from the TMPs indicate the majority of the latent heat remaining in the subsurface is being stored in the confining unit separating the water table and underlying aquifer. The latent heat is allowing VOC contamination once sorbed to the low permeability sediments of the confining unit to desorb and become more soluble in the groundwater. An increase in groundwater temperature at EW 1 has been observed to correspond with an increase in VOC concentrations (Figure 8). The EW 1 is screened from the water table, through the confining unit, and into the underlying aquifer. The EW 1 and EW 2, which are on the north and western side of the MASB, have been able to remove additional mass from the aquifer because of the latent heat associated with DUS. The east side of the MASB, however, is outside the zone

of capture of the two EWs. VOC concentrations at MW 3, one of the replacement wells on the east side of the MASB, are currently greater than $100\,\mu\text{g/L}$. The groundwater temperature at MW 3 is elevated above background. The high dissolved concentrations of VOCs and elevated temperatures provide an opportunity for additional corrective action to continue removing mass from the subsurface.

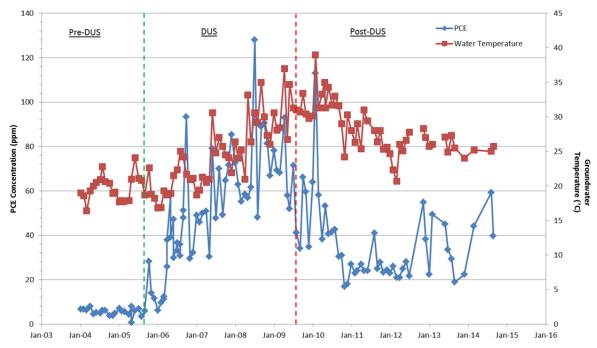


Figure 8. Groundwater PCE concentration and water temperature at EW 1.

CONCLUSIONS

It is evident from the data collected during the post-remediation evaluation of the DUS system that the deployment of DUS was able to heat the subsurface and reduce VOC concentrations in the TZ. Although DUS was commenced in 2009 the elevated subsurface temperatures allow for continued mass removal through vapor and groundwater extraction; therefore, preventing further impact to downgradient sources. The following are major points determined from this analysis:

- 1) The remedial effort was very successful in the removal (>99% based on direct comparison of pre- and post-heating analytical results) of volatile contaminants, dominantly PCE and TCE, particularly in the vadose zone throughout the TZ.
- Conditions are appropriate for a phased transition of SVE wells from active to lowenergy units. Eleven (11) SVE wells were converted to low-energy SVE units in September 2013.
- 3) Subsurface temperatures are declining, as expected and temperatures are estimated to be near background (~20°C [68°F]) by 2022.
- 4) Since latent heat in the area is still contributing to a higher solubility of the VOCs, groundwater concentrations of VOCs have increased in recovery wells EW 1 and EW 2 and surrounding monitoring wells. Elevated levels of PCE and TCE are also observed in deeper aquifer sediments from borings in the area surrounding the MASB.