Solar-Powered *In Situ* Soil Washing With Surfactant to Collect LNAPL

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This article presents the findings of a sustainable, surfactant-enhanced, product recovery pilot-scale study (PSS) completed between January 2010 and May 2010 at the Hydrocarbon Burn Facility located at the John F. Kennedy Space Center in Florida. The goal of this study was to implement a unique, simple, and sustainable light nonaqueous-phase liquid (LNAPL) recovery process and evaluate site-specific volumes and rates of LNAPL that could be collected and the degree of soil and groundwater cleanup that could be achieved. The recovery process was a combination of groundwater recirculation at a rate of approximately 2.9 gallons per minute (11.0 liters per minute), soil washing via LNAPL mobilization, and collection of LNAPL via a hydrophobic LNAPL skimmer. A biodegradable surfactant, ECOSURF™ SA-15, was added to the recirculation line to lower the interfacial tension and facilitate LNAPL recovery via mobilization. All equipment (submersible pump, LNAPL skimmer, surfactant feed pump, controls, and various other equipment) used was powered by a solar panel array. Approximately 60 gallons (227 liters) or 429 pounds (195 kilograms) of LNAPL were collected at the recirculation site over approximately three months during the PSS. The data suggest that surfactant amendments greatly enhanced free product collection. The maximum rate of free product collection was approximately 1 gallon (3.8 liters) per day. © 2012 Wiley Periodicals, Inc.

INTRODUCTION

Site Description

The Hydrocarbon Burn Facility (HBF) at the John F. Kennedy Space Center in Florida was operated between 1966 and 1994 as a fire-fighting training facility. Petroleum fuels mixed with volatile waste solvents and associated impurities were used during the training activities. These activities at HBF resulted in the accumulation of up to 1.5 feet (46 centimeters) of light nonaqueous-phase liquid (LNAPL) on the surface of the groundwater at various locations within the HBF site. LNAPL at the site is in the C10 to C15 range, which corresponds to mostly diesel fuel. The viscosity of LNAPL at the site is within the range of 1.4 to 10.9 centipoise, and the density of the LNAPL varies from 0.80 to 0.86 gram per cubic centimeter. Interfacial tension between LNAPL and groundwater at the site ranged from 9.0 to 21.0 dynes per centimeter.

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In Situ Soil Washing and Surfactants

In situ soil washing using surfactants is used to remediate an area by either solubilization or mobilization of the contaminant. By way of solubilization, a surfactant is dosed so the contaminant is encapsulated within surfactant micelles so that contaminant along with surfactant micelles can be removed. This formation of micelles, which is unique to surfactants (Parnian & Ayatollahi, 2008), occurs as the concentration of surfactant increases and individual surfactant molecules combine and agglomerate.

If mobilization is the chosen mechanism, a surfactant is typically dosed to lower the interfacial tension between the contaminant and the aqueous medium. As interfacial tension is lowered, mobilization of the contaminant becomes more achievable. The lowest interfacial tension that can be achieved using a surfactant addition is the critical micelle concentration (CMC) of a surfactant. The CMC is different for every surfactant and is the value where individual surfactant molecules begin to agglomerate and form micelles (Advanced Applied Technology Demonstration Facility Program [AATDFP], 1997).

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MATERIALS AND METHODS

The pilot-scale study (PSS) was implemented within an approximate 2,700-square-foot (251-square-meter) area with one extraction well, one injection well, and six monitoring wells installed. The extraction, injection, and monitoring wells and groundwater particle tracking model are illustrated in Exhibit 1. The monitoring wells were constructed as 2-inch (5-cm) diameter wells and were installed to total depths of 14 feet (4.3 meters) and were screened from 9 to 14 feet (2.7 to 4.3 meters) below ground surface (bgs). The injection and extraction wells were 5 inches (12.7 cm) in diameter and were installed to a depth of 25 feet (7.6 meters) bgs and were screened from 5 to 25 feet (1.5 to 7.6 meters) bgs.

Recirculation Pumping Rate and Zone of Capture

Based on a groundwater flow model using MODFLOW and particle tracking using MODPATH, 3 gallons per minute (gpm) (11.3 liters per minute [Lpm]) was selected as the optimal groundwater recirculation rate. An estimated minimum travel time of seven days for the injected groundwater and additives to travel from the injection point to the extraction point was determined under steady-state water-level conditions.

The footprint of the area estimated to be primarily influenced by the recirculation system was determined using the 3-gpm recirculation rate and the minimum travel time of seven days predicted by MODFLOW. At this pumping rate and minimum travel time, the volume of groundwater primarily influenced by the recirculation system was determined to be 32,240 gallons (122,000 liters). Considering the depth interval of injection and the volume of groundwater primarily influenced, the corresponding surface area of capture was determined to be approximately 2,695 ft^2 (250 m^2). The surface area of capture was then further refined by assuming that the area was elliptical in shape and extending over a length of 40 feet (encompassing the 30 feet between the injection and extraction wells and extending 5 feet beyond both wells). This assumption resulted in an ellipse with an estimated width of 80 feet. Considering the 80-foot width to be the outer

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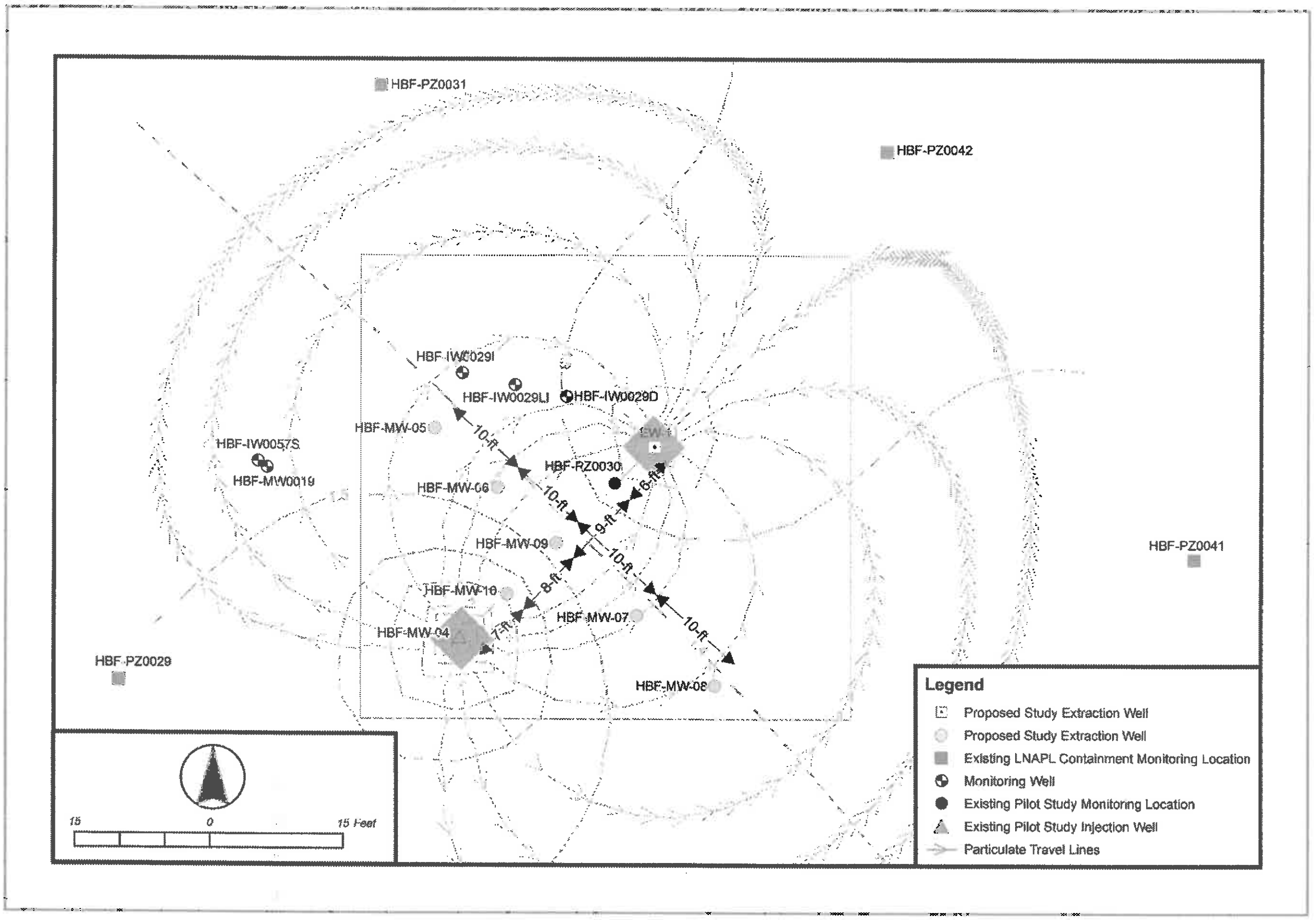

Exhibit 1. Well layout and groundwater particle tracking model

edge of the zone of capture, a maximum particulate travel time of approximately 90 days from the injection well to the extraction well was indicated by the model.

Surfactant Addition Rationale

The amount of surfactant to be added to groundwater was based on the mechanism of mobilization and the CMC of the surfactant chosen, which was ECOSURF™ SA-15, which has a CMC of 153 mg/L. The primary considerations for using mobilization rather than solubilization was that less surfactant would be needed during the study and LNAPL could be recovered via specific gravity separation because surfactant and oil emulsions are not expected to occur using mobilization.

The surfactant was added to the groundwater recirculation line to achieve a concentration of three times the CMC. Although the interfacial tension is typically the lowest at the CMC, the surfactant was dosed at three times this value to account for surfactant loss within the soil and groundwater and to ensure that the point at which the interfacial tension is at its lowest is met or slightly exceeded. In addition to dosing at three times the surfactant CMC, particular planning was given to achieving the designed surfactant concentration within the pilot-study area throughout the study. Consequently, a time-weighted approach to the dosing of surfactant was applied to minimize

Exhibit 2. Surfactant addition and dosage

Surfactant Concentration Calculations				
Particulate Travel Times From Figure (Days)	Average Time Between Lines (Days)	Zone	Approximate Pore Volume Flushes per Zone	Surfactant at Extraction Well (%)
7		1		
10	8.5	2	10.6	39
15	12.5	3	7.2	66
20	17.5	4	5.1	85
50	35	5	2.6	95
90	70	6	1.3	99.9
		Total	**26.8**	

Surfactant Feed Concentration				
Time Period (Days)	Dosage of Surfactant at Injection Well (mg/L)	Mass of Surfactant Injection Into Recirculation Line (g/hr)	Mass of Surfactant Required per Time Period (kg)	Surfactant Feed Concentration (g/L)
0–8.5	459	313	63.79	53.0
8.5–12.5	280	191	18.31	32.3
12.5–17.5	156	106	12.75	18.0
17.5–35	68.9	46.9	19.70	7.9
35–70	23.0	15.6	13.13	2.6
70–90	0.459	0.31	0.1501	0.1
		Total (lbs)	**127.85**	
		Total (kg)	**281.26**	

solubilization from occurring and allow mobilization to be the primary mechanism for remediation. The time-weighted approach was primarily developed using the particulate travel times predicted by MODFLOW, the estimated maximum travel time of 90 days, and the division of the estimated zone of capture into five zones. Each of the five zones represented areas of the zone of capture receiving a certain portion of recirculated groundwater. The approach provided the approximate time frame into the study when surfactant dosages were to be adjusted so that a steady concentration of three times the CMC of surfactant could be achieved. Exhibit 2 shows the surfactant dosages and the time frames that were determined.

Materials

A dual pumping system was installed at extraction well HBF-EW-01 and a 12-volt direct current (DC) submersible groundwater pump manufactured by SunPumps™ (Safford, Arizona) was used to extract groundwater from the extraction well at approximately 3 gpm (11.4 Lpm) and provide groundwater to the recirculation system. Surfactant

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addition was performed by a continuous-feed pump set to inject surfactant at the designated time-weighted concentrations. The Magnum Spill Buster™ (North Ferrisburgh, Vermont) was installed and operated simultaneously within the extraction well to extract partitioned LNAPL.

The Magnum Spill Buster™ unit and submersible pump were powered by four deep-cycle batteries that provided 24 volts charged by a six-panel solar array. One deep-cycle battery providing 12 volts of power was charged by a two-panel solar array, which provided power for the surfactant feed pump, tank mixer, and control panel.

Phase I Operations

Phase I consisted of operation of the recirculation system with no surfactant addition so that a baseline of LNAPL recovery could be monitored and eventually compared to operation with surfactant addition. The recirculation system was initially operated with no surfactant addition for approximately two months, from November 19, 2009, to January 26, 2010. During Phase I, a testing dose of surfactant was injected on December 16, 2009, to check operation of the injection system.

Baseline groundwater samples were also collected on December 16, 2009, and analyzed for total petroleum hydrocarbons (TPH). TPH samples were shipped to Gulf Coast Analytical Laboratories in Baton Rouge, Louisiana, for analysis via the Florida Petroleum-Range Organics (FL-PRO) method. System checks, including water levels, free product levels, free product collection volume, and flow rate, were recorded twice a week during this period.

Phase II Operations

Phase II of the recirculation system operation was from January 26 to May 28, 2010. During Phase II of the study, continuous surfactant injection was initiated and began on January 26, 2010, amending the groundwater returned to the injection well to contain 460 mg/L of surfactant. Dosage adjustments occurred on February 12, February 18, and March 9, 2010, with adjustments to 280, 160, and 280 mg/L, respectively. System checks including water levels, free product levels, free product collection volume, and flow rate were recorded twice a week during January 26 to May 6, 2010. From May 6 to May 28, 2010, only free product collection volumes and flow-rate information were recorded.

Groundwater samples were collected on February 11, February 25, March 15, and April 6, 2010, for TPH and surfactant analysis. Surfactant samples were shipped to Analytical Services, Inc., in Huntsville, Alabama, for analysis via Method SM 5540 B, D. TPH samples were shipped to Gulf Coast Analytical Laboratories in Baton Rouge, Louisiana, for analysis by the FL-PRO method.

RESULTS AND DISCUSSION

Free Product Collection

A summary of free product collected during the PSS is illustrated on Exhibit 3. Approximately 62 gallons (235 liters) or 441 pounds (200 kg) of LNAPL were collected during the PSS. During Phase I of the recirculation-only portion of the study,

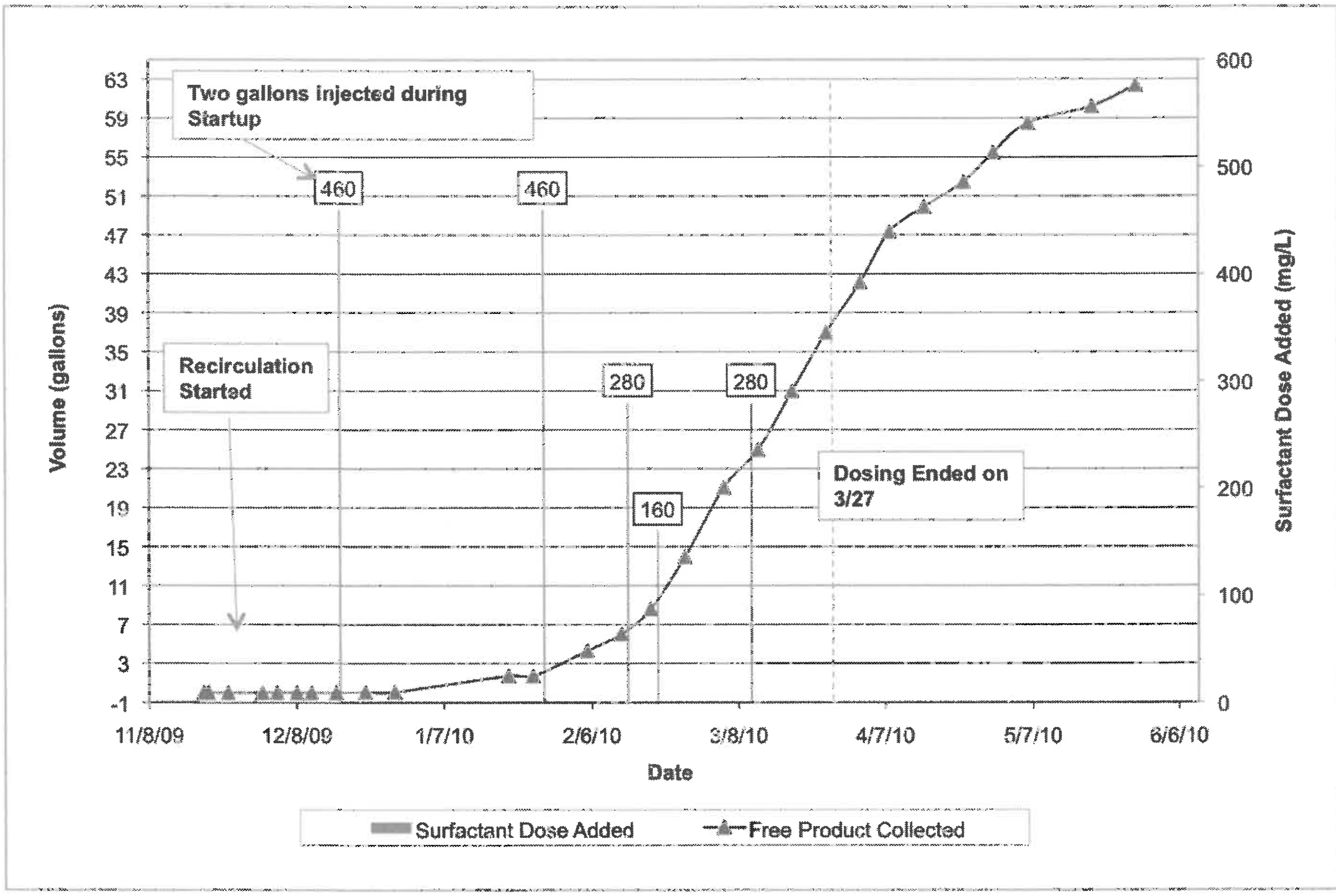

Exhibit 3. Free product collected and dosage of surfactant added

approximately 1.5 gallons (5.7 liters) of free product were collected. However, it was thought that this volume may have been a result of the testing dose of surfactant that was injected on December 16, 2010, as the 1.5 gallons (5.7 liters) were collected shortly after this event.

During Phase II (surfactant addition portion of the study), approximately 60.5 gallons (229 liters) of free product were collected. After continuous injection of surfactant, which began on January 26, 2010, the rate of free product collection increased steadily until approximately March 5, 2010. Immediately after March 5, the rate of free product collection began to decrease, so on March 9, the dosage of surfactant was increased back to 280 mg/L. After March 9, the rate of free product collection was steady at approximately 1 gallon per day until approximately April 8, 11 days after surfactant addition ceased on March 27, 2010. After April 8, the rate of free product collection decreased, suggesting that surfactant injection is directly related to the rate of free product collection. Considering the last three data points, on May 6, May 19, and May 28, 2010, the average rate of free product collection was significantly reduced to approximately 0.2 gallon (0.76 liter) per day.

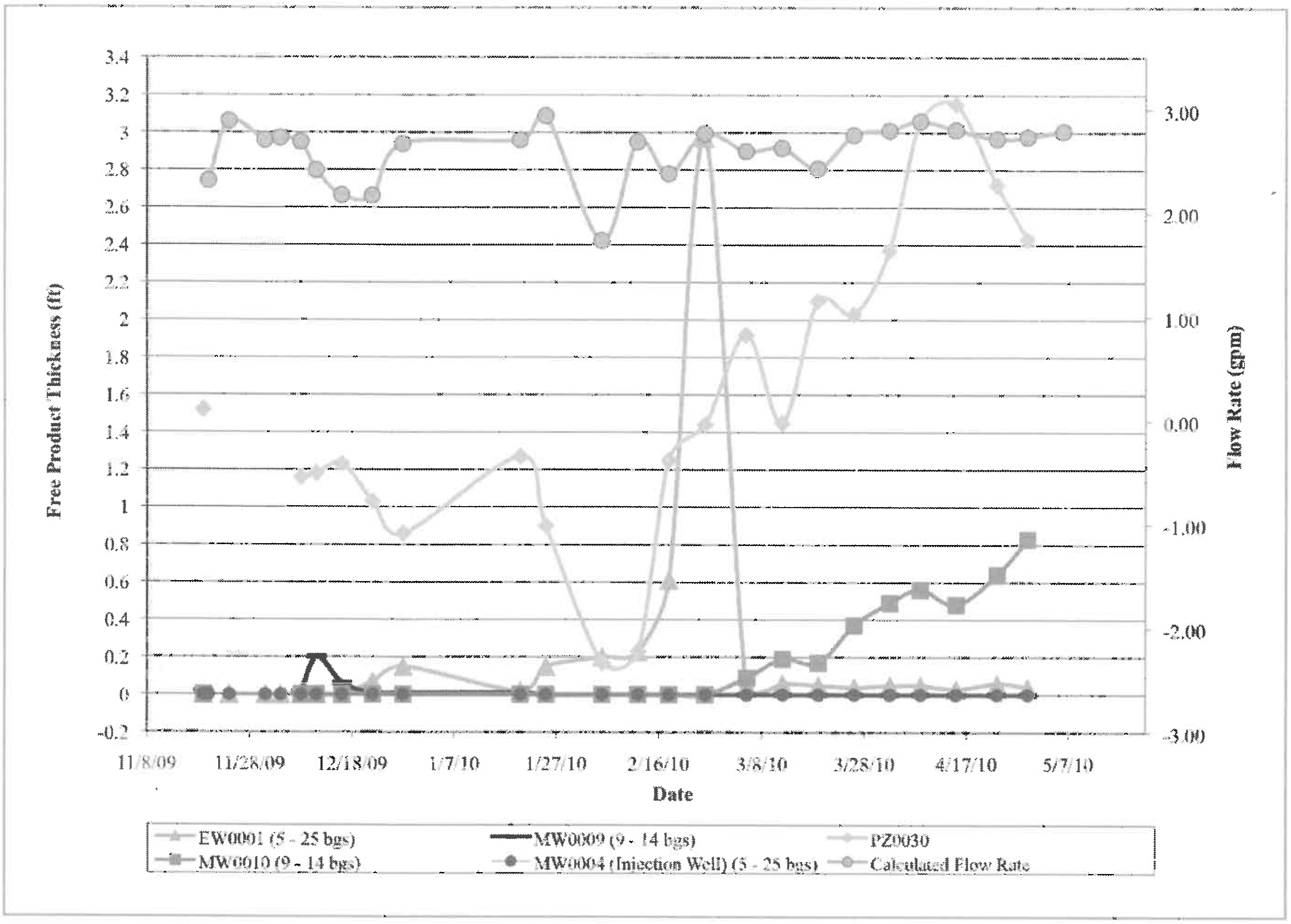

Exhibit 4. Free product thickness between IW and EW

Free Product Levels

Free product levels were measured in monitoring wells within the pilot study area, and the free product levels in wells between the extraction well and injection well are presented in Exhibit 4. Also illustrated in Exhibit 4 is the recirculation flow rate, which is plotted on the secondary y-axis. Free product thickness in PZ0030, which is in the approximate center of the PSS area and historically had high levels of free product, fluctuated throughout the study with a general trend of increasing thickness observed. However, one exception to the generally increasing trend was observed around February 5, 2010, and was associated with the reduced groundwater recirculation rate of the system. In the extraction well, free product accumulated up to approximately 3 feet (0.9 meter) in thickness on February 25, because of a skimmer malfunction. As shown in Exhibit 4, free product was observed in MW0010 starting on March 5 and continued to increase in thickness. On several occasions from November 19, 2009, to January 20, 2010, a thin layer of free product was observed at MW0009.

As described earlier, no product was observed at the injection well during the PSS, indicating that emulsions were not forming due to surfactant addition or pump action and that LNAPL was separating by gravity from the extraction well as designed. Free product

Exhibit 5. Groundwater TPH and surfactant concentrations

		TPH (μg/L)				
Location (HBF-)	**Screen Interval (bgs)**	**16-Dec-2009**	**11-Feb-2010**	**25-Feb-2010**	**15-Mar-2010**	**6-Apr-2010**
		Total Petroleum Hydrocarbons (μg/L)				
EW0001	5-25	NA	**10,400**	**9,510**	**5,090**	**5,270**
MW0004	5-25	1,110	**20,400**	2,850	3,320	**5,050**
MW0005	9-14	277	718	132	119	97.4
MW0006	9-14	1,120	2,020	949	737	578
MW0007	9-14	2,720	7,140	**8,520**	**7,350**	**13,200**
MW0008	9-14	**9,360**	**13,300**	**11,000**	**11,600**	**32,500**
MW0009	9-14	706	5,260	2,330	**6,350**	4,220
MW0010	9-14	1,530	**6,220**	3,940	FP	FP
		Surfactant (mg/L)				
EW0001	5-25	NA	ND	ND	0.4	1.3
MW0004	5-25	NA	73.6	ND	0.4	NA
MW0005	9-14	NA	ND	ND	ND	NA
MW0006	9-14	NA	ND	ND	ND	NA
MW0007	9-14	NA	ND	ND	ND	NA
MW0008	9-14	NA	ND	0.3	ND	NA
MW0009	9-14	NA	0.4	ND	ND	1.0
MW0010	9-14	NA	0.4	ND	NA	NA

NA = not analyzed

FP = free product observed

bgs = below ground surface

ND = nondetect

Bold value indicates TPH concentration is greater than FDEP Groundwater Cleanup Target Level (GCTL) of 5,000 μg/L.

thickness in PZ0030 increased throughout the PSS, indicating LNAPL movement and that possibly desorption was occurring. Free product levels also appeared to decrease when recirculation flow rates were reduced, as indicated by several periods of reduced flow rates, specifically around February 5, 2010.

ROI Determination

Groundwater samples were collected from monitoring wells within the pilot-study area and analyzed for TPH. The results are presented in Exhibit 5. Baseline samples were collected on December 16, 2009, and four subsequent sampling rounds were conducted on February 11, February 25, March 15, and April 6, 2010. TPH concentrations from the first sampling round increased significantly in all wells from baseline concentrations. More of an increase in TPH concentrations was observed in the wells between the injection well and extraction well because this was the area that received the most pore flushing and likely the most mixing of the LNAPL and groundwater interface. During the second sampling round, on February 11, 2010, sitewide TPH concentrations decreased compared to the first sampling round. During subsequent sampling rounds, TPH concentrations were quite variable, except for concentration differences in MW0005 and MW0006 (sidegradient wells to the north) compared to MW0007 and MW0008 (sidegradient wells to the south). The difference was most likely due to the locations of the monitoring wells as installed in the field compared to the symmetrical installation plan or, alternatively, the presence of pockets of free product in the MW0007 and MW0008 area.

Based on the first round of data collected, increased sitewide TPH concentrations suggest that sorbed LNAPL desorbed and mobilized within the recirculating groundwater. Based on subsequent rounds of data collected, highly fluctuating TPH concentrations in the groundwater samples also suggest that free product was continuing to desorb throughout the pilot-study area. The changes in TPH concentrations within the PSS monitoring wells over time suggest that the radius of influence (ROI) of the system included the furthest sidegradient wells, which were located up to 20 feet (6.1 meters) from the center of the PSS area.

Surfactant Demand

Groundwater samples were collected from monitoring wells within the pilot-study area and analyzed for surfactant. These results are also presented in Exhibit 4. Baseline sampling was conducted on December 16, 2009, and the four subsequent sampling rounds were conducted on February 11, February 25, March 15, and April 6, 2010.

During the first sampling round, surfactant concentrations at the wells were less than the dosage concentration of 460 mg/L at the time of sampling. The surfactant concentration at the injection well was the greatest at 73.6 mg/L, with all other wells having surfactant concentrations in the very low (1.3 mg/L) to nondetect range. Subsequent sampling on February 25, March 15, and April 6, 2010, was conducted when the surfactant dosage injected was 160 mg/L, 280 mg/L, and when surfactant injection ceased, respectively. During these sampling rounds, surfactant concentrations were all in the very low to nondetect range, indicating that the surfactant demand in the groundwater and surrounding subsurface exceeded the dosage injected. During the final sampling rounds, only MW0009 and the extraction well were sampled because surfactant injection had ceased and because surfactant was not detected at many wells during previous rounds. However, during the final two sampling rounds, a slight increasing trend in surfactant concentrations was observed at the extraction well, indicating that some residual surfactant was still in the pilot-study area.

Based on the data collected, low sitewide surfactant concentrations suggest that surfactant demand during the pilot study was significant. The surfactant concentration of 73.6 mg/L observed at the injection well while 460 mg/L was dosed suggests that surfactant demand at the site was likely approximately 390 mg/L.

> Overall, the recirculation system performed well, with no systemwide downtime.

Equipment Performance

Overall, the recirculation system performed well, with no systemwide downtime. In February, a skimmer malfunction occurred due to a faulty circuit board, which was replaced, but the recirculation system was still operational during that time. The 24-volt solar panel array and battery system maintained a supply voltage between 23.0 and 26.8 volts throughout the PSS to power the submersible pump and Spill Buster Unit. The groundwater recirculation rate varied from 2.1 to 3.0 gpm (7.9 to 11.4 Lpm) according

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to variations in the 24-volt supply, which coincidentally provided insight into how free product collection rates correspondingly varied with flows.

CONCLUSIONS

The PSS at the recirculation site was conducted for approximately 5.5 months from November 19, 2009, to May 28, 2010. The groundwater recirculation system and associated equipment performed very well with no systemwide downtime, were low cost, and incorporated solar power and a biodegradable surfactant. Approximately 62 gallons (235 liters), or 490 pounds (223 kilograms), of LNAPL were collected at the recirculation site during the PSS.

The data suggest that adding the surfactant greatly enhanced the free product collection rate. The maximum rate of free product collection was approximately 1 gallon (3.8 liters) per day. Low surfactant concentrations in groundwater samples suggest that sitewide surfactant demand in the subsurface of the pilot-study area is significant and should be considered in future applications in parallel with a time-weighted dosage approach. The optimum sitewide CMC of 153 mg/L was not achieved during analysis of the site groundwater, but, if the optimum CMC was met, free product collection rates in excess of 1 gallon per day could have been very likely.

Fluctuating sitewide TPH concentrations suggest that sorbed LNAPL desorbed and mobilized within the recirculating groundwater. Fluctuating TPH concentrations within the PSS monitoring wells over time suggest that the ROI of the system included the furthest sidegradient wells, which were located up to 20 feet (6.1 meters) from the center of the PSS area.

The goal of LNAPL removal by the primary mechanism of mobilization was considered realized, as LNAPL at the site was effectively mobilized to the extraction well and removed with no emulsion issues observed. Considering no emulsions were observed in either the extraction well or LNAPL collected, the nondesired mechanism of solubilization by means of micelle formation was not likely.

ACKNOWLEDGMENTS

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