

# COOPERATIVE LLNL/HAZWRAP PROJECT TO DEMONSTRATE FIELD-BASED MEASUREMENT OF RETARDATION FACTORS: PART 1. DISTRIBUTION OF PERCHLOROETHYLENE AROUND AND WITHIN PERMEABLE ZONES IN SATURATED ALLUVIAL DEPOSITS

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## ABSTRACT

As part of a cooperatively sponsored HAZWRAP and Lawrence Livermore National Laboratory (LLNL) project to evaluate field-based methods to measure retardation factors, we investigated some aspects of the variability associated with measuring the concentrations of perchloroethylene (PCE) within the saturated unconsolidated alluvial sediments beneath LLNL. Using the depth-sampling technique developed at LLNL, we are describing the relationship of VOC spatial variability to various sediment characteristics such as geophysical log results, grain size distribution, cation exchange capacity, total organic carbon, permeability, bulk density, skeletal density, and porosity. Using this information, an algorithm is being developed to calculate representative field-based partitioning coefficients ( $K_d$ ) and retardation factors ( $R$ ). A critical parameter used in the algorithm is the total mass of PCE present in a saturated sediment sample. The two major sources of sediment PCE concentration variability examined were those associated with (1) the analytical extraction methods and (2) the spatial changes in fine-grained materials within permeable and confining sediments.

To evaluate desorption efficiency during headspace extraction (EPA Method 3810) for VOC analyses (EPA Method 8010), a bulk thermal desorption chamber (BTDC) was constructed and calibrated. The BTDC extraction provided a reference method against which generally used EPA extraction methods such as headspace were compared. Compared to untreated control surrogate sediment samples, BTDC extraction efficiencies of better than 94 percent were obtained. The results of PCE comparisons between adjacent sediment samples indicated that there was no significant difference between headspace extraction techniques and the BTDC.

We used both headspace and BTDC analytical results to describe the vertical distribution of PCE in four adjacent boreholes. PCE appears to be largely confined to the permeable materials such that vertical distribution appears to be largely controlled by hydraulic conductivity. Within a permeable zone, significant changes in PCE concentrations occur on a vertical scale of 1 to 3 ft. Since a screened interval is placed across an entire permeable zone during construction of a monitor well, ground water collected as representative of sediment pore water will have been extracted from sediments with a variety PCE concentrations and is an integrated average, both vertically and horizontally, of the PCE concentrations in the pore water of that zone. Total VOC concentrations of well-completion-zone saturated sediments used during the calculation of partitioning coefficients should be sampled frequently enough to adequately represent the variability of total VOCs present in saturated sediments. In this way, total VOC concentrations on saturated sediments will represent the same vertical spatial scale as the the ground water extracted from the well.

## INTRODUCTION

As part of a cooperatively sponsored HAZWRAP and Lawrence Livermore National Laboratory (LLNL) project to evaluate field-based methods to measure retardation factors, we investigated some aspects of the variability associated with measuring the concentrations of perchloroethylene (PCE) within the saturated unconsolidated alluvial sediments beneath LLNL. The LLNL is located about 64 km (40 miles) east of San Francisco, California, in the Livermore Valley of eastern Alameda County, approximately 5 km (3.1 miles) east of the city of Livermore (Fig. 1).

LLNL, which is operated by the University of California for the U.S. Department of Energy (DOE), was estab-

lished in 1952 to conduct nuclear weapons and magnetic fusion research. LLNL also carries out a variety of projects for other federal and state agencies. Detailed descriptions of the LLNL site, climate, drainage conditions, and general environmental monitoring programs are described in Holland et al. (1) and Holland and Brekke (2).

In 1982, LLNL began ground water studies for the LLNL site and vicinity (3,4,5,6,7). Findings from these studies indicated that volatile organic compounds (VOCs), primarily tetrachloroethylene (PCE) and trichloroethylene (TCE), were present in local ground water. Sampling results showed several locations with VOCs in the part per billion range, and, subsequently, three areas where over one part per million  $\Sigma$ VOC concentrations were detected. A plume of VOCs originating from LLNL appears to be migrating

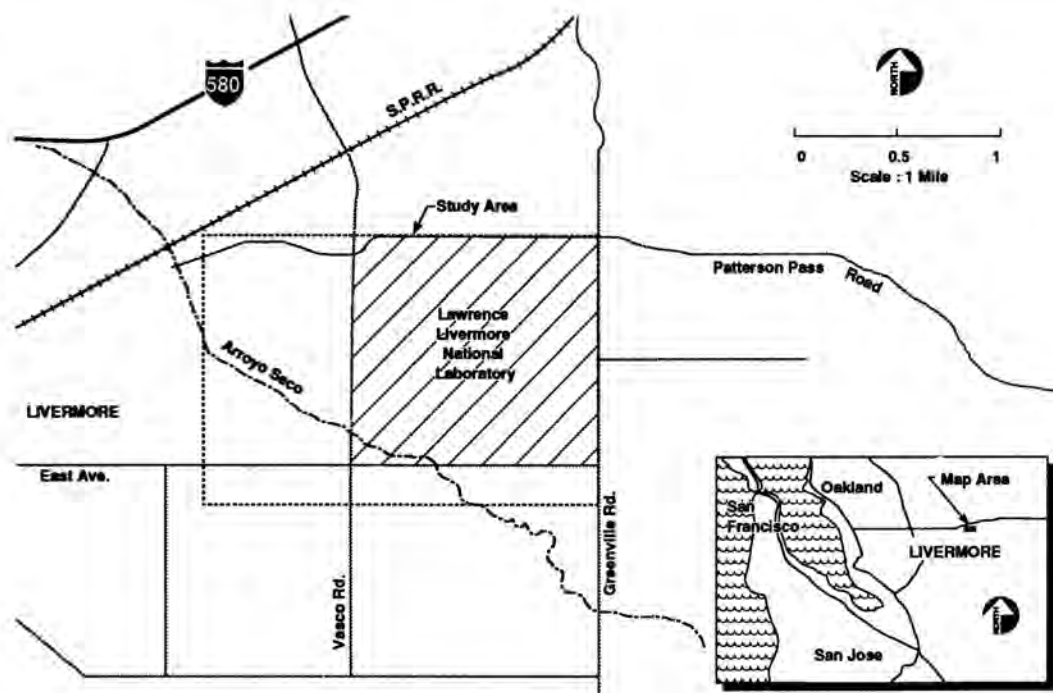


Fig. 1. Locations of LLNL and Study Area.

westward in the ground water. The LLNL Ground Water Project has installed over 250 monitor wells in the vicinity of the LLNL site to define the vertical and horizontal extent of VOCs in ground water shows an isoconcentration contour map of total VOCs in ground water beneath LLNL. Most of the VOCs present in ground water are believed to be the result of releases that occurred during the late 1940s and early 1950s while the site was occupied by the U.S. Navy. The site is currently undergoing Comprehensive Environmental Response Compensation, and Liability Act (CERCLA) investigations, and remediation of the site is the ultimate goal of the LLNL Ground Water Project.

The geology of the LLNL site and adjacent areas is described in Carpenter et al. (8). The LLNL site and low-lying areas of adjacent lands are underlain by complexly interbedded alluvial sediments of late Tertiary and Quaternary age consisting of clay, silt, sand, and gravel. Hydraulic conductivities of the more permeable sediments vary over three orders of magnitude. The hydrogeologic system is characterized as leaky, with horizontal hydraulic communication up to about 240 meters (m) (787 ft) and vertical communication up to 15 m (49 ft) (9).

In addition to onsite contamination, a VOC plume of primarily PCE, approximately 3600 ft long and 1700 ft wide, has been delineated west of LLNL along the Arroyo Seco. The source of the plume appears to be a storm drain near the southwest corner of LLNL. Near the source area, the VOCs are not present below a depth of about 90 ft. Near

the western or leading edge of the plume, the VOCs are not present below a depth of about 200 ft.

To evaluate field-based methods used to measure retardation factors, we investigated the variability associated with the measurement of the concentrations of perchloroethylene (PCE) within the saturated unconsolidated alluvial sediments in the area of the PCE plume (see insert in Fig. 2). Many mechanisms affecting transport are scale dependent and cannot be extrapolated from small-scale laboratory experiments or from a single-sediment core sample. Using the depth-sampling technique developed at LLNL, we are describing the relationship of VOC spatial variability to various soil characteristics, such as geophysical log results, grain size distribution, cation exchange capacity, total organic carbon, permeability, bulk density, skeletal density, and porosity.

Using this information, an algorithm is being developed to calculate representative field-based partitioning coefficients ( $K_d$ ) and retardation factors ( $R$ ) using measures of (1) average total VOCs in a series of saturated sediment samples taken from a monitor well screened interval, (2) VOCs in water extracted from the same monitor well, and (3) representative bulk density and skeletal density measurements (10). Initial determinations of field-based  $K_d$  and retardation were determined and are being compared to laboratory determined  $K_d$ s (11;12) and retardation factors predicted from site history matching models (13).

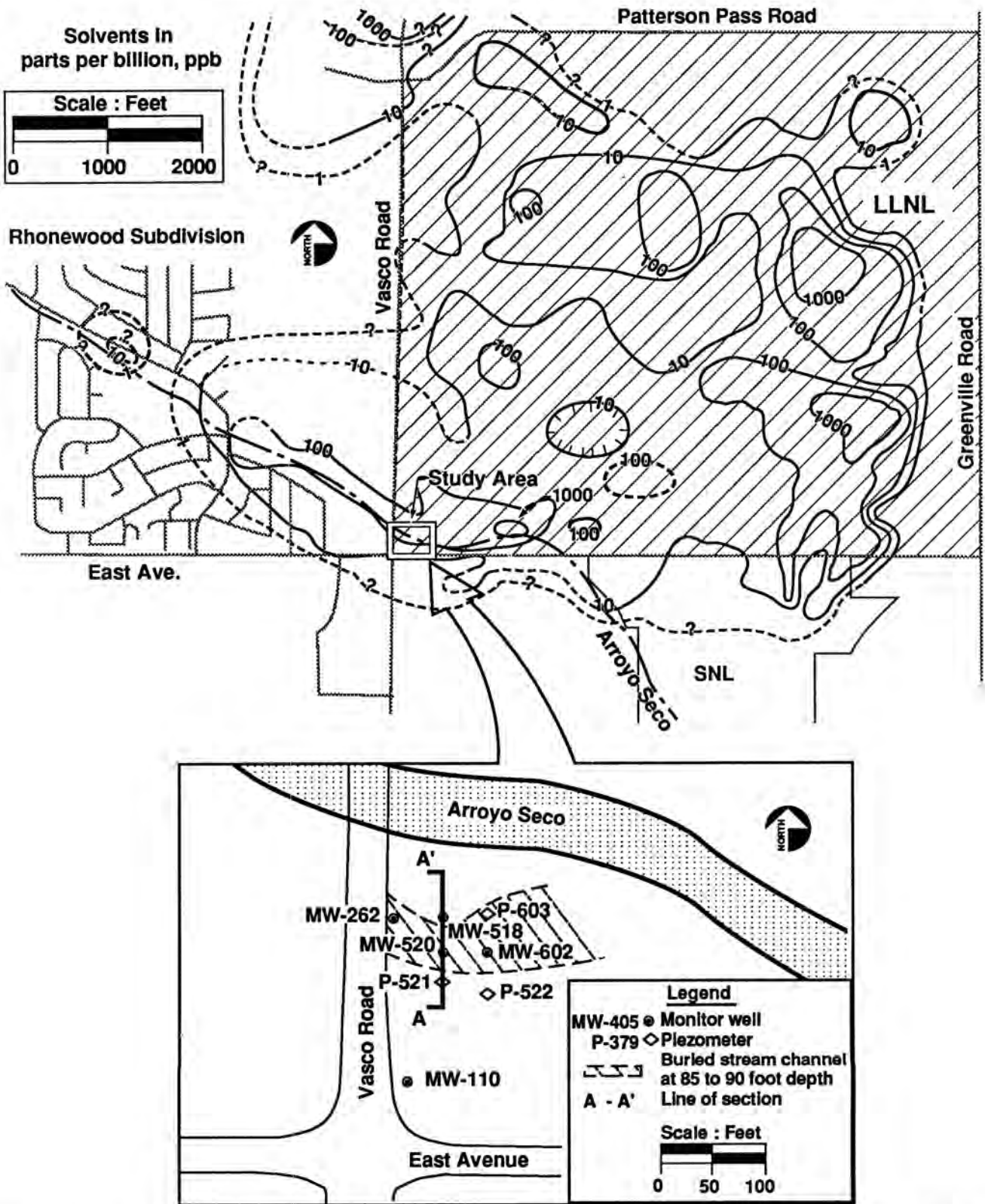


Fig. 2. Isoconcentration Contour Map of Total VOCs in Ground Water at LLNL, November 1989. Inset Shows Detail of Study Area.



A critical parameter used in the algorithm is the total mass of PCE present in a saturated sediment sample. Variable results are often reported when adjacent sediment cores are analyzed. These differences can be due to differences in the efficiency of the extraction method, or to spatial variability in the subsurface environment, or both. Thus, the two major sources of PCE concentration variability examined were those associated with (1) the analytical extraction methods and (2) the spatial changes in fine-grained materials within permeable and confining sediments.

### METHODS

To evaluate desorption efficiency during headspace extraction (EPA Method 3810) for VOC analyses (EPA Method 8010), a bulk thermal desorption chamber (BTDC) was constructed (Fig. 3).

The BTDC consisted of an 8.5-cm-diameter aluminum tube with end caps that used "O" rings to form a gas-tight seal. Fittings at either end allowed helium gas lines to be connected. Helium was passed through the chamber at a flow rate of 20 ml/min. VOCs such as PCE are extracted from the sediments by heating the core to 135°C for approximately 48 h and capturing them by sorption onto a calibrated Tenax column. Since the sediment sample pore

water is also extracted during the BTDC heating process, 0°C cold traps were used to separate VOCs from the pore water prior to sorption onto the Tenax column. The Tenax column and extracted VOCs were transferred to a Sulpeco Thermal Desorption Unit, which quantitatively transferred the PCE on to a 60-m gas chromatograph column by heating the Tenax column to 220°C in 10 seconds and transferring the desorbed compounds in a helium carrier gas flow. The BTDC extraction provided a reference method against which generally used EPA extraction methods such as headspace were compared. Since we used a complete core sample (approximately 400 g) for BTDC extraction, the issue of the representativeness of using 1- to 20-g aliquots of soil commonly used during headspace extractions was also addressed.

Core samples were recovered from the subsurface using a rotary mud, punch-core depth-sampling technique developed at LLNL (14) (Fig. 4). Briefly, this depth-sampling technique involves making drilling mud changes prior to each coring run to prevent cross contamination of samples. Cores were collected into 2.5-in. diameter x 3-in. long brass core sleeves. Immediately upon removal from the ground, the ends of those cores to be analyzed by headspace extraction were immediately sealed with teflon sheets, tight-

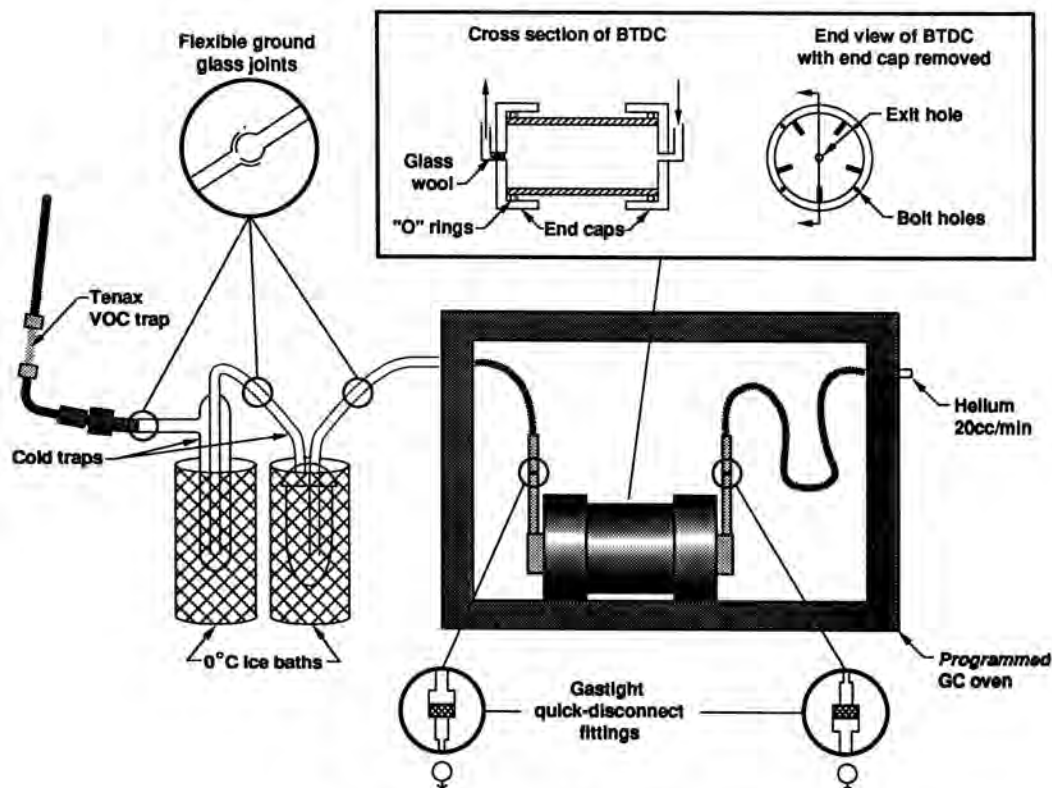
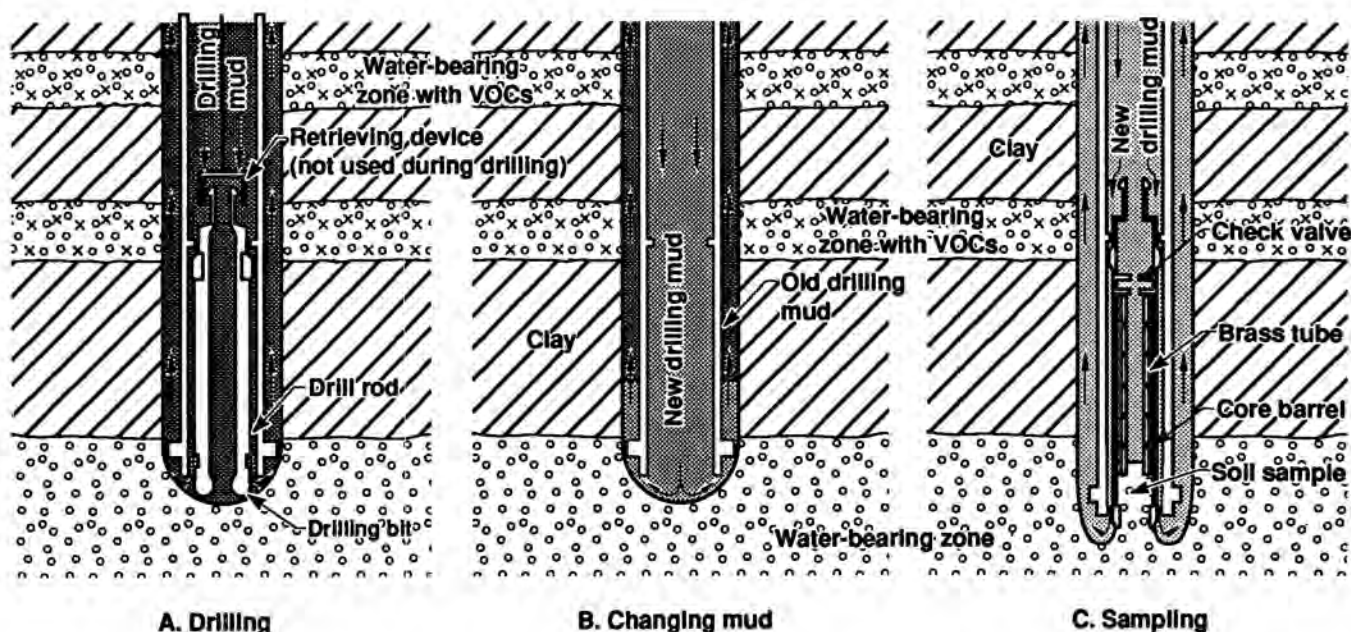


Fig. 3. Bulk Thermal Desorption Chamber.



Arrows indicate direction of drilling mud circulation.

Fig. 4. Schematic Diagram of Punch-Coring.

fitting plastic caps, and tape. The headspace cores were refrigerated at 4°C until extraction and analysis, which occurred within 6 to 8 hours of collection. Two different contact analytical laboratories performed the headspace extraction and VOC analyses. A core sample to be extracted in the BTDC was either immediately placed in the chamber upon removal from the borehole or sealed, frozen, and stored at -80°C. The frozen BTDC samples were stored up to two weeks before analyses.

Desorption efficiency of the BTDC was calibrated using both stable PCE and carbon-14 labeled PCE. Duplicate surrogate sediment cores were prepared using sediments collected during the construction of monitor wells in the LLNL site. The sediments were dried, sieved to < 2mm, homogenized, and placed into brass core sleeves. The surrogate cores were saturated with boiled, charcoal filter water that contained carbon-14 labeled PCE at a nominal concentration of 500 µg/l. The carbon-14 specific activity was 0.8 mmol/mCi. Immediately after saturating the surrogate samples, one sample was placed into the BTDC while the remaining surrogate sample was used as a untreated control. The extraction efficiency was calculated from the amount of carbon-14 remaining on BTDC treated sediments compared to the amount C-14 remaining in the control sample. The amount of C-14 retained in the water traps

was also evaluated. The BTDC carbon-14 desorption efficiency experiment was conducted twice.

Sediment samples to describe the spatial distribution of PCE were collected from four borings in the study area. The location of these borings is shown in Fig. 2. An attempt was made to collect sediments for ΣPCE analyses at a closely spaced interval, usually about every 1 ft, starting about 3 ft above, within, and below known permeable zones. Sediment sampling within the intervening confining zones was not as closely spaced, often about 3 ft apart. To compare analytical results, 11 duplicate samples (contiguous cores) were analyzed using BTDC and headspace extraction procedures. Samples from a variety of sediment types, ranging from gravelly sands to clayey silts, were chosen for comparative analyses. Two duplicate samples were analyzed by one of the contract analytical laboratories. Upon the completion of each borehole, geophysical logging for point-resistivity and natural-gamma were performed.

## RESULTS AND DISCUSSION

Compared to untreated control surrogate samples, BTDC extraction efficiencies of better than 94 percent were obtained (Table I). The water traps retained minor amounts of C-14 labeled PCE.

The results of a paired t-test comparison between the headspace extraction technique and the BTDC PCE concentrations indicated no significant differences ( $P = 0.13$ )

**TABLE I**  
Calibration of Sediment Bulk Thermal Desorption Chamber, Using Carbon-14 Labeled PCE

	Extraction efficiency (%)	Water trap retention (%)
Experiment 1	94.9	3.1
Experiment 2	97.7	0.9

**TABLE II**  
Comparison of BTDC to Headspace Extraction

Boring	Depth (ft)	Concentration PCE ( $\mu\text{g}/\text{kg}$ )			BTDC	Sediment type
		Headspace				
		Lab-1	Lab-2			
B-518	85	—	15	16	Gravelly sand	
	134	19	15	18	Silty sand	
B-520	90-92	24	—	28	Silty sand	
	95	62	—	61	Gravelly sand	
	96	67	—	76	Gravelly sand	
	119	4	—	2	Clayey silt	
B-521	132-136	16/12	—	16	Sandy gravel	
	83	2/3	—	2	Sandy silt	
	94	—	5	3	Clayey silt	
	98	1	—	2	Clayey silt	
	130	—	23	34	Gravelly sand	

(Table II). This finding indicates that the headspace extraction technique is providing relatively complete desorption of VOCs and that headspace derived PCE concentration in the sediments can be regarded as being as representative as the BTDC-derived PCE concentrations. Furthermore, the BTDC and headspace PCE desorption efficiency is the same regardless of sediment type. These findings also indicate that there is little variability in PCE concentration distributions within a 3-in.-long core and that the variability of PCE occurs on larger spatial scales.

Once we had established that the headspace extraction analytical results were representative, we used both headspace and BTDC analytical results to describe the vertical distribution of PCE in four adjacent boreholes (Fig. 5).

See Fig. 2 for the relative position of the borings. PCE appears to be largely confined to the permeable materials so that vertical distribution appears to be largely controlled by hydraulic conductivity, and, within a permeable zone, significant changes in PCE concentrations occur on a vertical scale of 1 to 3 ft. In addition, a gradient of PCE concentrations in the confining sediments was observed declining away from the permeable sediments. Since a screened in-

terval is placed across an entire permeable zone during construction of a monitor well, ground water collected as representative of sediment pore water will have been extracted from sediments with a variety PCE concentrations and is an integrated vertical and horizontal average of the PCE concentrations in the pore water of that zone. Total VOC concentrations of well completion zone saturated sediments used during the calculation of partitioning coefficients should be sampled frequently enough to adequately represent the variability of total VOCs present in saturated sediments. In this way, total VOC concentrations on saturated sediments will represent the same vertical spatial scale as the ground water extracted from the well is a reconstructed idealized cross-section through borings 518, 520, and 521 at a depth of 80 to 105 ft. This figure is based on interpretations of the geophysical logs, geologists physical observations of sediment type, and PCE chemical distribution. We believe that this cross-section represents a buried stream channel, possibly deposited by the Arroyo Seco. Since PCE is believed to have been present in the ground water in the study area for about 30 years, it is interesting to note that PCE migrated only a few feet into confining materials about the stream channel. Since the major mass



of PCE appears to be restricted to easily extracted ground water in permeable sediments, long periods of ground water extraction may not be necessary to adequately remediate the minor amounts of PCE that may be bound in fine-grained confining sediments.

### CONCLUSIONS

The main conclusions that can be drawn from our studies to date are that in the saturated alluvial sediments at LLNL, PCE distributions are largely controlled by hydraulic conductivity, and in areas distant from its release site, PCE is largely confined to permeable stream channel deposits with little movement into confining, relatively impermeable silts and clays surrounding the buried channels. Furthermore, the headspace extraction method used during analyses of sediments for PCE is representative, and the results are comparable to those obtained using a more rigorous extraction procedure. Finally, total VOC concentrations of well completion zone saturated sediments used during the calculation of field-based partitioning coefficients and retardation factors should be sampled frequently enough to adequately represent the variability of total VOCs present in saturated sediments.

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Work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract number W-7405-ENG-48.

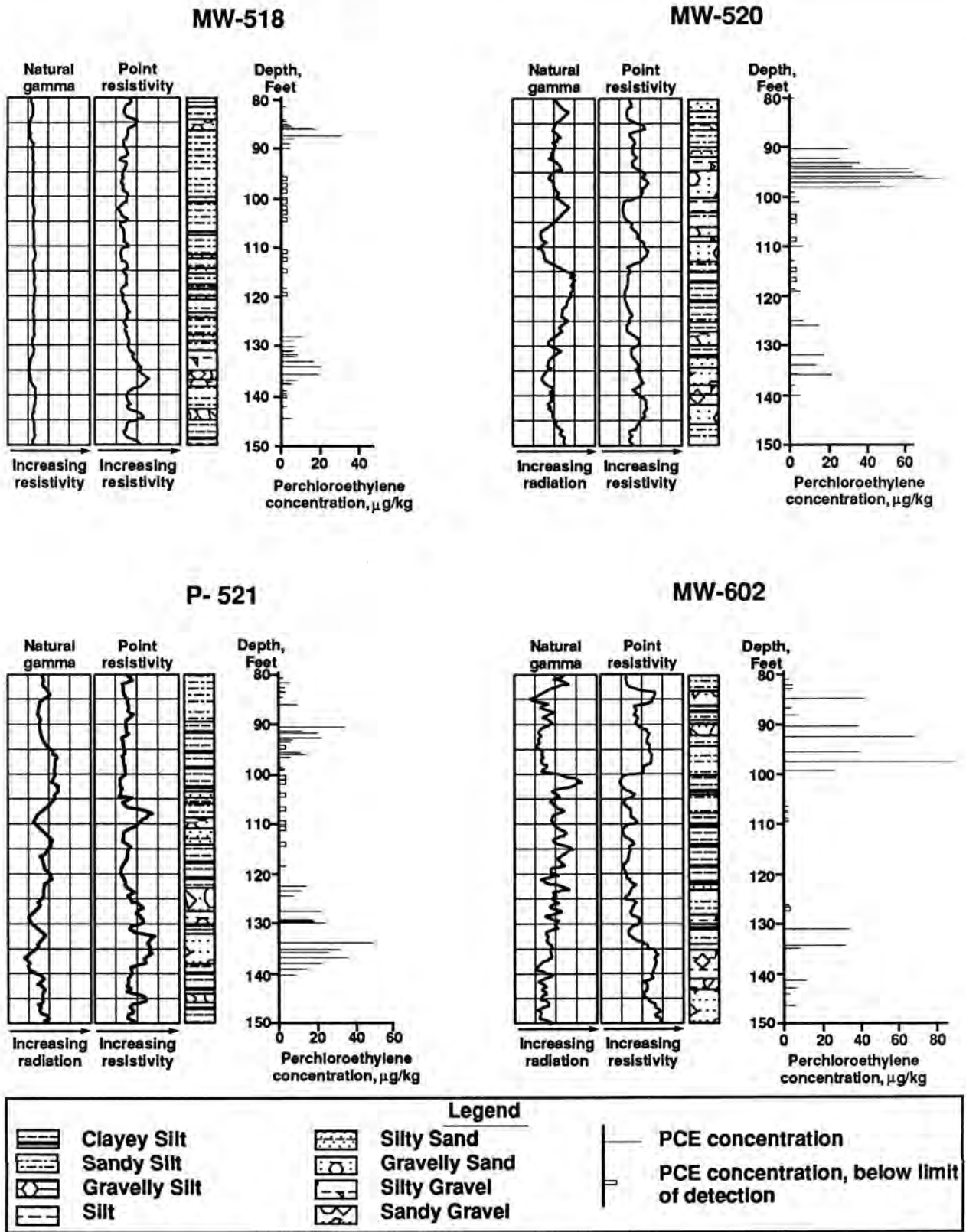


Fig. 5. Saturated Sediment Sample Results MW-518, MW-520, P-521, MW-602.



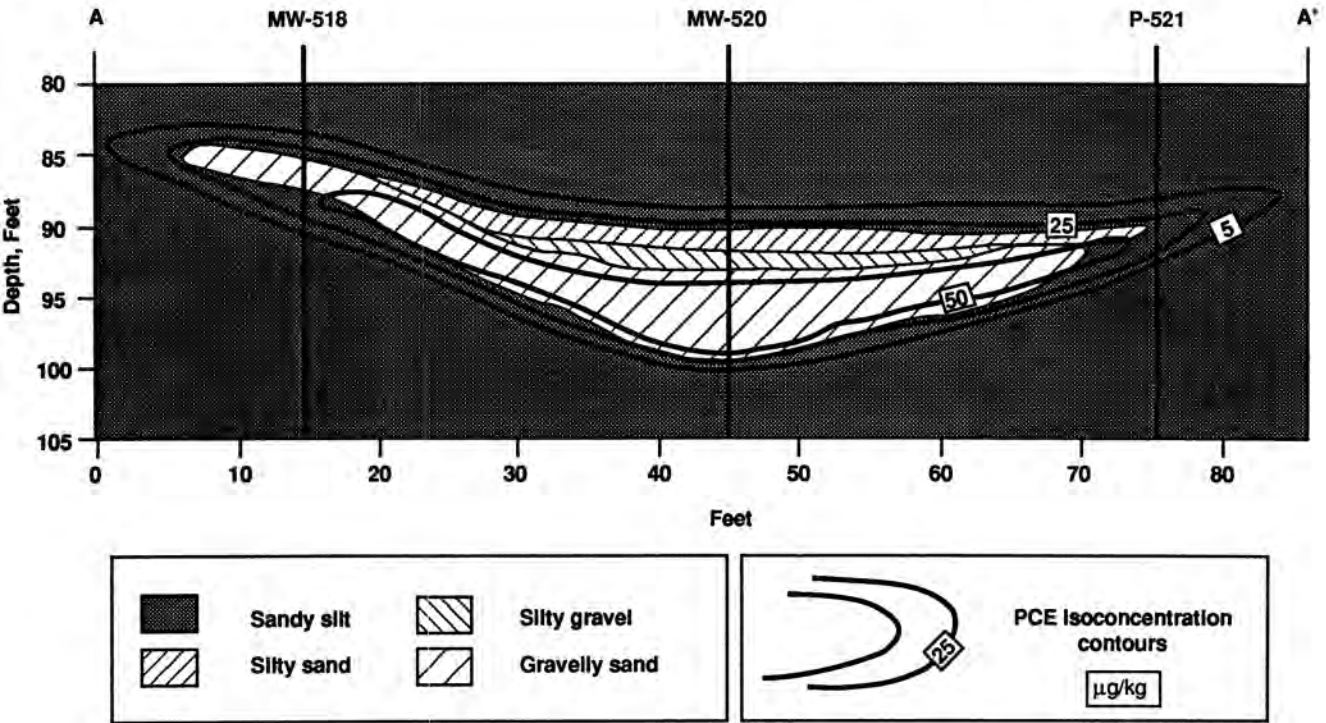


Fig. 6. Idealized Model of Buried Stream Channel Cross Section.