Evolution of a Pump and Treat Remediation System at the SLAC National Accelerator Laboratory, Menlo Park, California

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ABSTRACT: Pump and treat operations have been conducted over the past ten years at the Former Solvent Underground Storage Tank (FSUST) Area, located at the SLAC National Accelerator Laboratory (SLAC) located in Menlo Park, California. Soil and groundwater at the FSUST Area were impacted by historical releases of volatile organic compounds (VOCs) and semivolatile organic compounds (SVOCs) from a former 2,400gallon solvent underground storage tank used to store paint shop wastes in the 1960s and 1970s. A groundwater extraction and treatment system began operation in 2001 utilizing five groundwater extraction (GWE) wells and granular activated carbon (GAC) for treatment of extracted groundwater before discharge to a sanitary sewer. In 2007, the system was converted to dual-phase extraction (DPE) by adding simultaneous soil vapor extraction, substantially increasing VOC/SVOC mass removal rates. Migration of the groundwater plume has been contained with the operation of the GWE/DPE systems. Total VOC/SVOC concentrations in source area wells have declined over 99% in some wells since startup in 2001, and continue to decline toward remedial goals, with reductions accelerated during DPE operations. GWE and DPE system operational and performance data as related to attainment of remedial action objectives are presented along with observed system limitations. In addition, the unexpected destruction of 1,4-dioxane in the GAC groundwater treatment system is discussed.

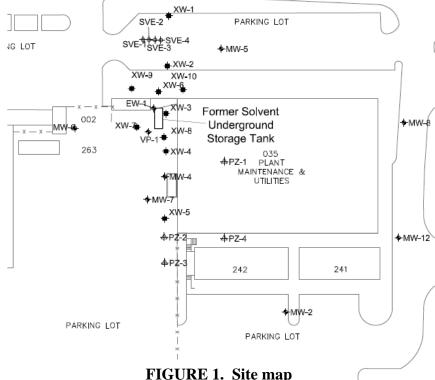
INTRODUCTION AND BACKGROUND

The FSUST Area is located at the SLAC National Accelerator Laboratory in Menlo Park, California. Soil and groundwater at the FSUST Area have been impacted by historical releases of chemicals from a former 2,400-gallon solvent underground storage tank that was used to store paint shop wastes and solvents in the 1960s and 1970s. The tank was removed in 1983. Between 1983 and 1988, a number of studies and remedial actions were completed and a limited amount of subsurface material was excavated. As of 2001, a significant mass of VOCs and SVOCs remained in the subsurface, necessitating the implementation of a remedial action to (a) reduce VOC concentrations in soil and groundwater, and (b) prevent migration of groundwater containing VOCs and SVOCs to surface water or a downgradient alluvial aquifer.

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Site Description and Hydrogeology. The FSUST Area and the location of the former underground storage tank are shown on Figure 1. The FSUST Area is primarily located

in the fine-grained siltstone and sandstone bedrock of the Miocene age Ladera Sandstone. The bedrock in this is several area thousand feet thick. The depth to groundwater across the FSUST Area ranges from approximately 3 to 6 feet (0.9 to 1.8 m) below ground surface (bgs), but is deeper in the area south of the former tank location. The groundwater gradient is primarily



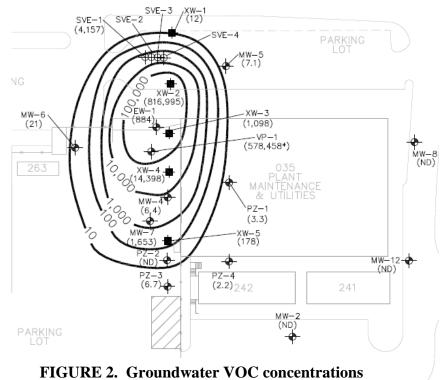
to the south and **FIGURE I. Site map** southeast and appears to be influenced by the subdrainage system for the SLAC linear accelerator (LINAC) located approximately 350 feet (107 meters) south of the former location of the underground storage tank at the FSUST Area. Groundwater flow at the FSUST Area appears to occur as both matrix seepage and fracture flow, but appears to be primarily fracture-controlled. Hydraulic conductivity of the bedrock in the FSUST Area is low, with laboratory-measured values of vertical hydraulic conductivity ranging from 3.16×10^{-7} centimeters per second (cm/sec) to 2.55×10^{-5} cm/sec, and field-measured hydraulic conductivity values during pump testing ranging from 4.4×10^{-6} cm/sec to 2.4×10^{-5} cm/sec.

Extent of Contamination. The distribution of total VOCs in groundwater as of 2001 is shown on Figure 2. In 2001, a maximum concentration of 617,822 μ g/L of total VOCs was detected in groundwater. Although high VOC concentrations were present in the immediate vicinity of the former underground solvent storage tank, the areal extent of the plume was limited due to the low hydraulic conductivity of the bedrock.

The primary chemicals of concern in groundwater included methylene chloride, toluene, trichloroethene, 1,1-dichloroethane, 1,1-dichloroethene, 1,1,1-trichloroethane, and 4-methyl-2-pentanone. However, over 25 halogenated and non-halogenated VOCs and SVOCs had been detected in at least one site monitoring well. The extent and distribution of VOCs and SVOCs in soil and soil gas is generally similar to the extent and distribution in groundwater.

METHODS AND RESULTS

Groundwater **Pump** and **Treat** System. In 2001, SLAC constructed a groundwater extraction and treatment system to address the elevated VOC and SVOC concentrations in groundwater at the FSUST Area. This pump and treat system consisted of five GWE wells and a treatment system consisting of two 2,000-pound GAC vessels in series. The groundwater and pump treat



 $(\mu g/L)$ in August 2001

system began operation in August 2001.

Due the low hydraulic conductivity of the bedrock in the FSUST Area, GWE flowrates were extremely low, generally ranging from 0.15 to 0.20 gallons per minute (gpm) [0.57 to 0.76 liters per minute for all five wells combined]. During design, the low anticipated GWE flowrates were a concern due to potential pump overheating. Air-driven pumps were therefore installed in the GWE wells, each with an internal float to automatically start and stop the pump depending on the groundwater level in the pump.

The extremely low influent flow rates resulted in some consequences for the pump and treat system that were not anticipated during design. The low flow rates combined with high naturally-occurring sulfate concentrations and high hydrocarbon concentrations in groundwater created an excellent environment for sulfate-reducing bacteria to flourish within the groundwater treatment system's GAC vessels. These bacteria converted sulfate in the groundwater into sulfide, causing a hydrogen sulfide odor to develop within the vessels. It was determined that the sulfide could cause an odor nuisance and potentially pose health and safety concerns for personnel servicing the GAC vessels. As a result, the system was temporarily shut down to flush out the carbon vessels and develop plans for mitigating the odor problem. An automatic chlorine feeder was added to the system in 2002 to reduce bacterial growth and the resultant sulfide formation. Since the installation of the chlorine feeder, hydrogen sulfide has not been detected in the GAC vessels or in influent groundwater samples.

An additional unexpected consequence of the low flow rate was related to 1,4-dioxane, which was present in FSUST Area groundwater at concentrations ranging

up to 7,300 μ g/L. Because of its high solubility and low octanol-water partition coefficient, 1,4-dioxane typically does not readily adsorb to GAC. Therefore, it was anticipated that elevated concentrations of 1,4-dioxane would be present in the treatment system effluent. However, based on the influent and effluent data shown in Table 1, 1,4-dioxane was indeed being removed by the treatment system down to non-detectable levels.

The reasons for the unexpected removal of 1,4-dioxane by the GAC are not entirely understood but have been speculated upon in the literature (Mohr, The most likely explanations are 2010). related to the low system flow rates. One potential explanation is possible cometabolism or biodegradation of 1,4dioxane on the carbon surfaces, with the low flow rates, large GAC surface area, and presence of potential cometabolites such as tetrahydrofuran in the influent groundwater allowing the vessel to essentially act as a bioreactor. A second potential explanation is that the low flow rates and large GAC surface area could allow 1,4-dioxane to diffuse into the GAC pore structures as opposed to adsorbing onto the GAC surface as part of the usual GAC sorption mechanism.

		Mid-	
Date	Influent	GAC	Effluent
8/17/01	100	<25	<25
8/17/01	200	<25	<25
8/20/01	470	<25	<25
8/29/01	1500	-	<25
9/5/01	1100	-	-
10/3/01	630	-	<10
10/17/01	900	-	<10
10/31/01	790	-	<10
11/14/01	590	-	<10
11/28/01	950	-	<10
12/12/01	660	-	<10
1/9/02	470	-	<10
2/7/02	470	-	<10
3/5/02	590	-	<10
6/13/02	880	<10	-
7/10/02	650	<10	<10

TABLE 1. 1,4-Dioxane in treatment system influent and effluent (µg/L), 2001-2002

Despite the low flow rates, significant VOC and SVOC mass was removed by the GWE system in its first years of operation. Over the first six years of system operation, over 300 pounds (136 kilograms) of VOCs had been removed by the GWE system. After six years of operation, total VOC and SVOC concentrations in influent groundwater had decreased from approximately 150,000 μ g/L to approximately 30,000 μ g/L. However, VOC concentrations in groundwater remained significantly above remedial goals and mass removal appeared to be approaching asymptotic levels as shown on Figure 3.

Pilot testing performed in 2004 suggested that GWE rates could be increased by the addition of a vacuum-inducing blower system to the existing GWE system, resulting in increased mass removal rates, larger groundwater capture zones, and faster progress toward remedial goals. An upgrade was therefore performed in Fall 2007 to convert the existing pump and treat system to a DPE system.

Dual-Phase Extraction System. The upgrade to DPE was performed during 2007 and consisted of (a) the installation of a 3-horsepower soil vapor extraction (SVE) blower at the existing groundwater treatment system pad, (b) installation of three new DPE wells, and (c) the conversion of three of the five groundwater extraction wells to DPE wells. For the wells being converted to DPE, soil vapor extraction tubing was installed within the existing secondary containment piping for the groundwater tubing. Soil vapor

extracted by the blower was discharged through a stack in accordance with a permit from the Bay Area Air Quality Management District. Startup of the DPE system occurred in October 2007.

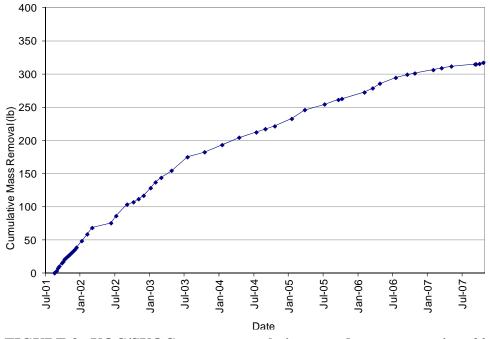


FIGURE 3. VOC/SVOC mass removal via groundwater extraction, 2001-2007

As was expected, the conversion to DPE and the addition of new DPE wells resulted in an increase in groundwater extraction flow rate. Prior to the DPE upgrade, the average annual groundwater flow rate was approximately 250 gallons (946 liters) per day (gpd). After the DPE upgrade, the average annual groundwater flow rate was approximately 330 to 340 gpd (1,249 to 1,296 liters per day). Although the groundwater extraction rate increased, the mass removal rate via groundwater actually decreased after an initial shortterm increase due to the continuing long-term downward trend in influent groundwater VOC concentrations (Figure 4).

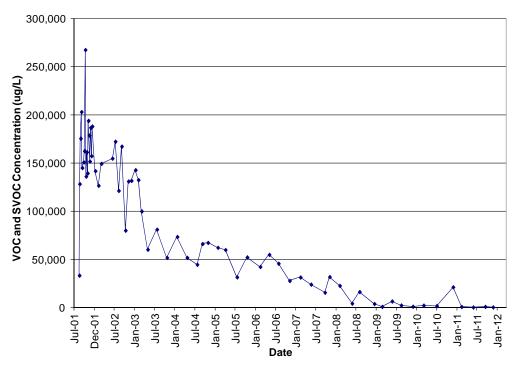


FIGURE 4. VOC/SVOC (total concentration in system influent), 2001-2012

Although the mass removal via groundwater extraction continued to level off following the DPE upgrade, the overall VOC/SVOC mass removal of the system increased dramatically due to the system's high mass removal rate in the vapor phase. The mass removal via SVE upon startup was over 6 pounds (2.7 kilograms) per day, as compared to the approximately 0.05 pounds (0.023 kilograms) per day that was being removed at the time via groundwater. Although the mass removal rate via SVE did decline in the months following startup, the mass removal rate in the vapor phase continued to be significantly higher than in the liquid phase. In fact, in the one year after the DPE upgrade, the VOC/SVOC mass removed via the soil vapor phase was greater than the cumulative VOC/SVOC mass removed over six years (2001-2007) via the groundwater phase. As of 2012, approximately 528 pounds (239 kilograms) of VOC/SVOCs had been removed in the vapor phase, as compared to 340 pounds (154 kilograms) of VOC/SVOCs in the groundwater phase. The comparative mass removals in the groundwater and soil vapor phase are shown on Figure 5. The graph in Figure 5 shows a leveling-off of mass removal in 2008, followed by surges in mass removal in late 2008 and early 2009 which reflected periodic "re-balancing" of system extraction rates and vacuums to increase soil vapor extraction rates at wells with the highest VOC concentrations.

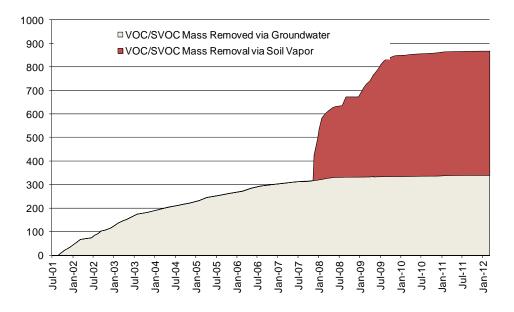


FIGURE 5. Cumulative VOC/SVOC mass removal in pounds, 2001-2012

One major challenge with DPE system operation has been continuously sustaining high vacuums. Some DPE wells experienced periods where they were unable to sustain high vacuums due to contribution of air directly from the atmosphere, or vapor "short circuiting." This was most pronounced at DPE wells with shallower screens, particularly those located in close proximity to a volume of pea gravel occupying the former tank excavation. To address the vapor short circuiting, two extraction wells (XW-3 and XW-8) were rebuilt with deeper screened intervals in January 2010. The rebuilding appears to have addressed the short circuiting issue at these two wells.

A second major challenge has been the continual balancing of SVE flow rates among the DPE wells, which is necessary to (a) optimize mass removal, (b) maintain the appropriate vacuums in the DPE wells, and (c) prevent potential "short circuiting." Flowrates and vacuums are checked on a weekly basis, with vapor sampling performed on a monthly basis, and flow rates are adjusted as appropriate based on the monitoring data. For example, flow rates at a given well can been increased if VOC concentrations in that well increase relative to concentrations in other wells. Alternatively, flow rates at a given well can be decreased if there is an upward trend in flowrate concurrently with a downward trend in vacuum, which is an early warning sign of vapor short circuiting.

DISCUSSION

Remedial Progress. Since the startup of the original groundwater extraction and treatment system in 2001, total VOC and SVOC concentrations in extracted groundwater have been declining. The declining concentrations in extracted groundwater generally reflect declining concentrations in groundwater in the source area where the extraction wells are located. Total VOC and SVOC concentrations in source area wells have

declined by 95 to 99 percent as shown in Table 2. The overall size of the VOC/SVOC plume has also reduced over the period of system operation, by roughly 15 to 20 percent based on the size of the area exceeding groundwater cleanup goals.

Although significant remedial progress has been made, groundwater VOC/SVOC concentrations remain above remedial goals, so operation of the DPE system is expected to continue.

Well	Total VOCs and SVOCs (μ g/L)			Change from	Change from
	2001	2007	2010-	2001 to 2011	2007 to 2011
			2011		
EW-1	853 (a)	24,474	3	-99.6%	-99.99%
SVE-3	11,337	480	80	-99.3%	-83.3%
VP-1	198,923	11,364	784	-99.6%	-93.1%
XW-2	802,995	2,008	580	-99.9%	-71.1%
XW-3	576,373	30,660	10,294	-98.2%	-66.4%
XW-4	15,129	3,811	679	-95.5%	-82.2%
XW-6	(b)	144,856	1,866		-98.7%
XW-7	(b)	1,391	523		-62.4%
XW-8	(b)	86,736	519		-99.4%

 TABLE 2. Trends in Total VOCs and SVOCs in Source Area Wells, 2001-2011

(a) Concentrations in well EW-1 were artificially low in 2001 prior to startup of groundwater extraction due to the well being screened within tank excavation backfill (i.e., gravel), meaning that the 2001 concentration partially reflects surface water that had entered the excavation backfill.
 (b) We have a water water water that had entered the excavation backfill.

(b) No data; well installed in 2007.

Future System Modifications. During 2010, i.e., two additional wells (XW-9 and XW-10) were installed at the FSUST Area. These wells may be incorporated into the FSUST DPE system in the future to accelerate remedial progress. Currently, SLAC is reviewing in-situ chemical oxidation (ISCO) as an adjunct remedial technology to accelerate remediation of residual chlorinated VOCs in the FSUST source zone.

ACKNOWLEDGEMENTS

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