

# **Treatment Facility F: Accelerated Removal and Validation Project**

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## **Executive Summary**

The Accelerated Removal and Validation (ARV) phase of remediation at the Treatment Facility F (TFF) site at Lawrence Livermore National Laboratory (LLNL) was designed to accelerate removal of gasoline from the site when compared to normal, single shift, pump-and-treat operations. The intent was to take advantage of the in-place infrastructure plus the increased underground temperatures resulting from the Dynamic Underground Stripping Demonstration Project (DUSDP). Operations continued 24-hours (h) per day between October 4 and December 12, 1993. Three contaminant removal rate enhancement approaches were explored during the period of continuous operation. First, we tried several configurations of the vapor pumping system to maximize the contaminant removal rate. Second, we conducted two brief trials of air injection into the lower steam zone. Results were compared with computer models, and the process was assessed for contaminant removal rate enhancement. Third, we installed equipment to provide additional electrical heating of contaminated low-permeability soil. Four new electrodes were connected into the power system. Diagnostic capabilities at the TFF site were upgraded so that we could safely monitor electrical currents, soil temperatures, and water treatment system processes while approximately 300 kW of electrical energy was being applied to the subsurface.

The first project activity, commencing on September 1, 1993, was day-shift operation of water and vapor pumping and treating. System automation and upgrades for reliable operations were begun. Training for operators needed for 24-h operation was conducted. Planning for the electrical heating system was started.

The next activity was institution of 24-h (three shift) operations on October 4, 1993. During this period, water was pumped continuously at a rate of about 50 gal/min (72,000 gal/d) simultaneously with vapor extraction at a rate of about 100 standard cubic feet per minute (scfm) (144,000 scfd) from the three central extraction wells at the site. Recovered hydrocarbons (initially about 30 gal of gasoline/d) were destroyed by two internal combustion engines (ICEs), while meeting Bay Area Air Quality Management District (BAAQMD) permitted conditions. Water was treated at the site using an ultraviolet (UV) oxidation system and discharged, after treatment, into the Livermore sewage system. Water was pumped from the lower steam zone (the lower of two zones of high hydraulic conductivity) in order to lower the water table and attempt to drain a confining zone located near the top of the original saturated zone. By draining this confining zone, which was at a temperature of around 90°C, we hoped to enhance the vaporization of any free-phase, adsorbed, or absorbed hydrocarbons. During the initial 30 days of pumping, the water table was lowered by about 16 ft at the pumping wells.

Between October 4 and November 8, while we were preparing the site for renewed electrical heating, we carried out vapor extraction with two different well configurations. Initially, we used the three central extraction wells for soil venting, switching to four of the steam injection wells (located about 72 ft radially outward from the extraction wells) after 14 days. Vapor flow rates generally were highly dependent upon the well configuration. Each configuration showed a high initial decline in recovery rate that tapered off to a very slow decline. During this period, 830 gal of gasoline was removed as vapor, condensate, and solute. Of this total recovered, about 710 gal was destroyed by the ICEs.

On November 9, we reverted back to venting from the three central extraction wells to establish a baseline for two periods of air injection (sparging) that were carried out during the weeks of November 15 and 22. The air injection applications were designed to better understand the processes that occur during air injection both below and above the saturated zone. The measurements addressed four questions: (1) how does injected air behave at the TFF site with various configurations of injection/extraction; (2) can we track injected air with electrical resistance tomography (ERT); (3) how useful are noble gas isotope tracers for monitoring the air injection process; and (4) is air injection a useful means to accelerate recovery of hydrocarbons?

Air was first injected into the lower steam zone (the 112- to 132-ft depth) on November 16 in well GIW820 at a rate of about 45 scfm while venting continued at two of the extraction wells at a rate of about 100 scfm. Neon, krypton, and xenon isotope gas tracers were injected into the input air stream. Separate vapor samples were taken at the extraction wells and at an additional nearby monitoring well to analyze for hydrocarbon recovery and for tracer gases. The results generally agreed with modeling that predicted that most of the air would flow radially outward and structurally upgradient from the injection well, with no recovery from the extraction wells. This injection, which lasted 7 h, was terminated once we had confirmed that most of the injected air was not being recovered. Later analysis of ERT images confirmed that the air from the injection well was moving upgradient, away from the extraction wells. The unrecovered injected air was not a major concern because it tends to oxygenate the ground water, thus enhancing microbial activity and hydrocarbon degradation.

The second phase of air sparging took place on November 22 and 23. Air was injected into one steam injection well and extracted from another injection well 65 ft away. In this case, air injection pressures were very close to atmospheric pressure, suggesting that the air was being injected into the vadose zone rather than the saturated zone. This was confirmed after the test, when the water table was found to be at a depth of 119 ft, 7 ft below the top of the 20-ft screened interval in the injection well. Trace gas analysis revealed that about 50% of the injected air was recovered in the extraction well. Analysis of the vapor chemistry was complicated by sampling problems that were identified and corrected during the operation. The concentration of hydrocarbons did not significantly change with time, even though the fraction of injected air in the extract vapor reached as high as 45%. Our interpretation is that the air injection focused the soil venting operation into a zone of higher vapor contaminant concentration near the top of, or within, the low-permeability zone. Both air sparging applications demonstrated the value of modeling and the importance of using tracer gases to better control and enhance the recovery of injected air. During November 8 to 30, an additional estimated 150 gal of gasoline was recovered by the soil venting and water pumping operations at TFF; 75% of this amount was destroyed by the ICE.

Operations were shut down over the Thanksgiving holiday (November 25 to 28). During this downtime, water levels rose about 6 ft (about 40%) at the extraction wells. In addition to the activities during October and November, described above, we also completed preparations to resume electrical heating and upgrades to the monitoring system. In order to resume electrical heating, a high-power switching unit was purchased and installed, and power cables were reconnected to heating wells used previously by the DUSDP. New power cables were routed to four new heating wells. These wells were drilled for post-DUSDP characterization analysis and were completed with heating electrodes at depth.

Operational safety procedures for electrical heating require that any electrically conductive signal wires running between the TFF site and the monitoring facility (which is located outside the personnel exclusion area) be disconnected while electrical heating is in progress. Thus, in prior activities, the water and vapor treatment systems had to be turned off and the well monitoring system disconnected during electrical heating. To overcome this limitation and to enhance the automation of TFF, a fiber-optic (nonconducting) data transmission system was installed so that water treatment operations and well physical parameters (temperature, current) could be continuously monitored while electrical heating was in progress. The entire system was installed and successfully tested by November 24. Electrical heating began on November 30. The monitoring system performed flawlessly from the very beginning of electrical heating. The ability to continuously monitor the water treatment process system and data from the heating wells and wells located nearby while hundreds of kilowatts of electricity are being applied below the surface represents a significant achievement of the ARV phase of remediation.

Electrical heating started on November 29 and continued through December 13. For safety, electrical heating was carried out only during the swing and overnight shifts, with 24-h operations during the weekend. The effect of the electrical heating on the subsurface was monitored by fixed thermocouples installed in several wells. Signals from the thermocouples and from current sensors at the heater wells were monitored, with the electrical power turned on, by means of the electrically isolated optical fiber monitoring system.

Initially, we could see no effect of the electrical heating on underground temperatures. Analysis of temperature data after completion of the electrical heating showed that some parts of the formation had been heated slightly. These results were very different from those experienced during the electrical heating phase prior to the start of steam injection in the DUSDP. If the ground was not being heated, where was all of the electrical energy going, what was different about this operation? There were several differences. First, we used longer electrodes which extended down into the lower steam zone aquifer, in the new heating wells. Second, we continuously pumped ground water, at a rate of about 50 gal/min, while electrical heating was carried out. Third, we carried out vapor extraction during electrical heating. Focusing on these differences and with the aid of computer modeling, we think we can explain the lack of significant heating of the targeted formation in the ARV electrical heating campaign.

We simulated electrical heating between two electrodes, in geology similar to that at the TFF site, with the three-dimensional NUFT code. The modeling showed a significant amount of heating near heater electrodes. These new, longer electrodes extend into the lower steam zone aquifer where a relatively inexhaustible supply of fresh water is available. High temperatures at the electrode cause the water near it to boil, which produces steam that then migrates upward into

the upper steam zone (in the vadose zone) where it comes under the influence of the vacuum from the vapor extraction. Thus, a great deal of energy is lost to latent heat of vaporization near the electrode. This hypothesis is supported by the observation that there was a large increase in the fraction of condensed water recovered in the vapor extraction system, which coincided exactly with electrical heating. In addition to the vaporization near the electrodes, the longer electrode tends to spread the current into several formational units rather than to focus it into the aquitard target zone. This causes a further lowering of heating efficiency. Thus, the longer electrodes installed in the new heater wells provide a combination of effects that results in a much lower heating efficiency.

On December 9, the water pumps in the extraction wells were shut off and the water table was allowed to rise. During this time, the electrical heating appeared slightly more efficient than when pumps were on. Throughout the electrical heating phase, we observed no increase in the amount of contaminant present either in the pumped water or vapor.

The system was shut down on December 13 and remained idle until mid-January 1994 when single-shift vapor extraction and ground water pumping activities were resumed. With the water again near its unpumped configuration, contaminant levels were much lower in both the vapor and aqueous phases compared to where they were at the start of the ARV operations.

In summary, the main accomplishment of the ARV phase at the TFF site was to remove an additional 1,000 gal or more of gasoline from the subsurface. This is a factor of about two or three higher than what would have been removed under normal operations with a gradually decreasing amount of contaminant present. Vapor concentrations in January 1994 were about 750 parts per million by volume (ppmv) total hydrocarbons (TH) compared to about 6,000 ppmv TH measured in the vapor at the beginning of October 1993. Concentrations of total petroleum hydrocarbons (TPH) in pumped ground water were about 6,000  $\mu\text{g/L}$  in January 1994 compared with about 14,000  $\mu\text{g/L}$  at the beginning of October 1993. Due to the desire to extract maximum contaminant during the course of this project, a definitive experiment correlating water level drawdown with contaminant recovery in the vapor phase was not conducted. This relationship could be useful for future operations and will be determined in the next phase of operation at TFF. Switching vapor extraction to four of the injection wells provided an increase in the contaminant removal rate, demonstrating that air flow patterns in the vadose zone are important for the effectiveness of the remediation. The two air sparging applications demonstrated the utility of noble gas tracer analysis, computer modeling, and ERT imaging for predicting where the injected air will go, and tracking its movement. It was difficult to tell whether the air sparging significantly enhanced contaminant removal rates, but the addition of oxygen into the ground water in the contaminated zone can only help enhance biogenic destruction of gasoline.

The development of the optical fiber monitoring system gave us the ability to safely apply hundreds of kilowatts of power to the subsurface while the TFF site continued to operate under remote control. This is a significant achievement. Even though the electrical heating campaign was unsuccessful in significantly heating the aquitard, we gained insight into some important processes that may be occurring near the heater electrodes. With the aid of computer modeling, coupled with further field trials, we will be able to better understand the near- and far-field processes in electrical heating and how they are influenced by geology and the environment. The predictive capabilities thus acquired will enable us to custom design more efficient systems for electrical thermal remediation.

# I. Introduction

The Accelerated Removal and Validation (ARV) phase work described here is the fourth in a series of remediation measures undertaken at Lawrence Livermore National Laboratory (LLNL) Treatment Facility F (TFF), also referred to as the Building 406 Gasoline Spill Area or the Gas Pad. Soil venting, carried out as a pilot study (Cook *et al.*, 1992) between August 1988 and December 1991, removed an estimated 545 gal of BTEX (benzene, toluene, ethyl benzene, and total xylenes), most of which probably came from depths of less than 75 ft. The Dynamic Under-ground Steam Demonstration Project (DUSDP) at TFF began operations in December 1992 with electrical heating. The DUSDP Phase I steam injection was carried out between February 3, 1993, and March 14, 1993. In this first phase, gasoline recovery peaked at about 350 gal/d on February 16. An estimated 2,100 gal of gasoline (from vapor, condensate, and ground water) were recovered during this first phase. The third remediation phase at TFF was Phase II of the DUSDP carried out between May 23 and June 30, 1993. An estimated total (vapor + condensate + ground water) of 4,900 gal of gasoline was recovered in this phase. Twenty-four hour extraction continued until July 9, 1993. Intermittent vapor and liquid extraction began on July 29, 1993, continuing until the reinstatement of 24-h/d operation on October 4, 1993. During this period, an estimated additional 1,400 gal of gasoline (recovered total from water, vapor condensate, and vapor) were recovered during single-shift operations.

After the DUSDP and by the beginning of September 1993, the temperatures underground in the steamed areas were still generally above 80°C, and in many areas above 90°C. The boiling point of benzene is 80°C at one atmosphere (Johnson *et al.*, 1990), so it is probable that any free product remaining in these heated areas will have been substantially stripped of the lighter hydrocarbon fractions. Analysis of soil samples taken from boreholes drilled into the steamed areas in Phases I and II of the DUSDP confirmed that free product had been removed and that residual contaminant levels were very low. However, because of the geometry of the injection well pattern, the relative permeabilities, and the relative rates of steam injection during the DUSDP remediation, an area still remained that was not substantially heated by steam. This "cold spot" occurs within the low hydraulic conductivity zone between the upper and lower steam zones; post-steam injection drilling confirmed that contaminant levels were still high in this zone.

The original volume of the spill at the Building 406 Gasoline Spill Area is unknown. As much as 17,000 gal of leaded gasoline may have leaked from storage tanks at the site between 1952 and 1979 (Devany, 1993). Subsequent weathering and biodegradation has removed an unknown fraction of the gasoline, although we would expect that the lighter fractions would be preferentially removed (Johnson *et al.*, 1990). Devany (1993), using site core sample data and a computer-based volume averaging scheme, estimated 3,890 gal of gasoline in the unsaturated zone and 2,660 gal of gasoline in the saturated zone within the volume of the steam injection ring used by the DUSDP. This estimate did not include free product and is clearly low, since over 7,000 gal of gasoline were recovered during both phases of steam injection, in addition to the estimated 2,200 gal (based on 545 gal of recovered BTEX) of gasoline recovered in the initial soil venting phase and the 1,400 gal recovered during July, August, and September 1993. An additional 1,000 gal of gasoline was recovered during this ARV phase; this sums to a total net

recovery to date of about 11,600 gal of gasoline. Details of the vapor extraction operations during the period of September 1 through November 11 are given in Section II. Section V addresses the questions: how much gasoline remains to be removed, and where is it? Details of the ARV project planning, scheduling, and cost are given in Appendix 1.

At the beginning of September 1993, the TFF site remained in much the same condition it had been at the completion of steam injection in June, with the exception of the ability to carry out electrical heating and steam injection. The rented boiler was no longer on site, and the LLNL exemption, from the Bay Area Air Quality Management District (BAAQMD), for steam injection had expired. The main power switch for the electrical heating part of the DUSDP was rented for the duration of that part of the project. At the completion of electrical heating, the power cables were cut, and the high power switch unit was returned to the manufacturer. In order to resume electrical heating, the power cables had to be reconnected and the same switch purchased and reinstalled.

One of the aims of this ARV phase of remediation was to enhance recovery of hydrocarbons from the "cold spot" mentioned above. The area had not been heated high enough to completely vaporize all of the free product in the soil, but it had been heated considerably above ambient. Additional thermal remediation of this zone would be most effective and efficient if it were done before the area cooled significantly. The most effective way to enhance recovery in this zone would be to heat the low hydraulic conductivity zone electrically. This contingency had already been planned for because the wells drilled for the post-steam injection evaluation had been completed as heating wells (installation of steel electrodes, thermocouples, and appropriate backfill) that could be used to direct electrical current into the "cold spot." Therefore, one of the initial goals of the ARV phase was to purchase and reinstall the high-power switch, complete power connections to the new heating wells, and reconnect several of the old heating wells so that we could resume electrical heating before the end of December. Details of the installation and design of the electrical heating and monitoring systems are given in Appendix 3. Electrical heating operations and results are discussed in Section III.

We also wanted to continue to pump ground water, carry out vapor extraction and destruction of gasoline vapor, and operate the ultraviolet (UV)/oxidation water treatment system during electrical heating. To do this while applying several hundred kilowatts of electricity to the subsurface, we had to redesign the monitoring sensor systems so that they were electrically isolated from the high-power, 600-volt heating system. This was accomplished by installing optical fiber links between the monitoring computers, located outside the heater system grid, and the wellheads and the treatment facility where the sensors were located. In addition, the ground water treatment system had to be automated so that system adjustments could be made from outside the site during electrical heating. Details of the system automation are given in Appendix 2; details about the optical system for power isolation are given in Appendix 3.

In addition to the above, it was generally agreed that additional recovery of hydrocarbons remaining in the saturated zone could be enhanced by injecting air, also known as air sparging, into the lower steam zone, below the low hydraulic conductivity aquitard separating it from the upper steam zone (which lies in the vadose zone). Air injected into the saturated zone would presumably move upward to the base of the aquitard and then spread laterally until it eventually found its way, through a fracture or lithologically conductive pathway, into the vadose zone. There, the injected air would eventually be recovered by drawing air from a well or wells

completed in the vadose zone. As the injected air passes through the ground water, free product or hydrocarbons dissolved in the water will partition into the vapor phase and be carried with the air flow, eventually to be recovered in the extraction well and destroyed. The partitioning into the vapor phase will be enhanced by the high temperatures existing underground; so this process, just like the electrical heating, is best completed before the subsurface cools significantly. The flow of air will depend on factors such as the geometry and lithology of the sediments, relative rates of injection and extraction, and position of the top of the saturated zone. It is very important to know where the air goes and how much is recovered because the air injection could cause contaminants to move away from the recovery area. On the other hand, air injection will result in oxygenation of the pore water. This should enhance microbial activity, leading to the destruction of additional hydrocarbons. For the ARV phase, we designed two simple air injection applications, described in Section III, to better understand the sparging process and its likely ability to enhance recovery of hydrocarbons at the TFF site.

In order to better design the air sparging and electrical heating operations, we carried out some computer simulations with a new code developed at LLNL called NUFT. NUFT is a suite of multiphase, multicomponent models for numerical solution of thermal and isothermal flow and transport in porous media. The code simulates the coupled transport of heat, fluids, and chemical components, including volatile organic compounds (VOCs). The code is a modification of one used to simulate air stripping (sparging) between horizontal wells at the U. S. Department of Energy (DOE) Savannah River Site (Buscheck and Nitao, 1992). Verification and benchmark testing of NUFT have recently been completed (Lee *et al.*, 1993). We used this code to make predictions—which turned out to be very accurate, given the limitations of the model—about what would happen under different situations for the air sparging operations. Under DUSDP, modules were added to the code to enable the simulation of electrical heating. We utilized this added capability to better understand what happened during the electrical heating operations at the TFF site and to help us design follow-up activities. However, in order to do the modeling accurately, we needed to obtain better knowledge of the temperature dependence of the coefficients that describe the solubility and partitioning between the dissolved and vapor phases of the VOCs. For application to this project, we decided that partitioning coefficients for xylene would be the most useful, so a series of laboratory experiments was carried out to obtain the data to define them. Details of the modeling and experiments are given in Appendix 5.

While we planned for the air sparging and prepared to resume electrical heating, we instituted 24-h operations at the site, running the internal combustion engine (ICE) vapor extraction system continuously while continuing to pump and treat ground water around the clock at a rate of about 50 gal/min. At these rates of ground water removal, we were able to lower the top of the saturated zone significantly over a wide area. By draining the rock units, we hoped to increase the volume of sediment accessible to vapor extraction. In addition, with temperatures already at the boiling point of benzene and higher, we could enhance our ability to recover any absorbed, adsorbed, or other free product available. Throughout the ARV phase, ground water was continuously pumped from the central extraction wells (GEW808, GEW816, and GSW16, refer to Fig. 1). We tried two basic configurations of vapor extraction. Initially, we pumped vapor from the central extraction wells, GEW808, GEW816, and GSW16. After about 2 weeks of operation, we switched to vapor extraction from the upper steam zone intervals of the injection

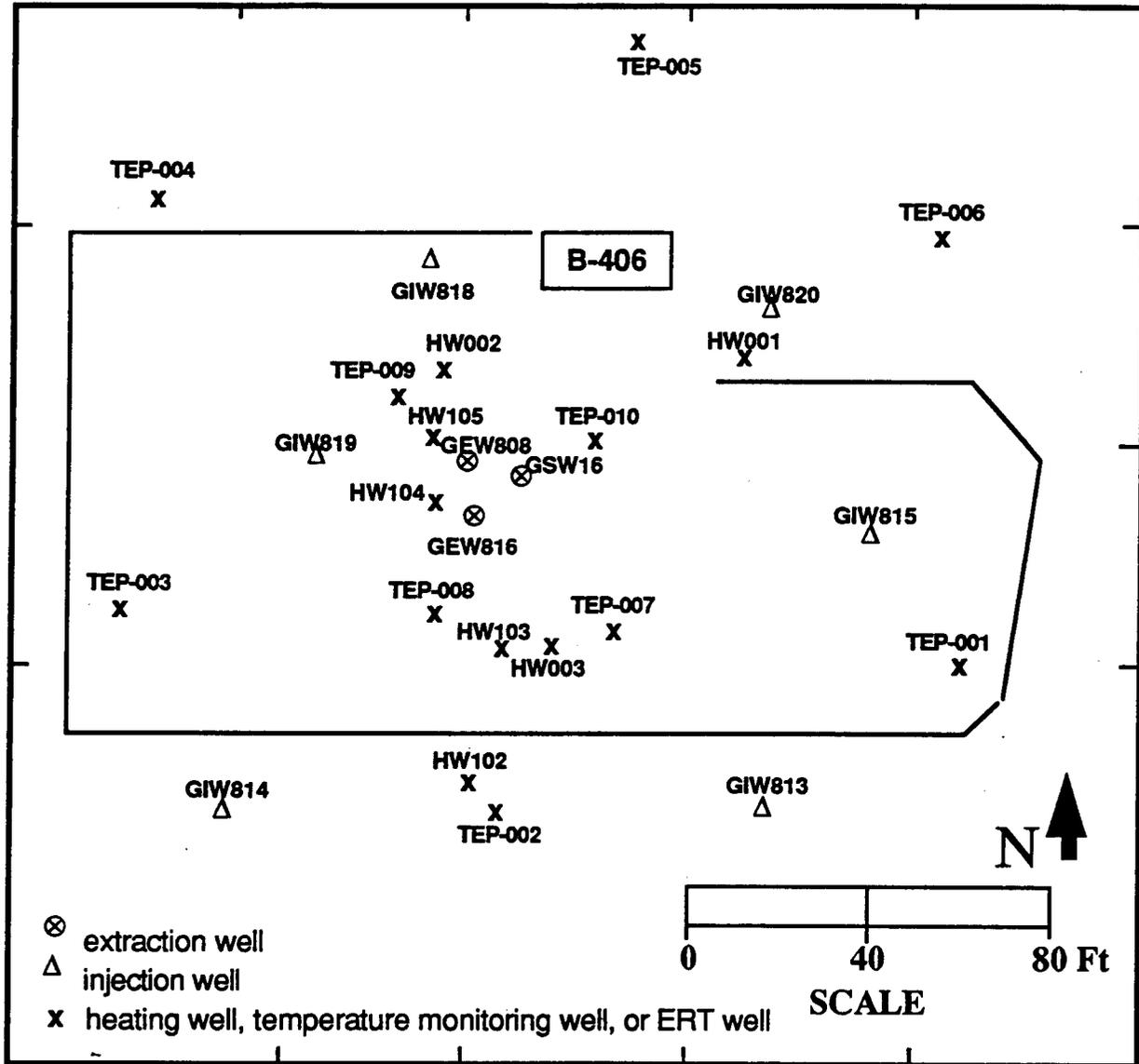


Figure 1. Location of wells at the TFF site.

wells, GIW820, GIW818, GIW815, and GIW813. In both cases, contaminant levels rapidly dropped off from initial highs with the removal rates decreasing with time. Details of these operations are given in Section II.

We end this introduction with a note of discussion (or caveat) concerning sampling of hydrocarbons and estimates of gasoline recovered. During the ARV phase, 75% or more of the hydrocarbons recovered were in the vapor phase. Condensate and hydrocarbons dissolved in water made up the rest. Therefore, estimates of recovery of vapor phase product drive the estimate for total product recovered. Sampling of vapor and testing for hydrocarbon concentrations is time-consuming and, hence, expensive. For these reasons, sampling for hydrocarbon concentrations was generally done only once a day. This single sample was then used, along with the average daily volume of vapor extracted, to estimate the total daily vapor recovery. Subdaily fluctuations in the contaminant level of the extracted vapor will not be detected this way, and we depend on our past experience during the DUSDP to support the assumption that the recovered sample is representative of the daily average. Potentially, recovery rates can also be monitored by tracking the amount of natural gas burned by the ICE (natural gas consumption increases as the vapor concentration decreases), but this correlation is not very sensitive to concentration variation at the concentrations seen during this phase and was not useful here.

The fact that we are forced to obtain vapor samples from a system under vacuum introduces additional difficulties, as we observed during the second air sparging operation (discussed in Section III). When sampling from a system under vacuum, there is always the possibility that air other than from the vapor stream can leak into the sampling system and dilute the sample. If this happens, the measured contaminant level will always be less than the true level and the corresponding estimates of recovery will be low. We found that improvements in our sampling technique and system were needed and these were made. Because of this possibility, the levels of product recovery reported herein should be considered as minimum values because any errors in sampling will tend to be on the low side. The issues of sampling, sample analysis, and data management are discussed in detail in Appendices 4 and 6.