A conceptual model and remediation strategy for VOCs in low organic carbon unconsolidated sediments

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Abstract

Field data collected during the first seven years of pump and treat remediation of ground water containing volatile organic compounds (VOCs) at the Lawrence Livermore National Laboratory (LLNL) Superfund Site in Livermore, California, indicate that ground water contaminant plumes can be divided into two distinct parts: source areas and distal areas. In source areas, located in the immediate vicinity of the contaminant releases, the contaminants are distributed in high concentrations throughout the vadose zone and below the water table in both fine-grained and coarse-grained sediments. In distal portions of the plume, downgradient of the source areas, the contaminants: (1) are primarily limited to coarse-grained zones, (2) may be orders of magnitude lower in concentration than in the source areas, and (3) have slightly diffused into the bordering aquitards and should not significantly affect the approach to or achievement of cleanup goals. The cleanup strategy for this distribution of contaminants calls for the hydraulic isolation of the source area followed by aggressive remediation of both the source and distal areas of the plume as needed to achieve remediation objectives most efficiently. In contrast to the currently perceived limitations of pump and treat remediation, our data and analyses indicate that distal portions of contaminant plumes can be expeditiously remediated; perhaps in less time than it took the contaminants to be transported to their pre-remediation locations.

Introduction

The transport of volatile organic compounds (VOCs) in saturated unconsolidated sediments with low organic carbon content (i.e. <0.1%) is controlled by ground water advection, hydrodynamic dispersion, chemical diffusion, and adsorption onto inorganic materials within the aquifer. Adsorption is partially responsible for the retardation of VOCs in ground water and remains poorly understood in the absence of organic carbon. We have identified three major factors that limit our ability to remove VOCs from ground water in a timely fashion: (1) retardation of VOCs, (2) diffusion of solutes across geologic contacts, and (3) the complex distribution of the VOCs in heterogeneous geologic media.

Mechanisms that control the distribution of VOCs in heterogeneous unconsolidated saturated sediments include advective and diffusive transport within geologic zones, as well as across geologic contacts between coarse- and fine-grained sediments. Due to the differences in the distribution of contaminants between 1) the source areas and 2) the plume of dissolved contaminants away from the source areas (distal areas), it is necessary to consider the transport mechanisms and rates, and cleanup strategies, as being distinctly different in these two areas. The importance of recognizing and planning for the characterization and remediation of the two different parts of a ground water contaminant plume was cited by the National Research Council (1994). Pankow and Cherry (1996) also draw a distinction between source areas and the dissolved portion of the plume. Both of these references define the source areas as the area where dense non-aqueous phase liquids (DNAPLs) exist in the subsurface. In this paper, we expand this definition of source areas to include areas where dissolved chlorinated solvents are present, in both fine- and coarse-grained sediments at elevated concentrations, and DNAPLs need not be present.

The conclusions of this paper are based on the interpretation of data from a perchloroethylene (PCE) plume beneath the southwest corner of Lawrence Livermore National Laboratory (LLNL) in Livermore, California. The initial releases of solvents to the ground took place circa 1944. Investigation of the plume began in 1984 and remedial action began in 1989. The 4,000-ft long, 1,500-ft wide plume extends from about 75 to 150 ft. below ground surface. The unconsolidated subsurface sediments consist of interfingered alluvial sediments with hydraulic conductivities ranging over many orders of magnitude and organic carbon contents below 0.1%. PCE concentrations up to 1,500 parts per billion (ppb) (µg/l) in addition to lower concentrations of other VOCs have been detected in ground water (Thorpe, 1990). Over 100 monitor wells and 18 remedial extraction wells are located within the study area. This PCE plume remediation is part of the ground water cleanup at the LLNL Livermore Superfund Site.

Conceptual Model

When VOCs, either as DNAPLs or dissolved in water at high concentrations, are released to the ground surface in an area of unconsolidated sediments, they are transported primarily downward through the vadose zone and to a lesser extent horizontally, by a combination of processes including gravity, capillary suction, and vapor diffusion. As the VOCs reach the water table, they are advected by ground water in a downgradient direction, at rates dependent on ground water flow velocities. However, downward contaminant transport in the saturated zone can also continue, driven by a number of possible mechanisms. If contaminants persist as separate phase DNAPL, density gradients, which are commonly greater than hydraulic gradients, may drive them downward. When DNAPL encounters fine-grained material, pore entry velocity limitations may cause it to pool at the contact, but some will enter the aquitard. High molecular diffusion rates, resulting from either DNAPL or high concentration dissolved contaminant, will continue to propel the VOCs, in the direction of the concentration gradients. While the transport velocity is primarily controlled by the hydraulic conductivity of the zone the contaminant encounters, the density and diffusive transport mechanisms are also important. While the mechanisms of downward transport may not be limited to those mentioned above and remain not completely understood, the result is that in the source area the contaminants are present at relatively high concentrations in both the fine- and coarse-grained zones. For the remainder of this paper, we will assume that the

VOCs are present in the source area, below the water table, as dissolved contaminants at high concentrations.

Dissolved VOCs are advected downgradient by ground water in all zones, but at velocities that are orders of magnitude higher in the coarse-grained, more permeable zones, as opposed to the finer-grained zones. In addition to the effects of variable hydraulic conductivities between the zones, contaminant retardation is higher in fine-grained zones. We assume that this retardation is a function of the larger surface areas of clay minerals and clay-sized particles. In conjunction with advection, hydrodynamic dispersion causes contaminant concentrations to decrease in an exponential-like fashion downgradient of the source area.

In distal parts of the plume, away from the source area, contaminants are transported into fine-grained zones only by molecular diffusion across the contacts between fine- and coarse-grained zones. Because concentrations are considerably less in the distal area as opposed to the source area, concentration gradients are lower and the rate of diffusion is much slower. As a result, relatively small amounts of contaminant mass are transported into the distal fine-grained zones. Figure 1a is a depiction of our conceptual model including a generalized characterization of contaminant distribution and directions of VOC transport in the source and distal areas of a plume, before and during remediation.

Remedial pumping in the distal parts of the plume can reduce concentrations in the most permeable coarse-grained zones in a relatively short period of time. When these concentrations become lower than the very low concentrations in the bordering fine-grained zones, the direction of the molecular diffusion will reverse and the solutes in the immediate vicinity of the contact between the zones will begin to diffuse back into the now cleaner coarse-grained zone. However, the contaminants at the leading edge of the original diffusive front in the fine-grained zones will also continue to diffuse further into that zone, resulting in two diffusive fronts: (1) further into the fine-grained zone, and (2) back out into the cleaner coarse-grained zone. The result is that the fine-grained zones in the distal part of a VOC plume will become sinks for a small amount of the contaminant mass, but because of the low concentrations, low diffusive rates, and double diffusive fronts, they will not become significant sources of contaminants to the coarse-grained zones in the late stages of remedial activity.

Conditions in the source areas, however, are quite different. Because of the low hydraulic conductivity of the fine-grained sediments and high concentrations of contaminants in them, these zones have the potential to become significant long-term sources of contaminants. It is this characteristic of source areas that causes the high costs of remediation and requires long periods of pumping to cleanup plumes to low concentration levels. Figure 1b depicts the distribution and directions of VOC transport shown in Figure 1a, during pump and treat remediation.

While there is certainly a transition zone between the source and distal areas of each plume, in the study area discussed in this paper we have defined the boundary between the two as that point where contaminant concentrations in the fine-grained zones decline by at least one order of magnitude.

This conceptual model is supported by field data collected during the past seven years of ground water remediation in the southwest corner of LLNL and by computational results. In addition, prior to remediation at virtually all known unconsolidated sediment VOC contaminated ground water sites in the southwestern United States, contaminant concentrations remain at their highest levels in the immediate vicinity of the point of contaminant discharge to the ground, even decades after the discharge has been eliminated or curtailed. Concentrations then drop, exponentially, away from the source area.

Site Remediation Background

At LLNL's Livermore site, VOCs detected in ground water in the early 1980s resulted in EPA's decision to place the site on the Superfund National Priorities List in 1987. The Record of Decision for the cleanup was completed in 1992. Pump and treat was the selected remedy to cleanup LLNL ground water, and by April 1996, six pumping centers and associated treatment facilities were operational. The LLNL approach to implementation of this remedy is to remove contaminant mass and reduce contaminant concentrations as quickly as possible, through a strategy called "smart pump and treat" (Hoffman, 1993).

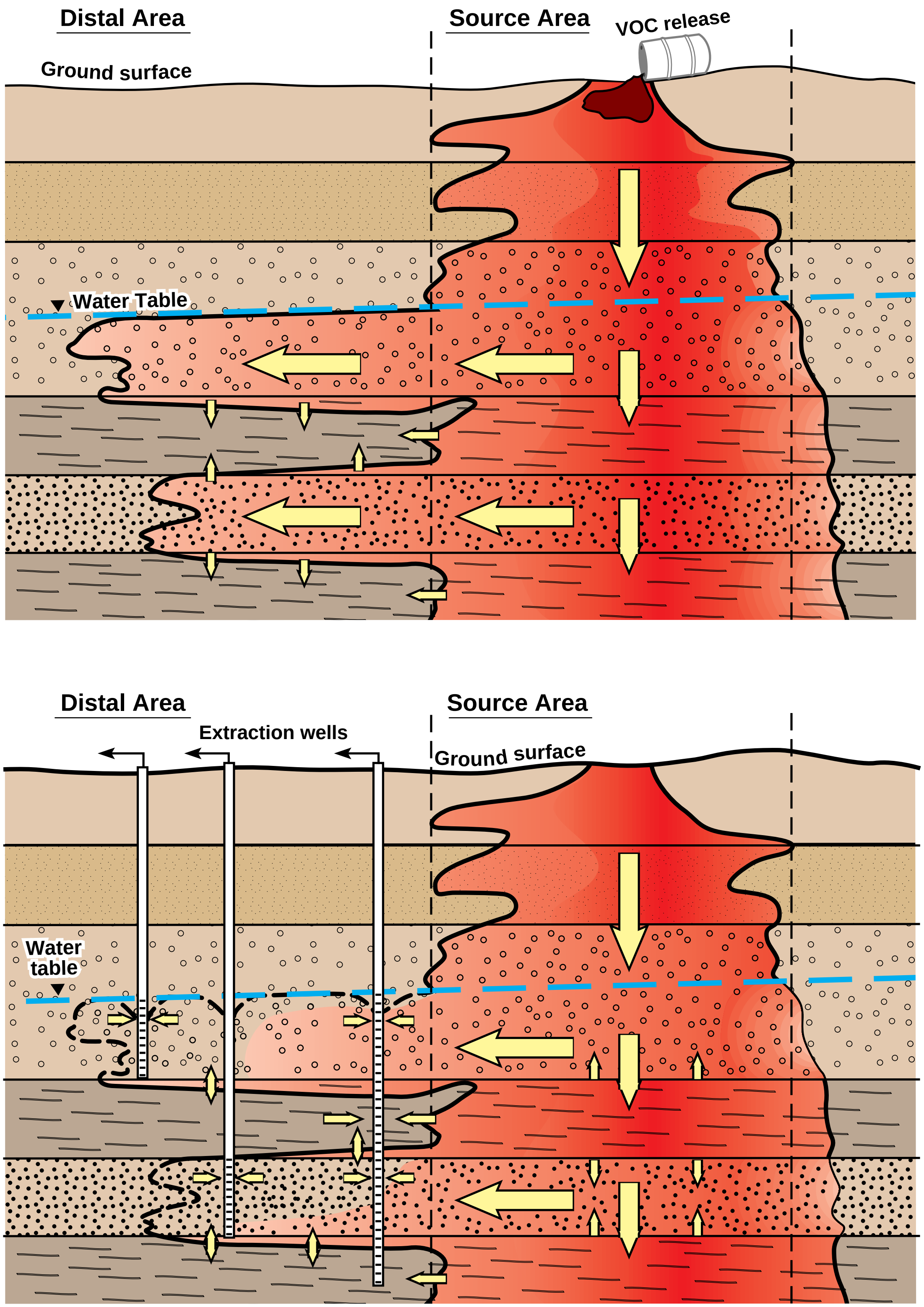

Fig. 1. Conceptual representation of the distribution of VOCs. Direction and magnitude of transport are shown by arrows (a) before remediation and (b) during remediation.

This strategy can be broken down to three major activities that are vigorously conducted throughout the life of the remediation:

- Characterization of the contaminant hydrogeology is continuously improved through the monitoring of extraction and monitor wells, and the drilling and construction of new wells as data and computer modeling result interpretations dictate.
- Modification of extraction well fields and treatment facilities is conducted whenever re-interpretation of subsurface conditions suggests that the time to attain cleanup goals can be reduced by such modifications. The most visible of these modifications occurs as the extraction wells are phased in. The initial wells are installed, pumped, and chemically and hydraulically evaluated for a period of months before decisions are made on the locations of other extraction wells within the wellfield.
- Operation of the remediation facilities is continuously altered as monitoring information indicate that portions of the aquifer needing cleanup require different stresses. For instance, when an area between extraction wells becomes stagnant, we may either alter the pumping rates of nearby wells to ensure remediation of all parts of the contaminant plume, or install new wells. Stagnation zones are identified from direct interpretation of field data and by 3-D data-calibrated flow and transport simulations.

This strategy has been implemented at LLNL, beginning with the initiation of cleanup of the ground water plume in the southwestern corner of the site in 1989. The extraction well field, monitor wells, pipelines, treatment facility and recharge basin are shown in Figure 2. LLNL began pumping W-415, located immediately downgradient of the source area, in 1989 and four wells south of the treatment facility in 1991. Four Six more extraction wells were added in 1994: four south of the facility and two along the western pipeline. Four extraction wells north of the facility came on-line in 1995, and LLNL began pumping three additional wells along the western pipeline in 1996. Two more northern extraction wells are planned for 1997. These seven years of active remediation and monitoring in the southwest corner of LLNL have produced the field evidence supporting our conceptual model.

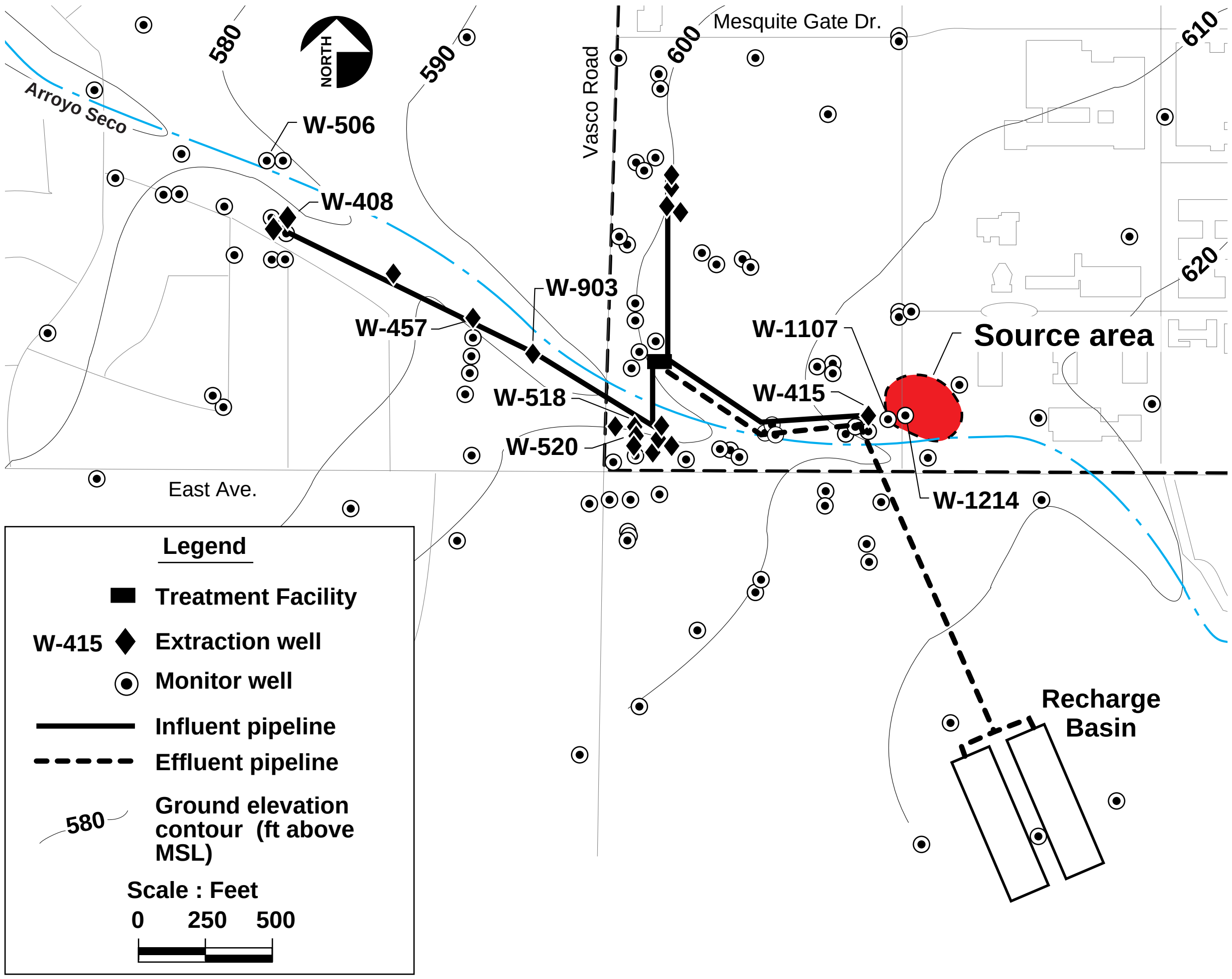

Fig. 2. Map of study area showing location of the major components of ground water remediation in the southwest corner of LLNL.

Field evidence supports this conceptual model

Depth-sampling

At LLNL, we use a mud-rotary drilling and sediment sampling technique that allows us to evaluate the vertical distribution of VOCs in a single borehole (Hoffman and Dresen, 1990). The technique involves the collection of a core sample of saturated sediment from each zone of interest for analysis. The methodology uses a wireline coring system in which the mud-rotary drill stem remains in the borehole at all times. New drilling mud is pumped down the drill stem and part way up the annulus prior to sampling each zone of interest so that the sampling equipment and sampler pass through uncontaminated drilling fluid. This drilling and sampling procedure provides a semi-quantitative analysis of the VOCs in the saturated sediment which allows us to determine the presence or absence of contaminants in each geologic zone with minimal contamination from a shallower contaminated zone.

While the vast majority of the samples collected during the investigation phase of the project are from coarse-grained sediments, there are several samples of intervening aquitards from boreholes that were drilled in the distal portion of the southwest corner plume. Plots of the PCE concentrations in saturated sediment superimposed on portions of the geologic logs of three of these wells in the distal portion of the southwest LLNL plume are included in Figure 3a. In each of the distal wells, the highest concentrations were in the coarse-grained zones, and concentrations dropped dramatically in the fine-grained zones. Since ground water chemistry indicates that the dissolved solvents have been present at this location for tens of years, the low levels of VOCs in the fine-grained zones are evidence of the slow VOC transport from the coarse-grained to the fine-grained zones in the distal portions of the contaminant plume.

In order to gain further information on the source areas, we are now sampling fine-grained zones in all boreholes drilled in suspected source areas. Figure 3 includes partial geologic logs and semi-quantitative saturated sediment analyses from two boreholes in the southwest corner plume source area and from three boreholes in the distal portion of the same plume. In contrast to the distal boreholes, the contaminants in the source area boreholes are distributed in relatively high concentrations in the fine-grained as well as in the coarse-grained zones.

Concentration history

By analyzing the multiple independent data sets collected over the years, we have characterized this very complex alluvial setting and have mapped several hydrostratigraphic units (HSUs) beneath the LLNL site. HSUs are defined as sedimentary sequences whose permeable layers show evidence of hydraulic communication and interconnection. These permeable layers have common geologic, geophysical, contaminant, and hydraulic characteristics (Blake et al. 1995). Hydraulic test results indicate a high degree of connectivity between water-

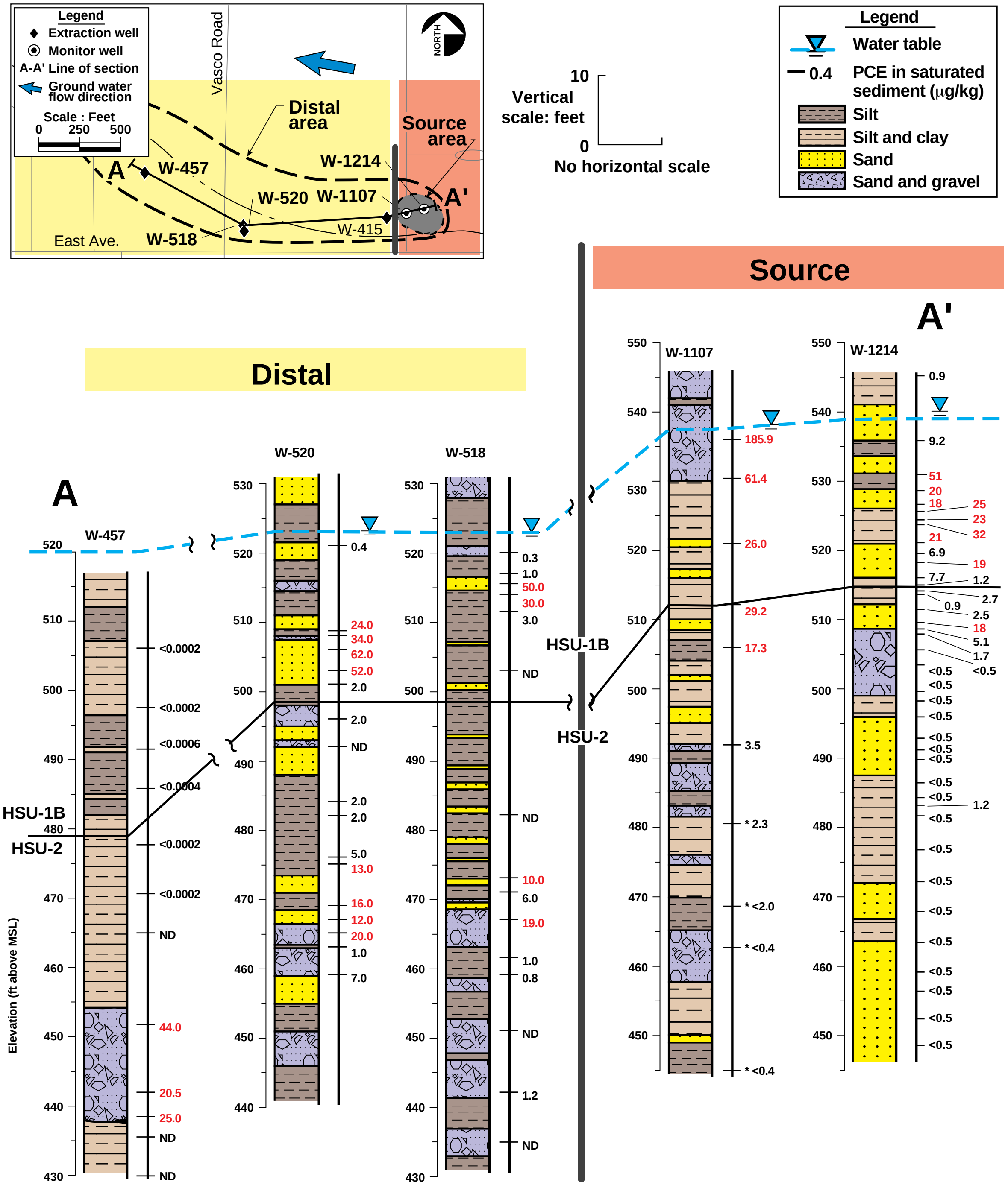

Fig. 3. Partial geologic logs of wells in the distal and source area portions of the southwest corner plume, with semi-quantitative saturated sediment PCE concentrations.

bearing zones mapped within each HSU as opposed to a low degree of connectivity to the zones in adjoining HSUs. Eight HSUs have been identified at LLNL and comprise the upper 400 feet of unconsolidated saturated sediments.

PCE contamination in the southwest corner ground water plume is present in both HSU-1B and HSU-2. Figures 4 and 5 show isoconcentration contour plots of PCE in these HSUs between 1988 and 1996. The time periods were chosen to show significant concentration changes from just prior to initiation of pumping to July 1996. As shown in Figure 4, in the distal portion of the HSU-1B plume, the 500 ppb contour has been drawn back approximately 1,200 ft. toward the source. In HSU-2, PCE concentrations are currently below 200 ppb and the 100 ppb contour has been dramatically reduced in size (Figure 5). In contrast, the high PCE concentrations in the source area have remained relatively unchanged.

Extraction well W-415 is located immediately downgradient of the source area and is screened across both HSU-1B and HSU-2, throughout the thickness of the plume. LLNL began pumping well W-415 in 1989 at a flow rate of about 50 gpm. At this pumping rate, the capture area of the well encompasses the entire source area, thus eliminating any further downgradient movement of source area VOCs. The cutoff of the influx of further contaminant mass to the distal portion of the plume, combined with the phased-in pumping in the distal portion has resulted in the dramatic and steady reduction of VOC concentrations away from the source area. This result supports our contention that distal portions of many contaminant plumes can be cleaned up in a more reasonable period of time (perhaps one to two decades) than the many decades to centuries projected by Travis and Doty (1990).

In order to evaluate the quality of the contour plots shown in Figures 4 and 5, we calculated the PCE mass that would have to be removed from each HSU in order to produce the changes in the contour lines for each time step. These calculations assumed that the coarse-grained zones within each HSU produced all of the extracted VOC mass and that these zones comprised 35% of the thickness of the HSU. The 35% estimate was derived from the average fraction of coarse-to fine-grained zones taken from the geologic logs of HSU-1B and HSU-2 from over 100 monitor wells and boreholes within the study area. We also assumed an average porosity of 0.25 which was estimated from 31 porosity measurements of core samples from four boreholes in the southwest corner of LLNL. We then compared the estimated PCE mass to the actual PCE mass

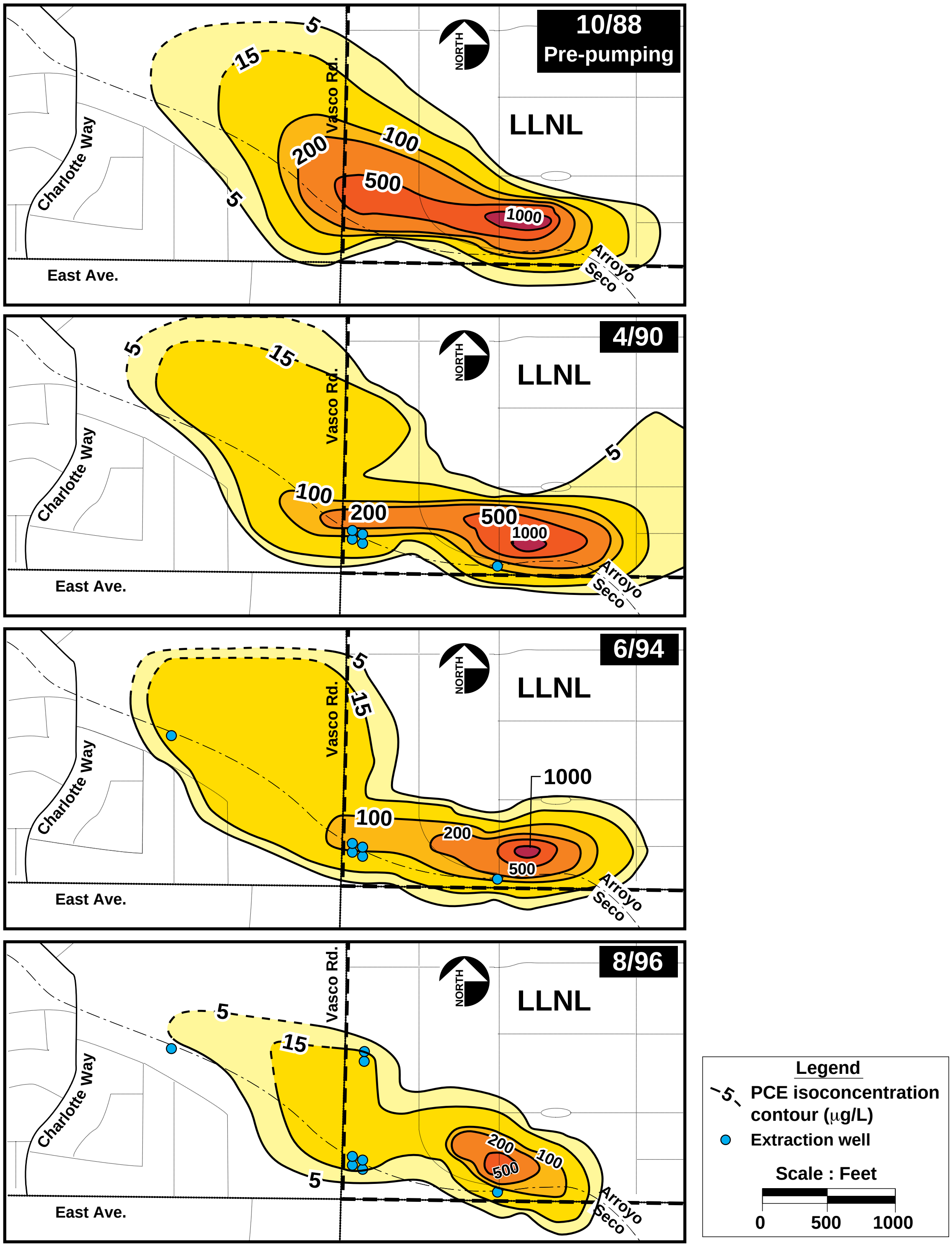

Fig. 4. Isoconcentration contour maps of PCE in HSU-1B from pre-remediation to July 1996.

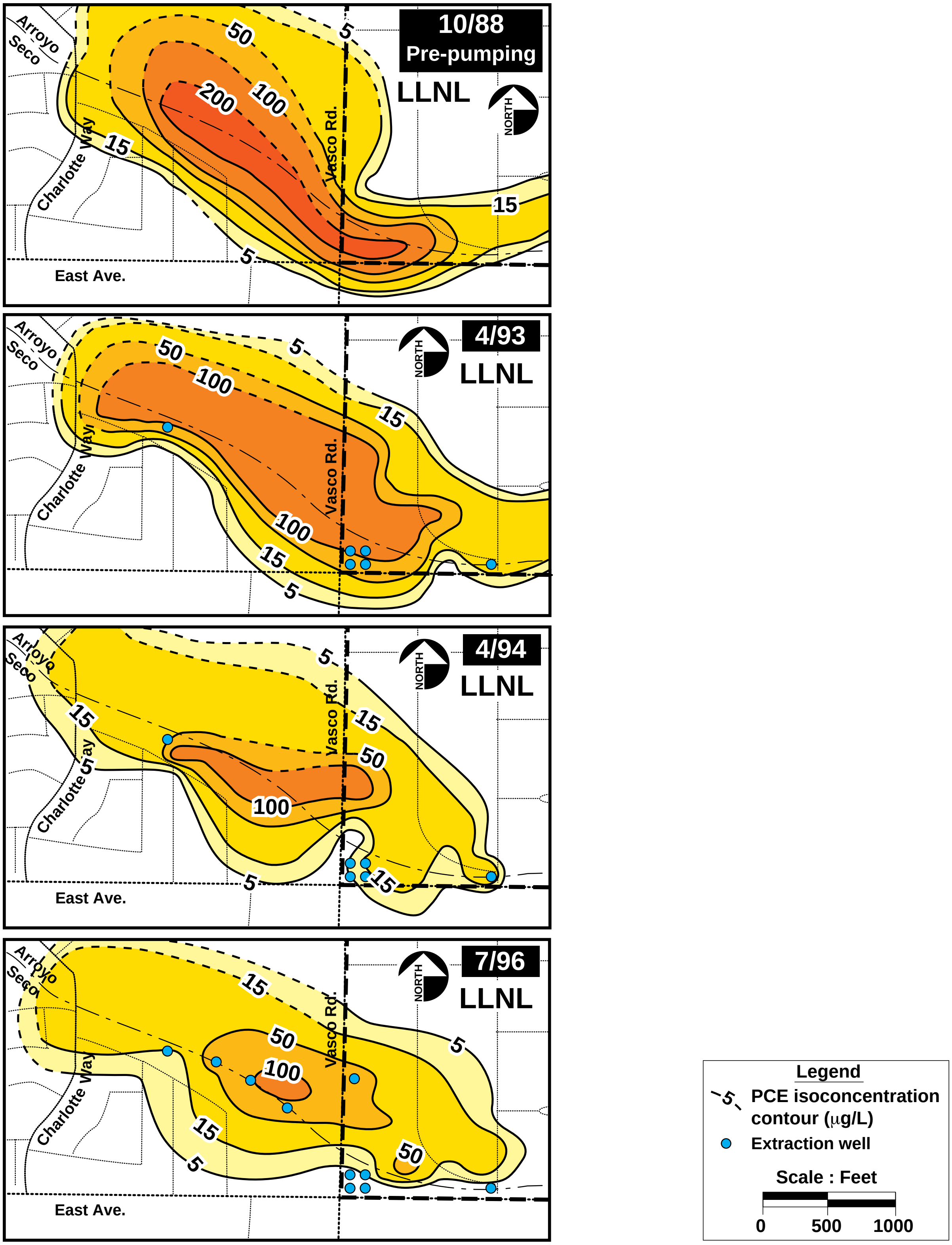

Fig. 5. Isoconcentration contour maps of PCE in HSU-2 from pre-remediation to July 1996.

removed by the ground water treatment facility. The actual PCE mass removed was calculated using treatment facility monthly influent concentrations and flow volumes. The estimated 47 kg of PCE mass removed from the aquifer compares quite well with the 38 kg removed at the treatment facility. A graph of the estimated PCE mass removed from each HSU plotted with the calculated mass removed at the treatment facility is shown in Figure 6.

Given the degree of uncertainty in both the placement of the isoconcentration contour lines and the estimate of effective thickness, (i.e. fraction of permeable zones within the HSU), this analysis indicates that the time-series concentration contour plots are reasonable and that the reduction in PCE concentrations in the ground water is directly related to the remediation efforts over the last seven years.

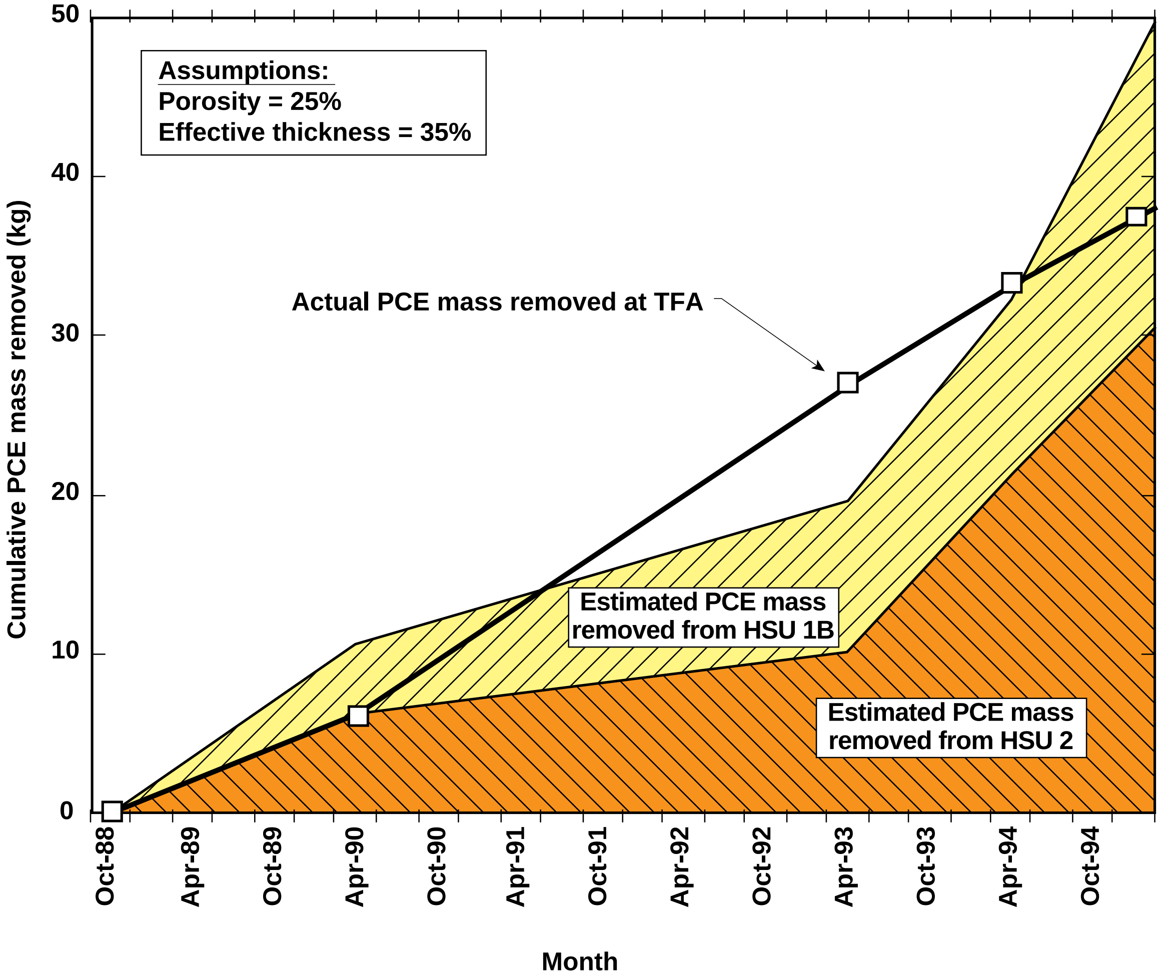

Fig. 6. Estimated PCE mass removed from each of the HSUs (from 1988 and 1995 contoured contaminant distributions) and actual PCE mass removed at the treatment facility.

If this conceptual model is correct, then ground water VOC concentrations in the distal parts of the plume should continue to decline during remediation and not show any appreciable recovery resulting from diffusive transport from fine-grained zones during a hiatus in pumping. Although remedial pumping has been interrupted for periods of several months during treatment facility modifications, in the seven year concentration histories of over 100 wells in the distal portion of the plume, we have seen no evidence of VOC concentration rebound resulting from VOC diffusion out of fine-grained sediments. Figure 7 is a graph of the monthly flow from extraction well W-408 and the concentration of total VOCs from the same well and the concentration of total VOCs from monitor well W-506 located about 50 m north of W-408. The location of both of these wells is shown in Figure 2. The monthly flow of extraction well W-408 was reduced or eliminated following September 1995, when VOC concentrations decreased below 5 ppb. The graph shows the decrease in contaminant concentration, in both wells, in response to pumping and no change in concentration in response to the cessation of pumping.

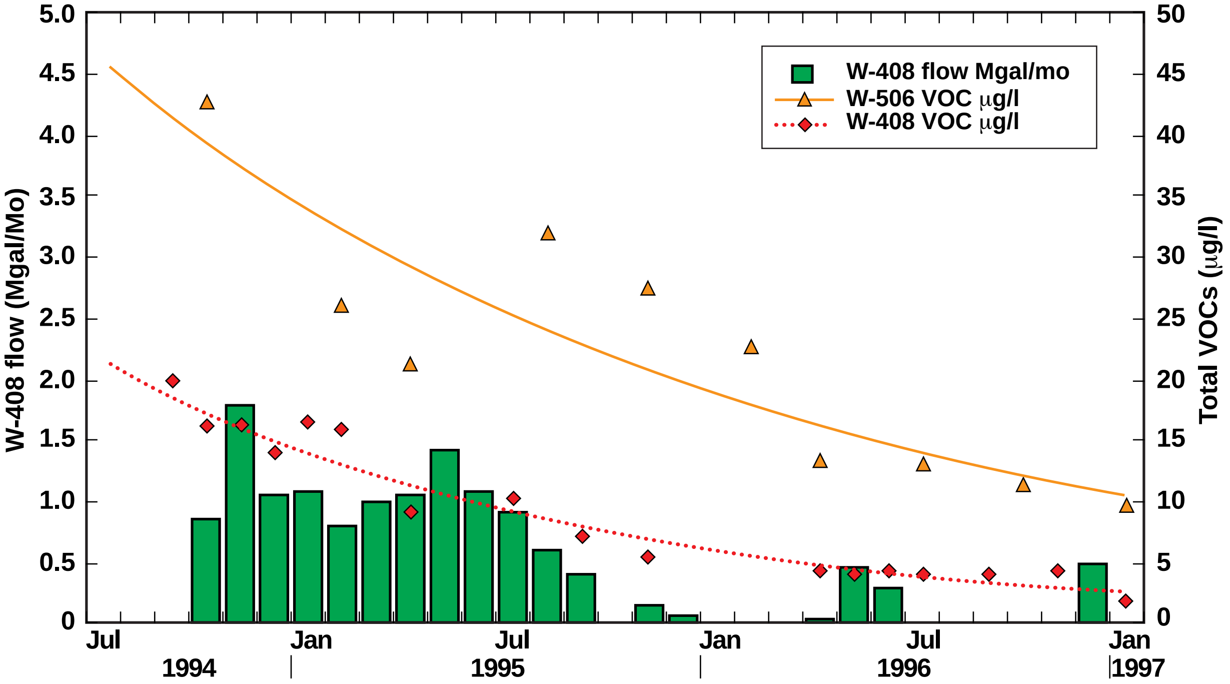

Fig. 7. Graphs of the total VOC concentrations in extraction well W-408 and monitor well W-505 show the response to pumping W-408 and the lack of response to the cessation of pumping.

Computational Results Support the Conceptual Model

Diffusion

To test our assumption of low mass transport of contaminants into fine-grained zones in the distal portions of the plume, we used the one-dimensional complementary error function solution for Fickian diffusion (Fetter, 1993). Our calculations indicated that PCE concentrations of 5 ppb would extend 0.5 m into a low-permeability sandy aquifer in 7.5 years and 1.0 m in 30 years. To make this calculation, we assumed a constant PCE concentration of 300 ppb at the boundary. Our estimated effective diffusion coefficient of 9.4×10^{-7} cm^2/sec was based on a typical tortuosity coefficient for aquifer materials of 0.1 (Freeze and Cherry, 1979), and a diffusion coefficient in water was calculated from the molar volume of PCE (Schwarzenbach et al., 1993).

3-D modeling

As part of the effort to monitor progress of the cleanup at the Livermore Site, a three-dimensional data-calibrated ground water flow and contaminant transport model was developed using the finite element computer code CFEST (Gupta et al., 1987). The model primarily simulated the ground water flow and PCE transport in HSU-1B and HSU-2. The flow portion of the model was calibrated to measured ground water elevation data collected from the Livermore Site wells using representative hydraulic parameters for each HSU. Simulations included the actual pumping history of all of the extraction wells through 1995. Using the initial (pre-1989 initiation of pumping) distribution of PCE concentrations, shown in Figures 4 and 5, the contaminant transport portion of the model was calibrated to measured aqueous PCE concentration study area data from 1988 to 1995.

These preliminary results indicate that, with the source of the southwest plume effectively cut off by an extraction well since 1989, no further contaminants were advected into the distal portion of the plume, and the current well-field can hydraulically control and cleanup the distal PCE plume. An isoconcentration contour map of the area based on analysis of samples collected from monitor wells in HSU-1B during the fall of 1995 is shown in Figure 8. The CFEST simulation results for October 1995 are also shown in this figure (Vogele et al., 1996).

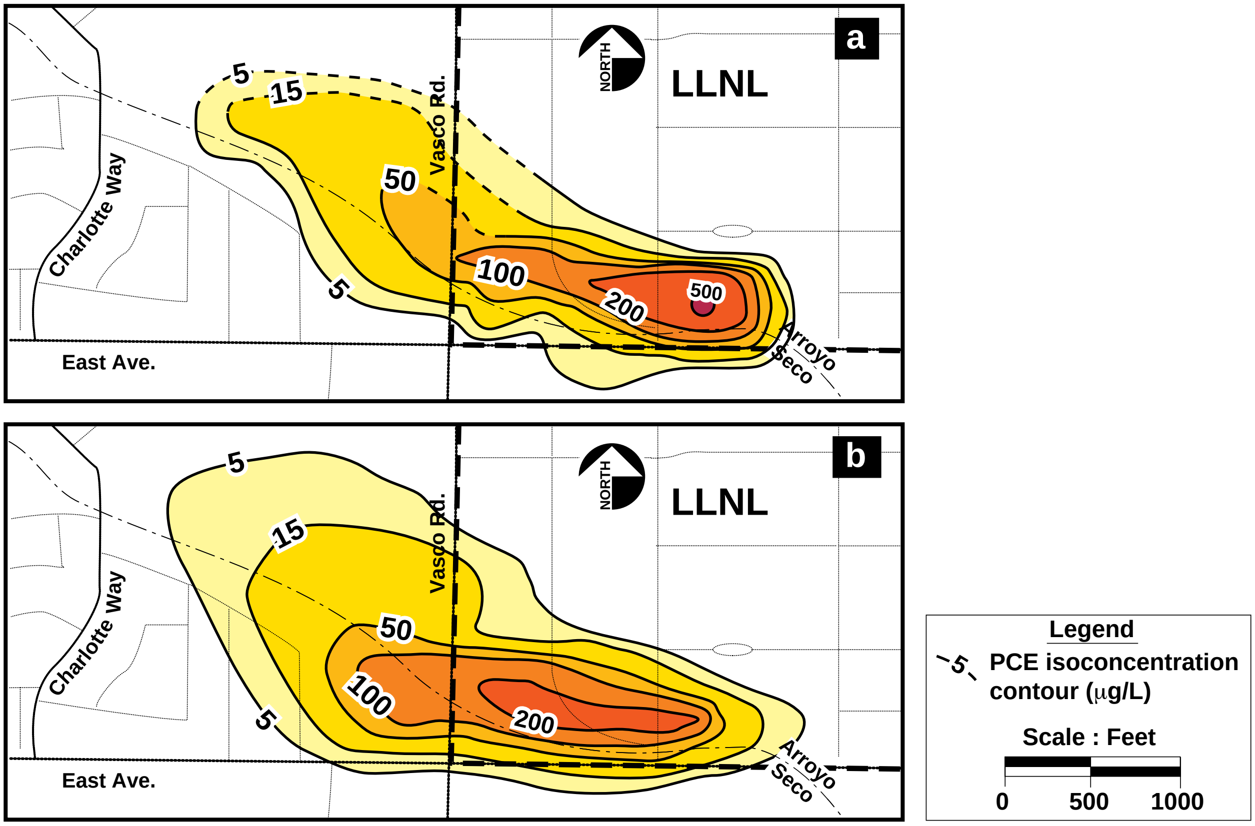

Fig. 8. Isoconcentration contour maps of PCE in HSU 1B: (a) measured in October 1995, and (b)estimated by CFEST 3D numerical model computations.

Conclusion and Proposed Remediation Strategy

Organic solvent plumes in ground water in low organic carbon sediments can be divided into two distinct areas with very different characteristics. The source areas contain high concentrations of the contaminants throughout the geologic column in both coarse- and fine-grained zones. Although water in the coarse-grained zones can be quickly removed from the aquifer along with large quantities of contaminant mass, high concentration gradients between the coarse- and fine-grained zones will continue to allow contaminant mass to diffuse into the coarse-grained zones. As a result long periods of pumping will probably be necessary to approach cleanup goals.

In the distal portions of the plume, the contaminants are essentially contained in the coarse-grained zones and can be readily removed with a carefully controlled pump and treat program. Any contaminants that diffuse into the fine-grained zones in this part of the plume will do so at low concentrations and are not likely to significantly lengthen the cleanup when they diffuse back out in the late stages of the remediation. In contrast to the currently perceived limitations of pump and treat remediation, our experience indicates that distal portions of contaminant plumes can be expeditiously remediated; perhaps in less time than it took the contaminants to be advected to their pre-remediation locations.

The remediation strategy suggested by this conceptual model has the following three elements:

- Begin by installing extraction wells immediately downgradient of the source area to effectively cut off the source area and eliminate the influx of any new contaminant mass to the distal portion of the plume. Proceed with simultaneous remediation in both distal and source areas.
- As contaminant concentrations reach low asymptotic levels in the distal portions of the plume, extraction wells can be shut down, allowing the remedial well field to contract toward the source areas. This reduces the cost of pumping, treating and discharging large amounts of water.
- A small number of extraction wells guarding the source area can remain to prevent any further downgradient movement of contaminants (Pankow and Cherry (1996) refer to wells positioned here as "source containment wells"), while continued pump and treat or more aggressive new cleanup technologies are employed to accelerate remediation of the low mobility contaminants from fine-grained sediments in the source areas.

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