Cleanup Operations

Goals of the Experiment

Dynamic Underground Stripping was originally designed for the removal of separate-phase organic liquids from highly contaminated areas both above and particularly below the water table. The goals of the first application of the method were:

1. To determine the effectiveness of the process in removing free product.
2. To evaluate the effectiveness of the monitoring methods for controlling heat input and mapping heated zones.
3. To examine whether any deleterious effects (such as dispersal of contaminant) might occur.
4. To demonstrate the necessary engineering and operational practices required for effective and safe operation of this high-energy technique.

All goals were met and the site and process were turned over to the Laboratory's site remediation team (funded by DOE's EM 40) for final site cleanup (Sweeney et al., 1994).

Experimental Operations

Operations at the site were conducted in four distinct phases:

(1) Electric Preheating: November and December 1992
(2) First Steam Pass: February 1993
(3) Second Steam Pass: May–July 1993 (drill-back characterization followed)
(4) Polishing Operations (accelerated removal and validation): October–December 1993
Table 1 summarizes the project history.

The electrical preheat of the site began in November 1992, before the treatment facility was completed. No extraction data are therefore available from this phase. The electrical preheat phase is described in detail by Buettner and Daily (1994b). The 1-MW electrical system operated at a maximum power output of about 800 kW. The chief monitoring methods used during the electrical preheating were temperature measurements and ERT. Temperatures were measured using both fixed thermocouples in individual boreholes and, for continuous logs, an infrared-sensor system in the 11 2-in.-diameter fiberglass monitoring/imaging wells (Newmark, 1994b; Goldman and Udell, 1994).

The goal of an average 20°C temperature rise in the clay zones was achieved; some of the clay layers were heated to a maximum of 70°C (Figure 7). The effects of this phase on the extraction of gasoline were not tested, but several of the groundwater monitoring wells on the site showed increases in the concentration of gasoline components, indicating that free-phase gasoline was being mobilized in the vicinity (Figure 8). Gasoline concentrations in these wells had been decreasing previously, apparently due to localized bioremediation or venting resulting from the increased air circulation to the borehole area.

Steam injection began in early February 1993 into the lower of two steam zones (permeable layers) using a 24,000 lb/hr (50 gallons water/minute, energy approximately 8 MW) natural-gas-fired, skid-mounted boiler (Figure 9). Siegel (1994) describes the steam operations in detail. Steam injection rapidly heated the permeable zones to above the boiling point of water, and initial steam breakthrough to the extraction wells occurred in 12 days (Figure 10). During the first steam pass, it was learned that, although a bank of cold, free-product gasoline may precede the steam front to the extraction wells, it contains only a small fraction of the recovered gasoline (Jovanovich et al., 1994; Aines et al., 1994) (Figure 11). None of the 1700 gallons recovered during the first steam pass could unambiguously be associated with the liquid front ahead of the steam. The great majority of the gasoline came out after a steam zone was fully established, and the extraction continued without further steam injection. The reduced vapor pressure forces residual pore fluids and contaminants to boil. At this point, the forced boiling generated large amounts of water and gasoline in the vapor stream, and our potential removal rates greatly exceeded our dual-bed activated-carbon trailer's design limit of about 25 gallons/day. During the planned shutdown following the first steam pass, the vapor treatment system was redesigned to increase capacity (Sorensen and Siegel, 1994).

The monitoring and imaging systems utilized at the gasoline spill site provided excellent control of the steam injection process (Newmark, 1994b; Goldman and Udell, 1994; Ramirez et al., 1994; Boyd et al., 1994). Initial steam breakthrough to the extraction wells occurred in only 12 days; each subsequent breakthrough occurred sooner as

Table 1. Project history of the Dynamic Underground Stripping project LLNL gasoline spill site cleanup.

Phase	Dates	Objectives	Accomplishments
Vacuum Extraction, Vadose Zone EM 40 Operations	9/88 to 12/91	> Extract vadose gasoline contamination. > Evaluate extraction effectiveness.	> Pilot Test permitting received. > 2000 gallons removed > Biological activity confirmed
Clean Site Engineering Test EM 50	2/91 to 9/91	> Demonstrate establishment of steam zone below water table. > Evaluate and optimize monitoring, imaging systems. > Optimize resistance heating electrode design. > Evaluate personnel and environmental safety.	> 10,000 yd^3 steam zone established below water table with no steam rise. > ERT, thermal logging, and tiltmeters demonstrated, chosen for gas pad use. > Individual electrode capacity raised from 20 kW to (2) kW. > Safe procedures established for personnel; no detrimental environmental effects .
Electrical Pre-Heat EM50 operations, EM 40 Treatment Facility F construction	11/92 to 1/93	> Raise temperature of clay/silt layers 20^{o}C so conductivity always above steam-temperature gravel zones. > Test electrical safety at high current in industrial area. > Optimize electrical heating methods.	> Clay pre-heating accomplished. > Maximum heating to 70^{o}C in clay layer. > Safety measures and procedures adequate. > 850 kW continuous power achieved. > Nighttime operations with daylight construction of treatment facility.
1st Steam Pass Joint EM40/EM50 operations	2/93 to 3/93	> Heat target zones to steam temperature. > Optimize monitoring/control methods. > Evaluate treatment procedures and facility. > Quantify possible deleterious effects (such as contaminant spreading). > Demonstrate safe handling of steam and hot gasoline effluent.	> Upper and Lower steam zones heated to boiling point. > ERT established as control system with 12 hr turnaround on 10 planes/day. > Non-contact thermal logger demonstrated with no hysteresis, 100^{o}C/2 ft gradients. > Gasoline found to be mainly recovered in vapor phase, greatly exceeding capacity. No liquid phase free-product recovered. > No spreading of contaminant to outer monitoring wells/ > Safe handling of steam and hot gasoline. > 1700 gallons gasoline removed.

Table 1. (Continued.)

2nd Steam Pass **Joint EM40/EM50 operations**	5/93 to 7/93	> Operate re-designed vapor treatment system with 10x capacity of first pass. > Optimize steaming/recovery technique to maximize vacuum recovery. > Heat zones which were insufficiently heated in first pass. > Accurately measure gasoline flux in vapor and condensate paths, reduce uncertainty in total recovery rate, continuously monitor gasoline flux.	> 100,000 yd^3 heated to boiling point. > Recovery rates in excess of 250 gal/day achieved. > Tiltmeters used for imaging of horizontal extent of steam zones from individual wells. > Most cool zones from 1st pass fully heated to steam temperature (one "cold spot" remained at 80°C). > Fluxes measured to ± 10 % accuracy, continuous monitoring systems demonstrated. > 4600 gallons gasoline removed.
Post-Test Drill-Back Characterization **EM 50**	7/93 to 9/93	> Measure soil concentration changes along six-hole cross-section > Ascertain from soil concentrations whether spreading had occurred (outside original contamination) > Evaluate process effectiveness. > Examine possible changes to soil. > Examine effects on existing microbial gasoline-degrading ecosystem.	> Soil concentrations reduced dramatically. > No spreading of contaminant; only inward motion seen. > Vadose zone completely clean (< 1ppm) > Saturated zone contaminant remained around extraction cluster only. > No significant soil changes. > Active microbial ecosystems at all locations and soil temperatures up to 90°C, makeup varies by soil temperature.
Accelerated Recovery and Validation (ARV) **EM 40 Operations**	10/93 to 1/94	> Remove remaining free product, especially in cool zone. > Make use of existing heat and high extraction rates to continue removal. > Electrically heat clay/silt zones to enhance removal. > Test sparging, injection well extraction.	> Remaining free-product gasoline removed (1000 gallons). > Ground water concentrations of 5 of 6 regulated compounds reduced to MCL. > Benzene down to 100 ppb in ground water. > Sparging monitored with noble-gas tracers. > Electrical heating maintained site soil temperatures during extraction.

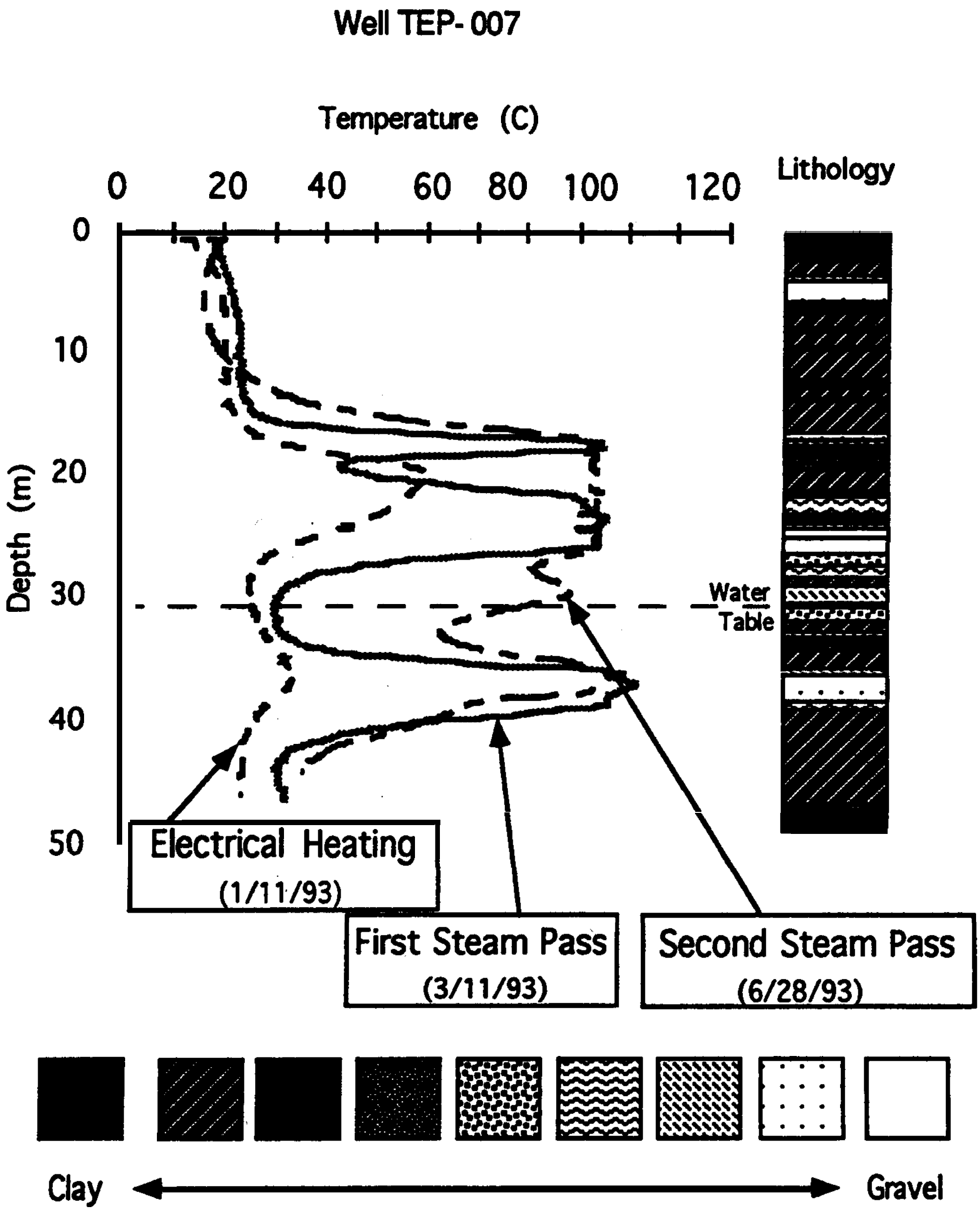

Figure 7. Temperature logs from a monitoring well inside the ring of injection wells, along with the lithology. These logs show electrical heating of the clay-rich layers during the electrical preheat, steam passing through the most permeable layers during the first steam pass, and conductive heating of and later penetration by steam into less permeable layers during the second steam pass. (From Newmark, 1994b).

the formation gained heat. This made the day-to-day process monitoring critical in order to ensure that the correct amount of steam was injected to drive contaminant to the center without adding excessive amounts of steam outside the pattern. Each of the twelve injection ports (two each in six wells) would inject a different amount of steam at a given pressure, ranging from 600 lb/hr to one well that would apparently have taken the entire output of the boiler had we so permitted. This range is expected in such a heterogeneous site, but it requires that the location and size of the steam zones be measured *in situ*, not merely calculated from injection volumes.

Temperature measurements made both with fixed thermocouples in the field and with the

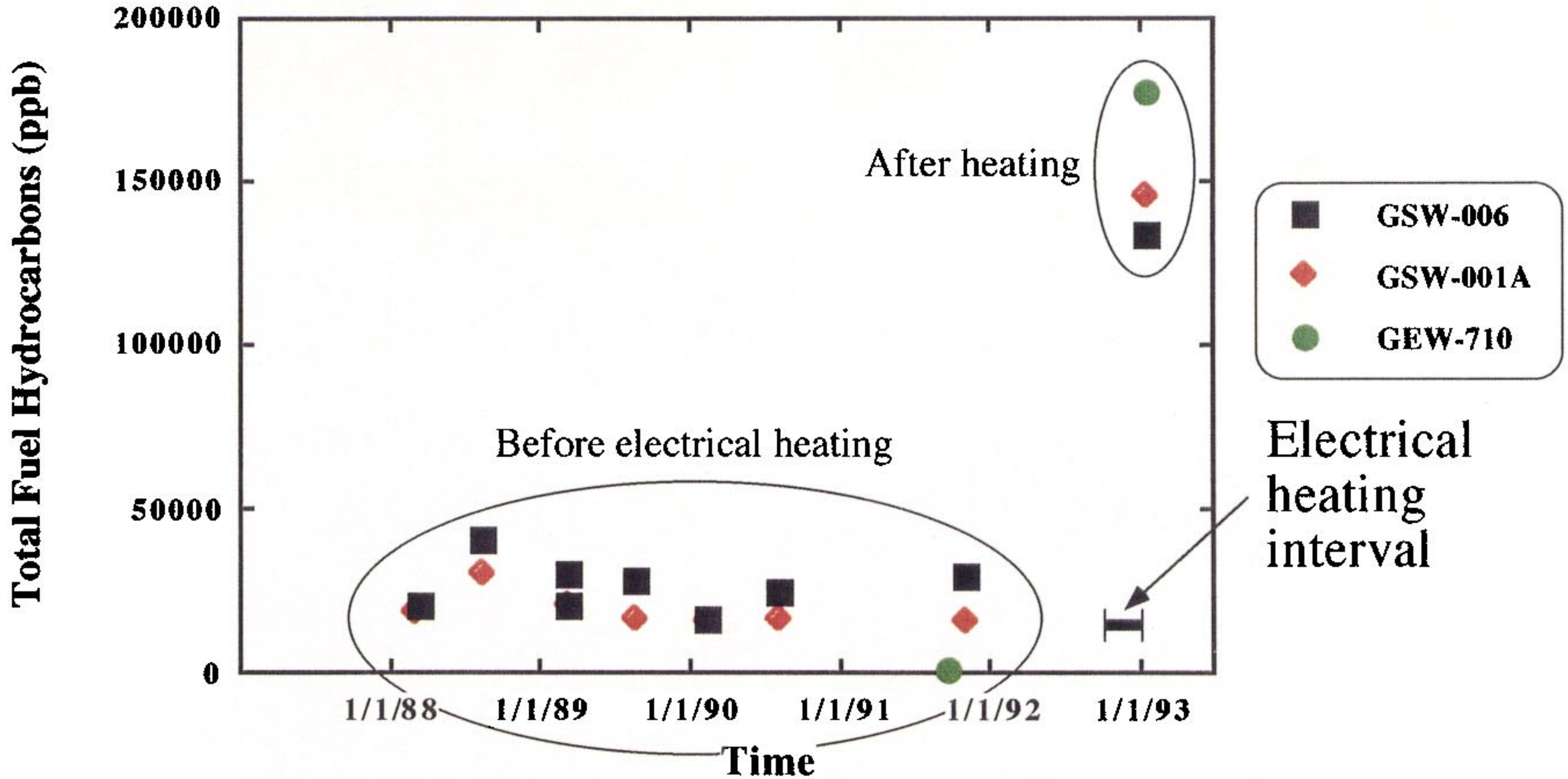

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Figure 8. Chemical signatures of groundwater in monitoring wells in the central gasoline spill area. Before electrical heating, total fuel hydrocarbon concentrations (TFH) were below 50,000 ppb and generally decreasing, most probably due to localized enhanced bioremediation in the vicinity of the boreholes. After electrical heating, high TFH concentrations were found, indicating contact with free-product gasoline (Buettner and Daily, 1994b).

Figure 9. Portable steam plant used for the Dynamic Underground Stripping demonstration at the LLNL gasoline spill area. The 24,000 -lb/hr boiler is skid-mounted; this particular unit was leased by the month. A steam injection/electrical heating well can be seen in the foreground. Steam is distributed to the injection wells via flexible rubber hoses. The boiler is fired by natural gas and fed by Laboratory drinking water, both from Laboratory utility lines. An injection well is seen in the foreground, with two injection lines (one for each steam zone). Steam is piped to the wells using flexible reinforced-rubber steam lines.

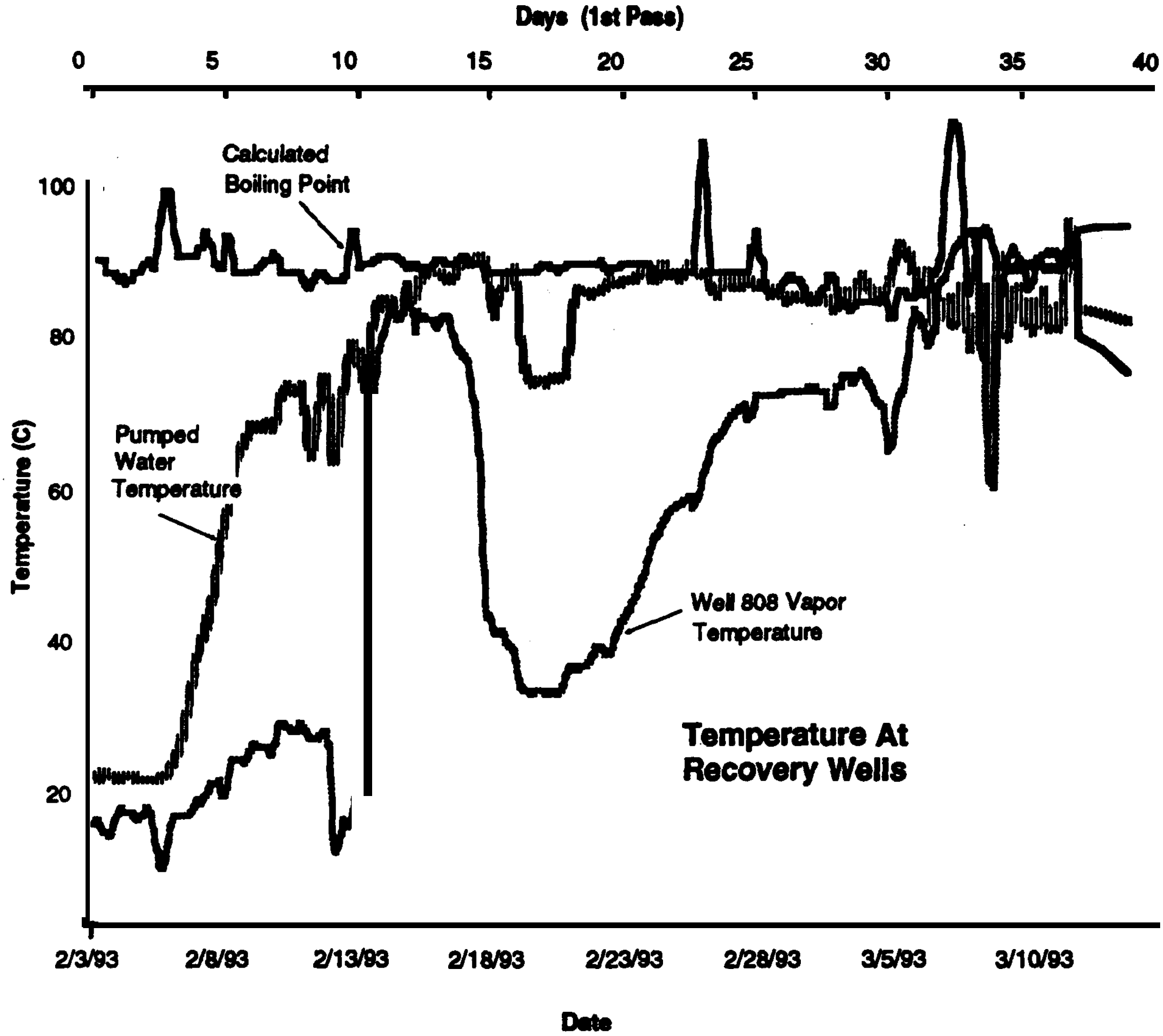

Figure 10. Extraction well temperatures during the first steam pass. Steam breakthrough to the extraction wells occurred about 12 days after steam injection began in the lower steam zone. Calculated boiling point based on the vacuum applied to the well. (After Aines et al., 1994).

continuous temperature loggers showed a rapid temperature rise in the more permeable zones (Figures 6 and 12). The temperature logs revealed thermal gradients of up to 100°C over just a few feet depth during initial steam injection, and provided the most accurate measurements of the vertical distribution of the steam at the 11 locations (Newmark, 1994b; Kenneally, 1994).

Between the wells, ERT proved to be a rapid and accurate way to map steam progress at 1–2-m resolution, providing actual images of the heated zones by comparing the electrical resistance distribution before heating to that afterwards (Ramirez et al., 1994) (Figure 13). Daily ERT images showed the vertical extent of the steam zones and the lateral movement between imaging wells. They revealed a number of areas where steam was moving vertically in the formation that were not detected by the temperature logs in individual wells. The total cycle time to obtain and process the data for each image was about an hour. This made ERT the principal control method, and decisions on steam injection rates made at the morning operations meetings were based principally on ERT images from the previous day. Coupled with the temperature profiles from the continuous temperature loggers, steam

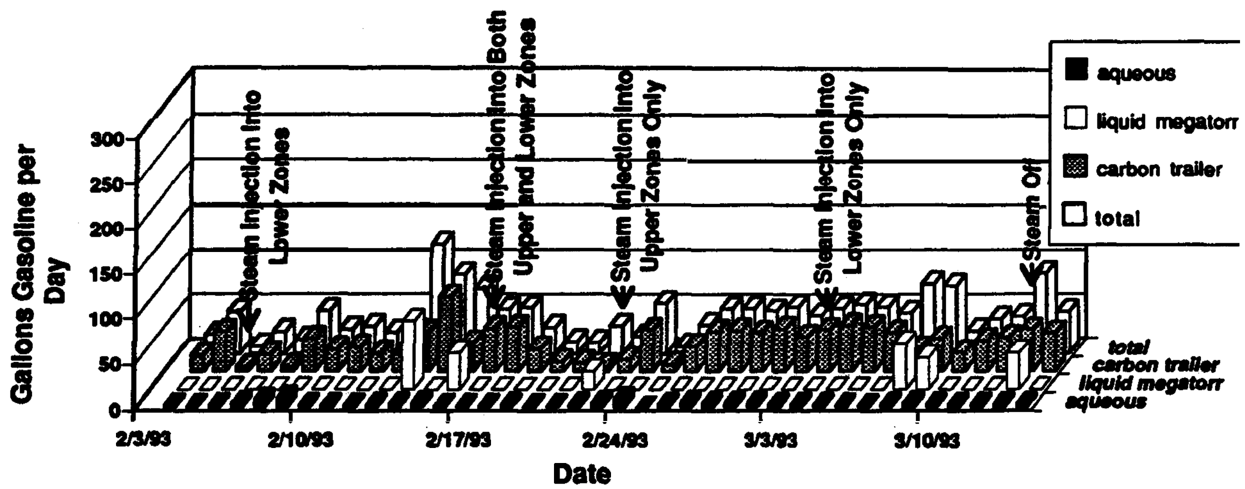

Figure 11. Daily average gasoline recovery rates during the first steam pass. (From Udell, 1994a,c).

progression through the formation was seen to occur in multiple horizontal permeable zones, with significant vertical motion occurring in some areas. The combined ERT/temperature 2-in. fiberglass wells were placed to allow optimal monitoring of the interior of the treated zone (extending about 30 ft outside the ring defined by the steam injection wells) and lower-resolution monitoring of the surrounding area. Induction logs run in the monitoring wells revealed the changes in the electrical properties of the heated soils in detail. These results were used to calculate fluid saturation in the steamed zones (Boyd et al., 1994) (Figure 14).

An array of tiltmeters was installed near-surface in a double ring surrounding the site to monitor the lateral extent of the steam zone outside the treated area (Hunter and Reinke, 1994). The array was used in two modes: passive and active.

In the passive mode, tiltmeters measure the small deformations in the ground surface that result from a subsurface pressure transient in terms of tilt. As the steam front moving in the subsurface approaches a tiltmeter, it produces a pressure transient and causes the ground to deform. If the signal is sufficiently large, the tiltmeter will detect the slight tilt resulting from that pressure transient. Using this method, we mapped the outer extent of the steamed region during steam injection.

In a more active mode, the tiltmeter array was used to measure the slight deformation in the ground surface resulting from a pressure transient induced into the steam zone by shutting off an injection well for a fixed time. Maps of the areal extent of the steam zone emanating from each well could then be obtained, particularly for the lower steam zone (located below the pre-steam water table). This technique was extremely effective in mapping the lateral spread of steam and the development of any preferential steam pathways.

During the first steam pass, tiltmeters were primarily relied upon to delineate the outer extent of the steam front. We tested and validated the processing technique whereby the individual steam zones could be mapped during this pass, where the subsurface monitoring network of temperature measurements and ERT image planes could provide ground truth.

The second steam pass was begun after a 3-month hiatus to redesign the effluent treatment capacity, establish better analytical control on the effluent stream based on our new knowledge of the comparative flows in vapor and water, and evaluate the cost-effectiveness of the process. In this pass, we optimized the amount of time the formation was kept under vacuum (no steam injection) and greatly increased the extraction rate, hitting a contaminant recovery peak of more than 250 gallons/day and routinely removing more than 100 gallons/day (Figures 15 and 3).

The focus of the various monitoring activities was somewhat different during this pass, where steam was being injected into previously heated soil. Although the ERT images continued to provide valuable information, interpretation was

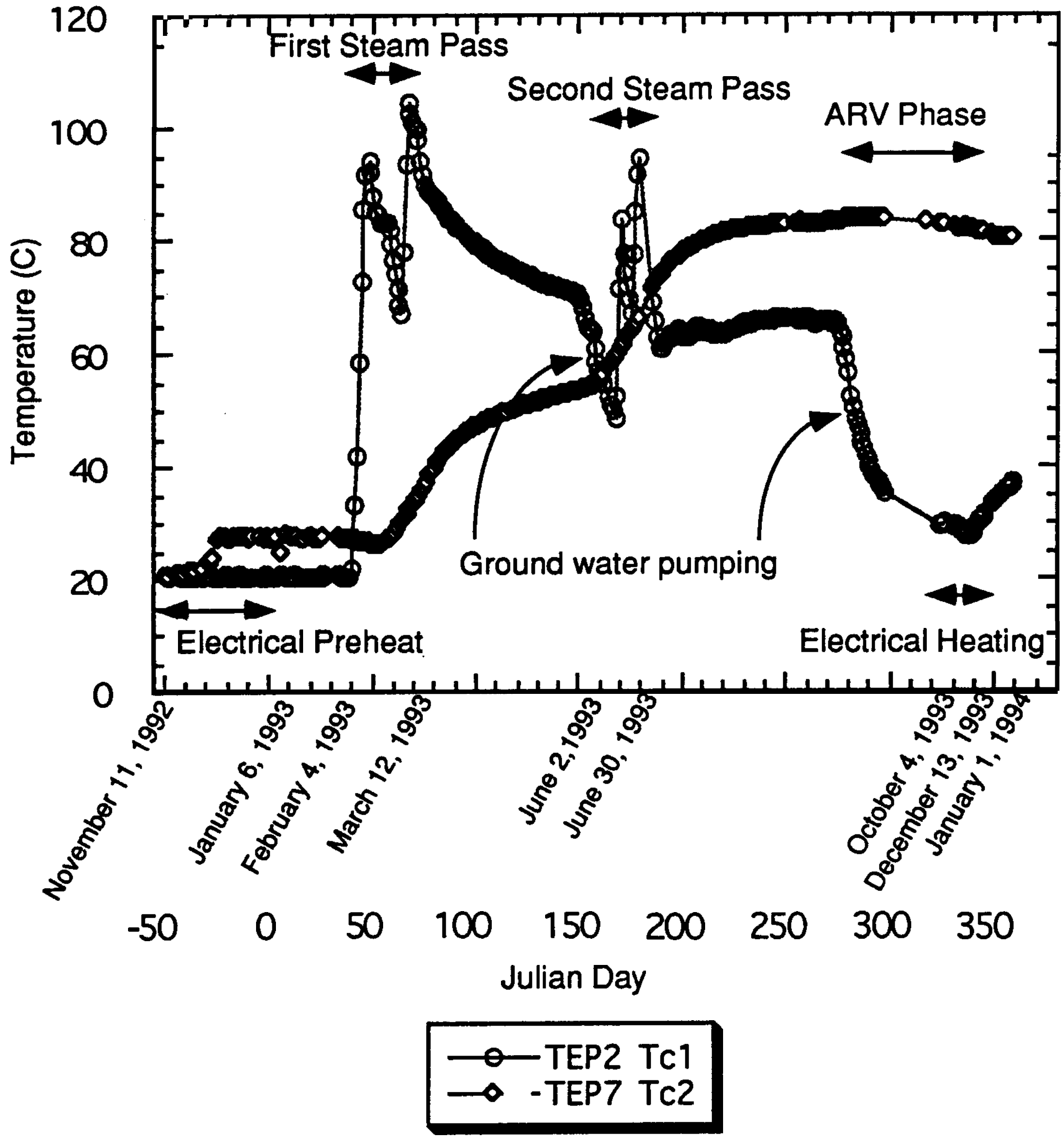

Figure 12. Individual thermocouples reveal the thermal history of different soil types at fixed locations in the field. A temperature record of a thermocouple positioned at about 40-m depth in a permeable gravel unit in the lower steam zone in well TEP 2 shows rapid temperature increases during steam injection. During groundwater pumping, cool fluids are drawn across this location from outside the steamed area, causing temperatures to decrease. By contrast, a thermocouple positioned at about 34-m depth in a clay-rich unit in well TEP 7 shows gradual temperature increases resulting from electrical heating and steam injection. Both fixed thermocouples lie below the standing water table. (After Newmark, 1994b).

more difficult, as the contrast between steam and hot soil was diminished by nearly an order of magnitude. Temperature measurements were similarly more difficult to interpret, as the relative temperature changes in the treatment area grew smaller.

The tiltmeter array was used to determine the horizontal dimensions of the steam zone, and we relied more heavily on the tiltmeter maps of individual steam zones (Figure 16). This was particularly important during the second steam pass, when steam was alternately injected into selected wells to target the remaining cooler zones. Using the tiltmeter maps and temperature logs for guidance, we injected steam into two or three wells at a time to selectively heat portions of the pattern

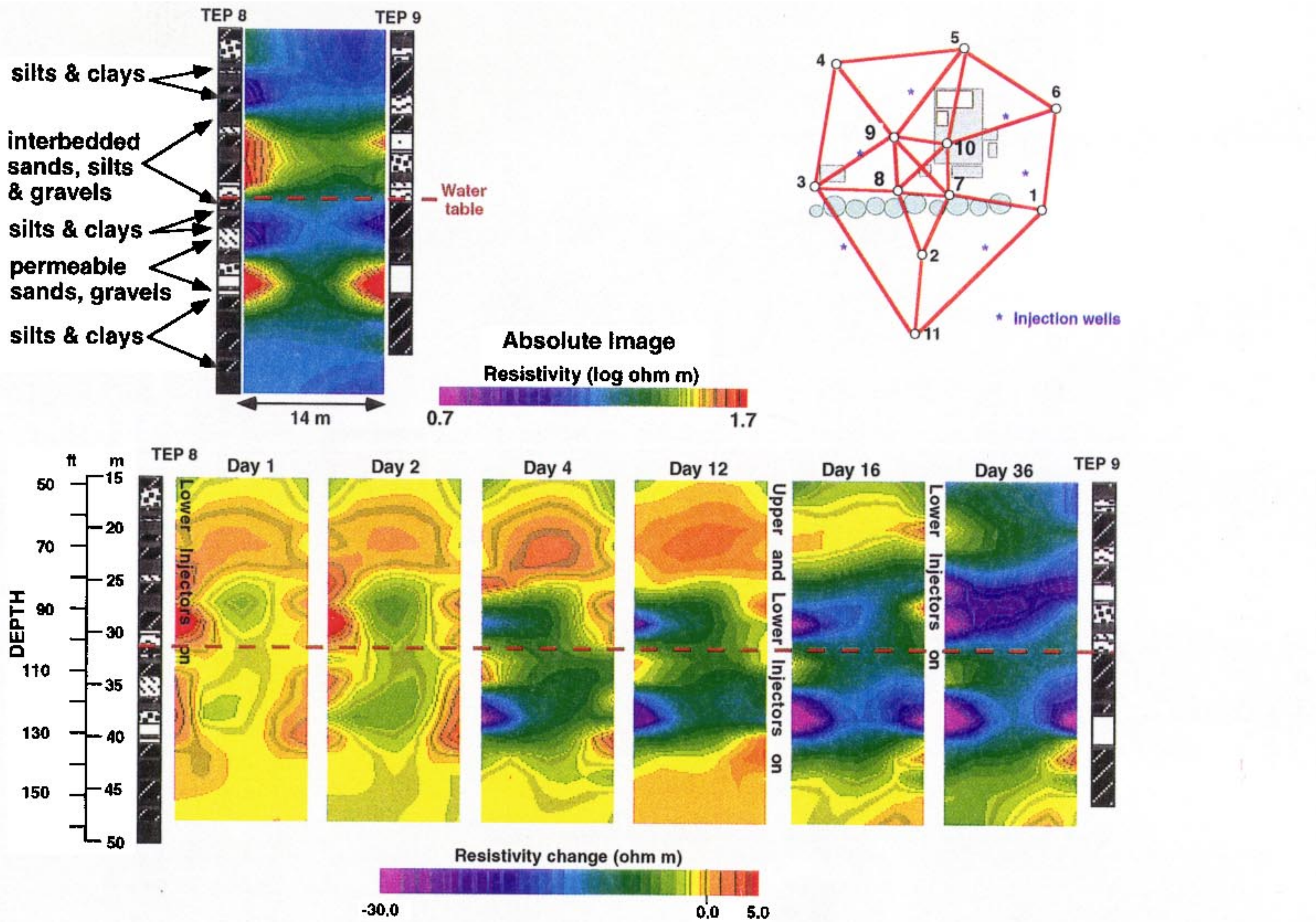

Figure 13. Electrical Resistance Tomography (ERT) images. Top: ERT absolute images reveal the continuity of soil units across image planes. The resistive units correspond to the more permeable sand and gravel zones; the conductive units correspond to the clay-rich intervals. (The apparent pinching-out of units in the center of the image is due to the increase in resolution radius toward the center of each image). Bottom: ERT difference images show the progress of the steam fronts across the image plane, starting from the first day of steam injection. This image plane (between wells TEP 8 and TEP 9) is located approximately 6 m from the nearest injection well, and is oriented nearly perpendicular to a line linking it and the extraction wells. Small decreases in electrical resistivity are observed within hours of the start of steam injection. Although steam was initially injected into only the lower steam zone (centered at about 35-m depth), steam leaked into the upper steam zone (centered at about 25-m depth) through the well completion in the nearby injection well; this is evidenced by the resistivity decreases in both zones in these images. By the end of the first steam pass (Day 36), both the upper and lower steam zones were at or near steam temperature, with conductive heating occurring in the neighboring clay-rich units. The preferential steam paths closely follow the more resistive units seen in the absolute images. (From Newmark, 1994b).

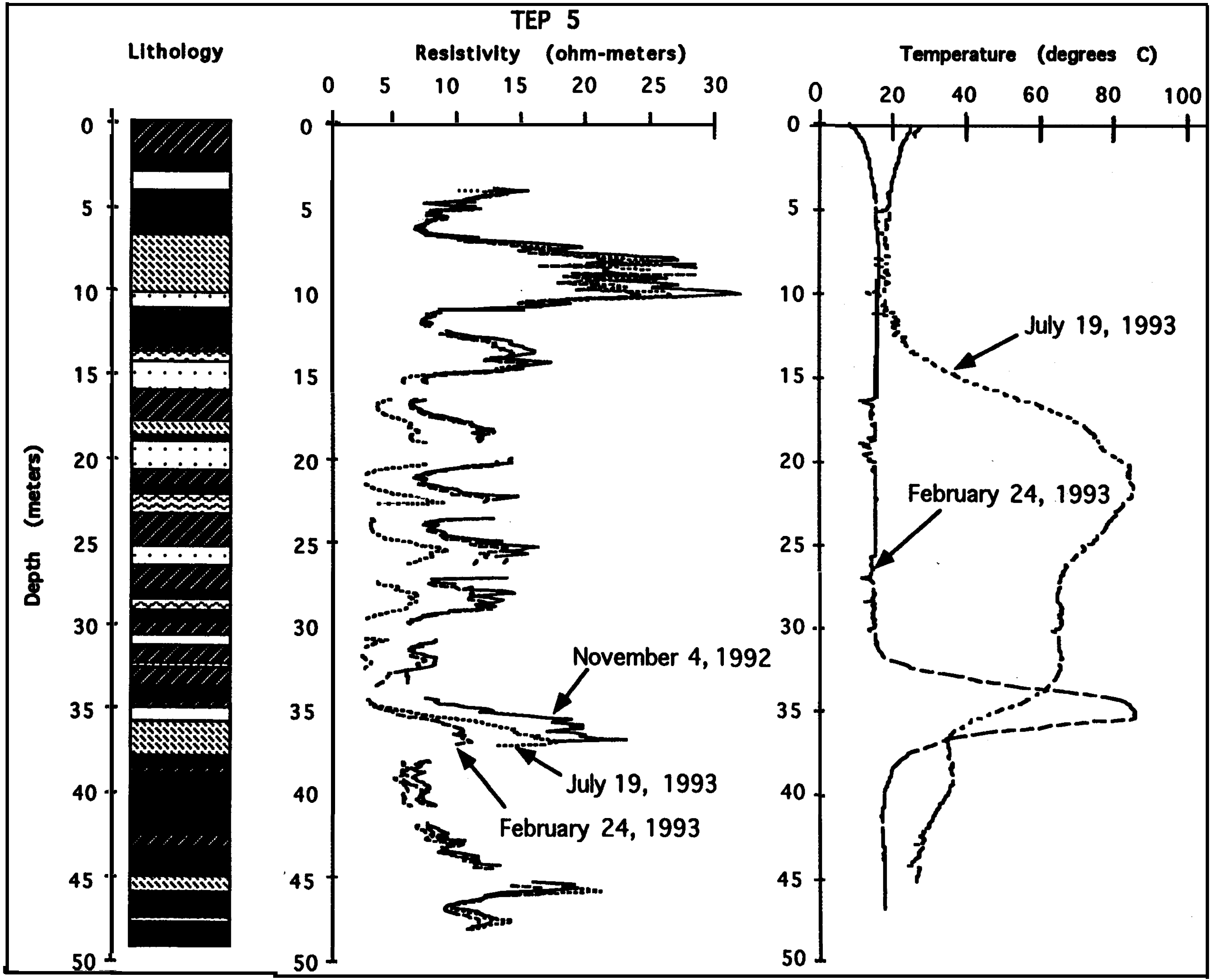

Figure 14. Induction logs such as these obtained in well TEP 5 reveal the changes in soil electrical properties in detail. In the baseline log (11/4/92, solid curve), the permeable zones have high resistivity. During the first steam pass (2/24/93, dashed), the narrow heated zone at about 35 m displays lowered resistivity. After the second steam pass (7/19/93, dotted), a broad zone from about 15-40 m exhibits both elevated temperatures and diminished resistivity. The narrow aquifer at 35 m has experienced groundwater recharge; hence, its resistivity is indicative of heated saturated conditions compared to the hot, dryer conditions existing during the first steam pass. (From Boyd et al., 1994; Newmark, 1994b).

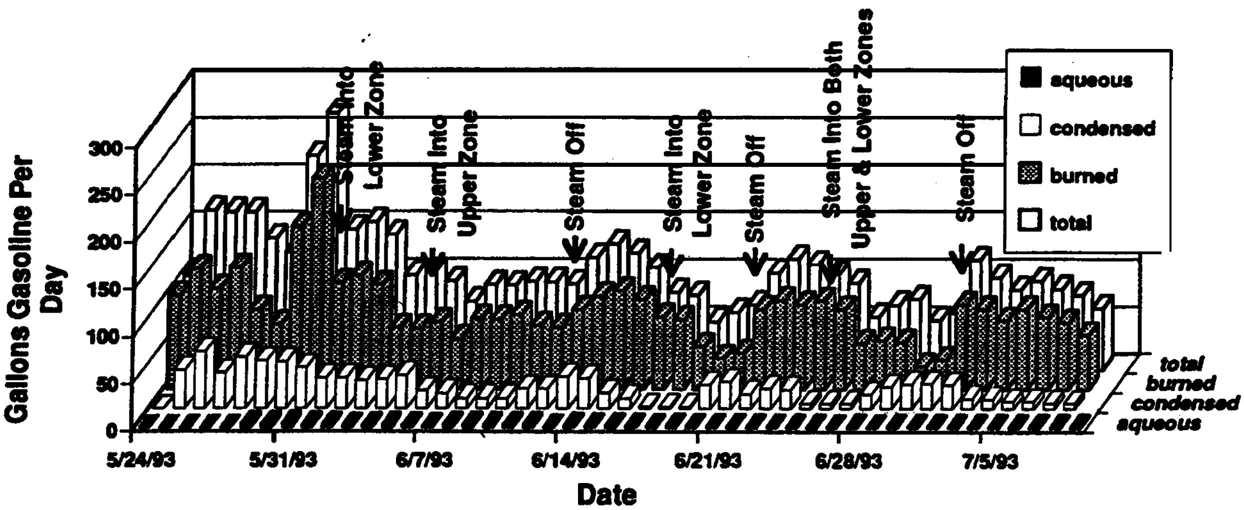

Figure 15. Daily average gasoline recovery rates during the second steam pass. (From Udell, 1994a,c).

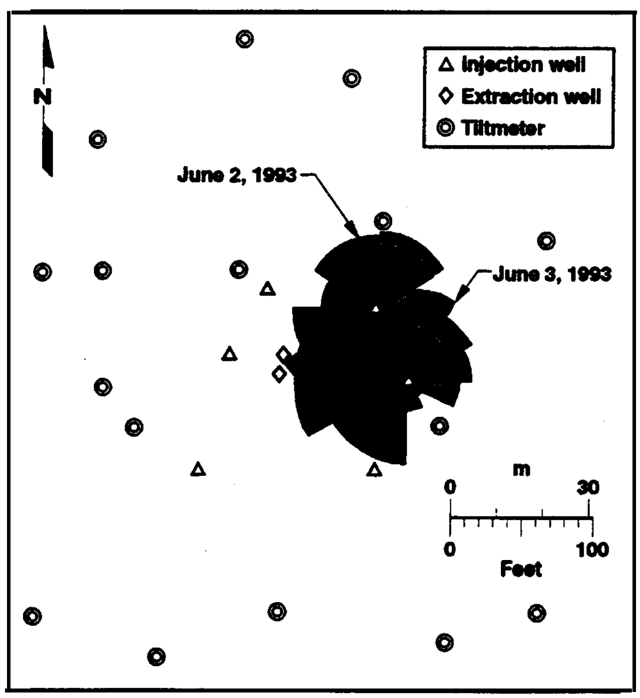

Figure 16. Tiltmeter maps show the growth of the team fronts emanating from two injections wells on consecutive days. At this time, steam was being injected into only two wells, below the water table. Steam broke through to the extraction wells the third day. (From Hunter and Reinke, 1994).

and "sweep" the steam across the remaining cool areas. The pulsed mode of operation, alternating steam and vacuum-only on a 5–6-day cycle, was very effective at maximizing contaminant removal. We terminated this phase on schedule on July 9, 1993, while the extraction rates still ranged between 50 and 100 gallons/day.

Evaluation of the gasoline concentration in the effluent from the extraction well proved difficult in the first pass, but was significantly improved in the second pass (Jovanovich et al., 1994; Aines et al., 1994). Most of the gasoline was removed in the vapor phase, and much of that was condensed along with a large amount of water in the heat exchanger (Aines et al., 1994). The second-pass addition of an oil-water separator on this part of the effluent stream allowed an accurate determination of the condensed part of the flux by simple volume measurement (Sorensen and Siegel, 1994). The remaining dried, cooled vapor was burned in two internal combustion engines; the flux of gasoline in this stream was highly variable, as a function of the amount of steam in the injection wells, total vacuum applied, and time of day (temperature of the heat exchanger).

Because of the cost and hazards associated with sampling and analysis, off-line vapor samples were collected only once or twice daily. This sampling frequency provides somewhat limited insight into the Dynamic Underground Stripping process, and cannot provide sufficient data for detecting short-term fluctuations in system performance or for real-time optimization and control of the system.

We employed a series of continuous in-line chemical sensing systems to measure this flux and to allow the same level of control for the chemical extraction rate as was obtained for the thermal injection systems. These included a standard Fourier-transform–infrared (FT–IR) spectrometer equipped with a gas sample cell, an automated gas chromatograph (with photoionization detector), and the experimental Differential Ultraviolet Absorption Spectroscopy (DUVAS) system. The trends indicated by the in-line sensors were in agreement with standard off-line laboratory analyses, and were obtained continuously in near or real-time (Figure 17a).

Continuous monitoring allowed transient events and mid- to long-term trends in the extraction process to be measured. For example, the DUVAS data showed significant diurnal fluctuations in the absorption of total aromatic compounds; these fluctuations corresponded with recorded variations in ambient temperature and changes in the pressure and flow rates within the vapor extraction system (Barber et al., 1994a,b) (Figure 17b). The correlation between ambient temperature and sensor response led to an analysis of the vapor system's efficiency. The fluctuations appear to be caused by changes in condensation efficiency resulting from variations in ambient temperatures (higher condensation rates during the cooler nighttime temperatures.) This explanation also resolved the apparent scatter between the contaminant concentrations measured in the morning and afternoon vapor samples. (The morning values showed significantly lower concentrations than the afternoon samples.) Thus, the in-line sensors, due to their high sample frequency, revealed trends that occurred between samples and provided a context in which to interpret the analytical results.

During the second steam pass, about 5000 gallons of gasoline were recovered. Extraction rates were extraordinarily high at the beginning of the second pass because of the 3-month heat soak of the formation and the accompanying release and volatilization of gasoline (Aines et al., 1994).

By the end of the two steam injection phases, most of the soil within the treatment volume was heated to the boiling point of water. Only the thick clay layer at 95 to 110 ft in depth did not reach this value, in places reaching only 80°C. It was within this "cold spot" that the largest concentrations of gasoline remained (Figure 18).

Drill-back characterization utilizing six boreholes in a line across the spill site after these first two phases indicated that, as expected, there was still free-product gasoline in the vicinity of the extraction wells but that it was now restricted to a small area just below the water table (Figure 19). Based on the observed soil concentrations, it was estimated that about 750 gallons remained in the clay unit. Gasoline had been substantially removed from the edges of the spill and from the vadose zone.

Of significant importance to this experimental application of Dynamic Underground Stripping was the finding that gasoline concentrations were not increased in the soil outside the treatment volume. However, groundwater and vapor gasoline concentrations were still very high.

At this point, operational control of cleanup activities at the gasoline spill site was transferred

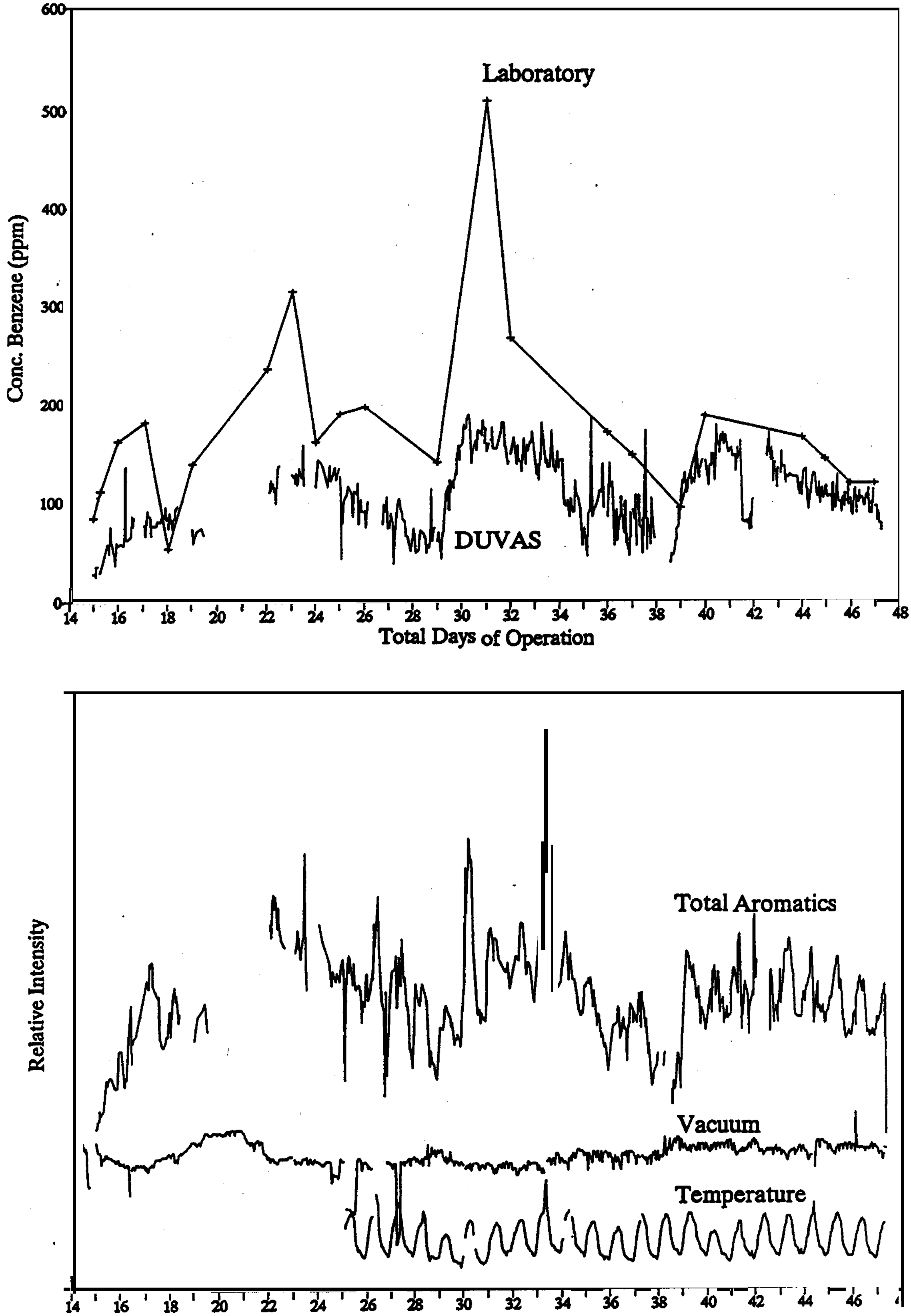

Figure 17. (a) Comparison of the benzene concentration measured by DUVAS and off-line laboratory analyses, (b) Observed variations of relative total aromatic concentration from DUVAS, extraction line vacuum, and vapor temperature. (From Barber et al., 1994a).

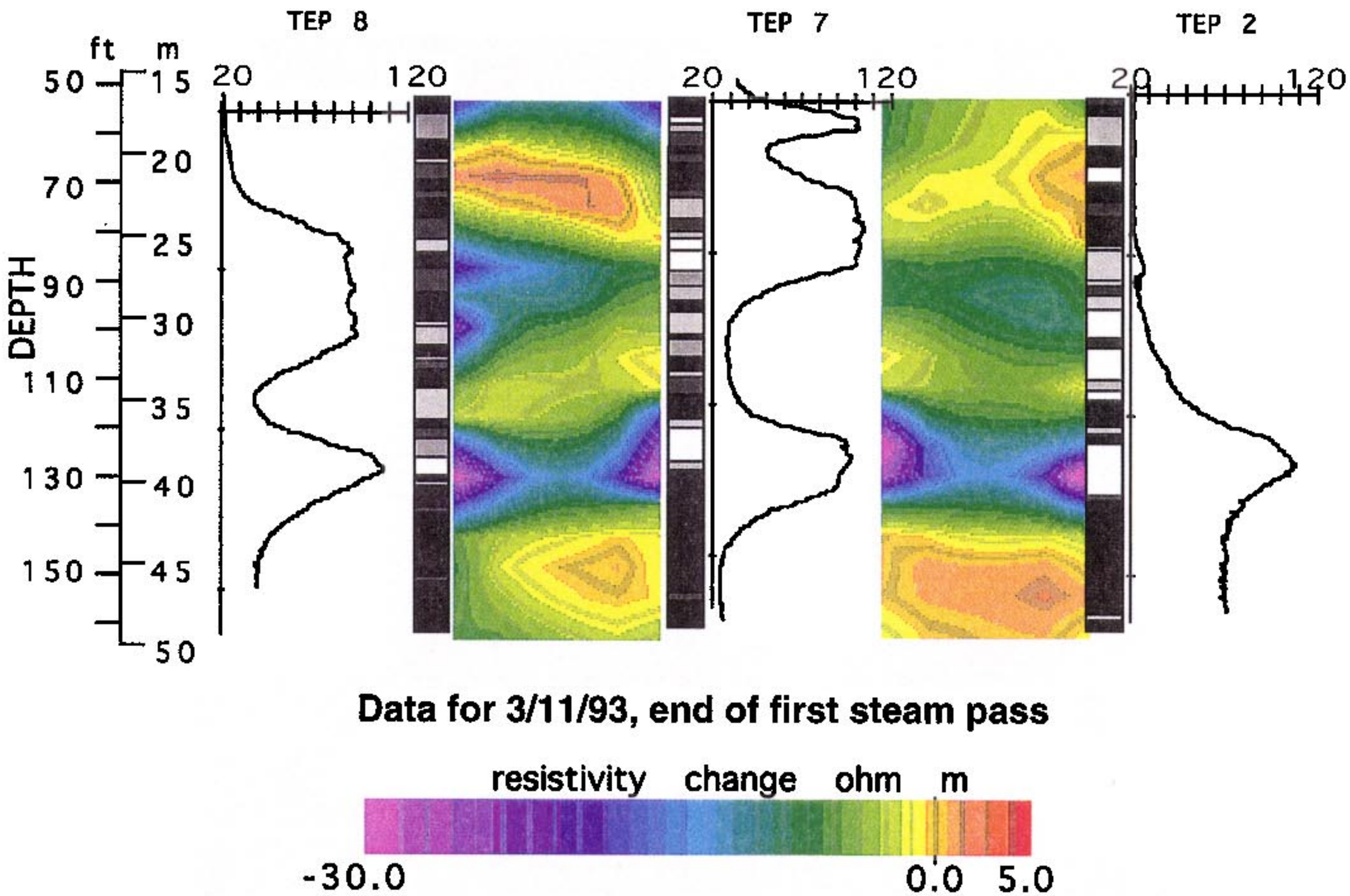

Figure 18. ERT and temperature surveys detected a "cold spot" after the first steam pass. Data from March 11, 1993, at the end of the first steam pass, reveal a zone between about 32 m and 37 m where temperatures have not risen much above ambient. The ERT images indicate the lateral continuity of this zone between wells in which temperatures can be measured.

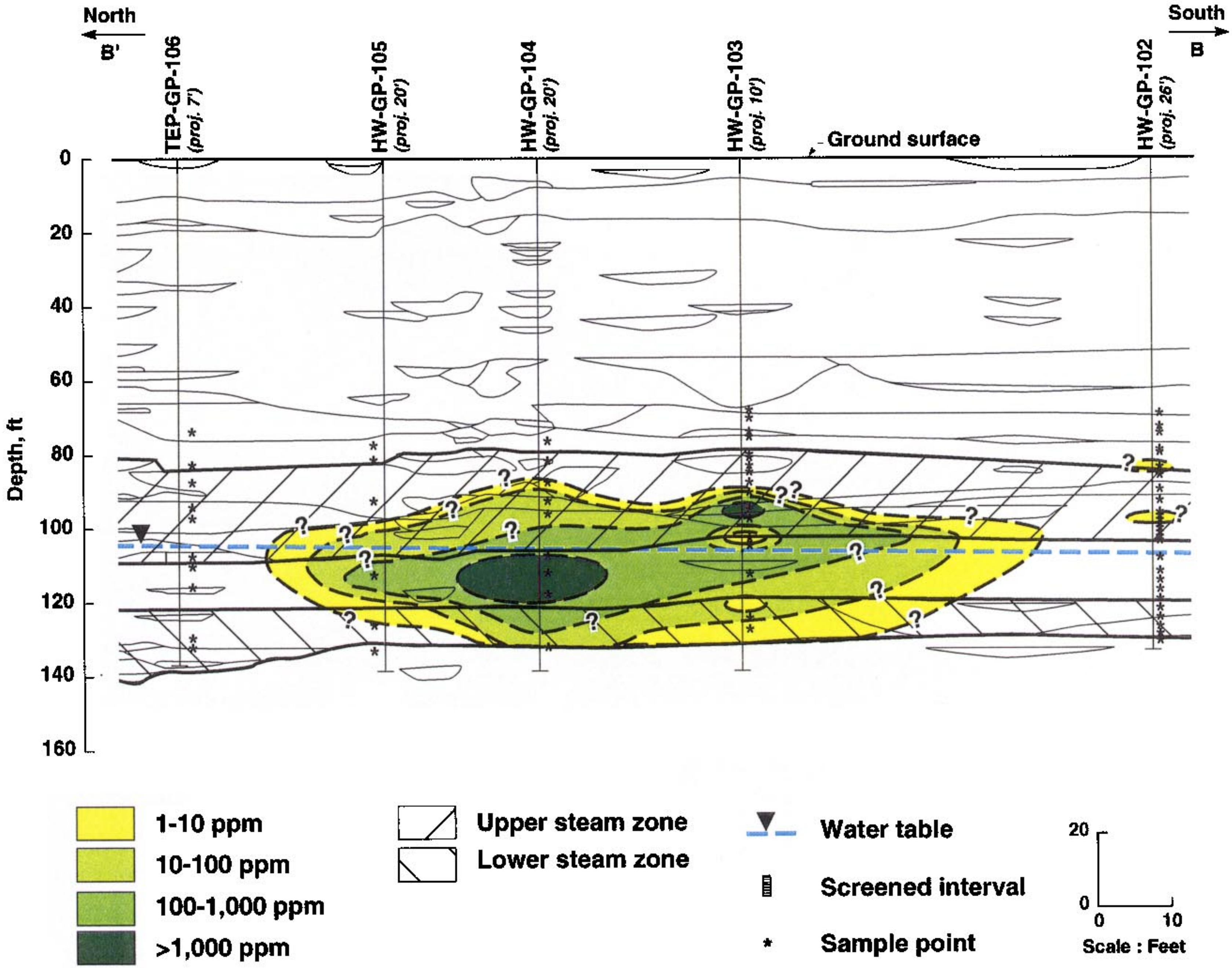

Figure 19. Approximate cross section of the treatment site from the characterization drill-back after the two steam passes (compare with Figure 2). The area of gasoline contamination has contracted greatly, and there are no indications of free product remaining in the treated area outside the volume immediately around the extraction wells. No gasoline has been dispersed outside the treated volume. (From Bishop et al., 1994).

from the more experimental Dynamic Underground Stripping demonstration team to the LLNL site cleanup organization. Subsequent activities focused on the final cleanup of the site.

Extraction of groundwater and vapor resumed as part of the Accelerated Recovery and Validation (ARV) project (Sweeney et al., 1994) in October 1993; the spike in initial extraction rates was smaller than observed after the first pass (Figures 20 and 3). Electric heating was applied to the system in November. Approximately 1000 gallons were removed during this phase, with the concentrations and extraction rates falling dramatically. Electric heating raised the overall temperature of the treated zone only slightly, apparently because the extraction systems were removing large amounts of heat (50 to 100 kW) at the high temperatures prevailing at the time.

When the extraction systems were turned off, temperatures in the clay zones began rising (Figure 21). The electric heating was terminated on December 16, and the system was shut down for the holidays. At this point, at least 7600 gallons of gasoline had been removed from the site. The discrepancy between this and the 6200 gallons estimated to be present is not surprising due to the extreme heterogeneity of the site and the difficulty in characterizing gasoline trapped in soil capillaries. Historically, very few measurements of total hydrocarbons were made at the site, since measurements of BTEX (benzene, toluene, ethylbenzene, and xylenes) were sufficient to delineate the contamination and quantify the regulated contaminants (Dresen et al., 1986). The error in converting the BTEX measurements to total gasoline is therefore fairly large, and the estimated total volume of gasoline subject to an error of several thousand gallons (Devaney, 1994; Aines et al., 1994).

In January 1994, groundwater pumping and vapor extraction resumed. During the 1-month shutdown during the 1993–1994 year-end-break, concentrations in the vapor increased only slightly, and water concentrations decreased. Benzene concentrations in the extraction wells continued their downward trend, now at less than 200 ppb from a peak of 7000 ppb before the start of steam injection. At a groundwater monitoring well within the pattern, benzene concentrations have decreased dramatically, from several thousand parts per billion before Dynamic Underground Stripping to less than 30 ppb in January 1994. Other wells show similar decreases. These factors indicate that there is no significant free-phase gasoline remaining in the treatment volume, although significant contamination may still lie outside the treatment volume.

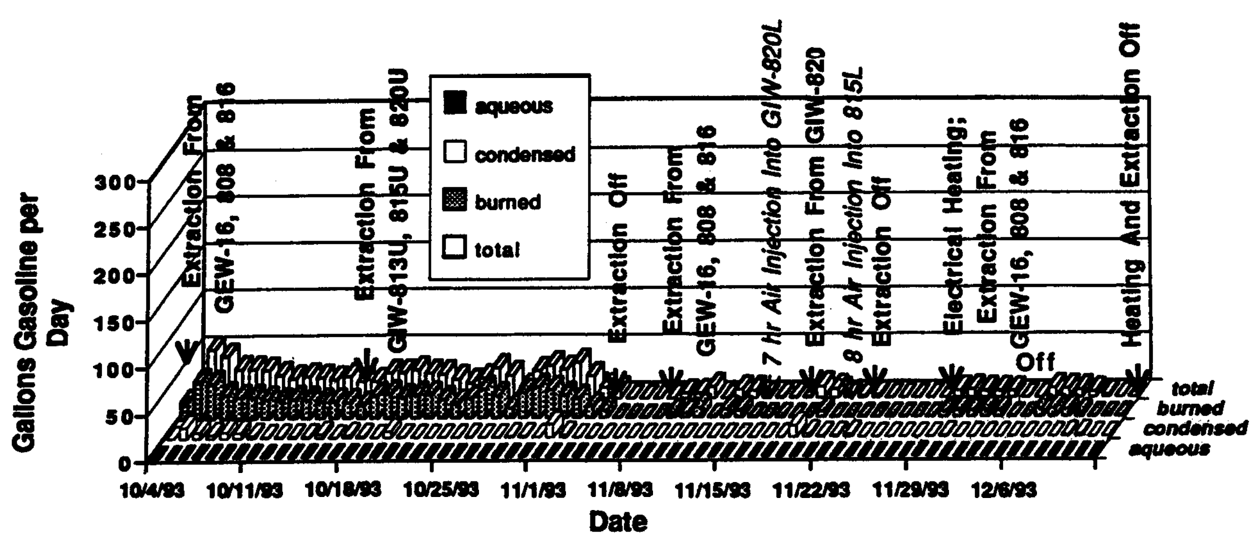

Figure 20. Daily average gasoline recovery rates during the ARV phase. (From Udell, 1994a,c).