

**COOPERATIVE LLNL/HAZWRAP PROJECT TO DEMONSTRATE DETERMINATION  
OF FIELD-BASED RETARDATION FACTORS: ALGORITHM TO  
DETERMINE A FIELD-BASED RETARDATION FACTOR**

Leah L. Rogers, David W. Rice Jr., Dorothy J. Bishop, and Norman D. Stout  
Lawrence Livermore National Laboratory  
Livermore, CA 94550

**ABSTRACT**

Current limitations of field and laboratory technologies make it difficult to determine a field-based distribution coefficient which is necessary to calculate a field-based retardation factor. At a well-characterized Superfund site, Lawrence Livermore National Laboratory, an ongoing study is refining a method to assess the existing partitioning of TCE and PCE between the solid and liquid phases of the aquifer system. The three main components of this method involve (1) measurement of the total VOCs in saturated alluvial deposits, (2) measurement of sediment properties, and (3) measurement of the VOCs in pore water. The design and implementation of new measurement techniques and protocols are being compared to traditional measurement protocols. An overview of these new measurement protocols is presented here along with the algorithm that calculates the field-based retardation factors. A sensitivity analysis is presented to demonstrate the required accuracy of the individual measurements needed to meet the desired accuracy of the final retardation factors.

The algorithm begins with a measure of total contaminant concentration in both the solid and liquid phases of the saturated alluvial sample. The concentration in the liquid phase is then measured. The difference is assumed to be the concentration of the sorbate on the solid phase of the alluvial sample. The distribution coefficient is determined as the ratio of concentration of the sorbate on the solid phase to concentration of the solute in the liquid phase. Bulk density measurements and porosity measurements combine with the distribution coefficients to calculate field-based retardation factors.

To attain an accuracy in the distribution coefficients to within 1 to 5 percent, sensitivity studies indicate measurement of sediment properties such as skeletal density, bulk density, and porosity need to be more accurate than traditional volume displacement or wet weight/dry weight measurement procedures. In this study, mercury porosimetry is examined as a more accurate technique. Presented here is a comparison of the mercury porosimetry results obtained from vacuum oven drying versus freeze drying of the sample. Minimal disruption of the sediment structure was sought in comparing the drying methods.

One difficulty in measuring the VOC concentration in the pore water is the scale at which the sample is taken. Traditional water sampling methodology is designed to yield a representative sample of the aquifer. Consequently, this results in an average concentration over a much larger zone of influence than the spatial scale of the saturated sediment sample that was used to determine the VOC concentration on the sediment and water. The field-based retardation factors resulting from this study have thus far employed the traditional water sampling methodology. Centrifuge techniques are being examined as an alternate methodology.

In this study, progress has been made to increase the accuracy of sampling and subsequent laboratory analyses to determine the actual partitioning of contaminants that exist at a specific site. Results compare favorably with laboratory partitioning data determined from equilibrium batch sorption experiments. These results should improve the quality of data incorporated into predictive solute transport modeling.

**INTRODUCTION**

The transport of volatile organic compounds (VOCs) in ground water systems is significantly affected by sorption, the partitioning of VOCs between the solid and fluid phases of the system. Failure to incorporate retardation into an analysis of the system may lead to significant error in evaluating the magnitude of contamination and the difficulty of remediation. Any predictive mathematical model is only as rigorous as the degree to which the flow and transport

mechanisms considered describe the vital characteristics of flow and transport in the system.

A common approach to understanding the sorption-desorption behavior of contaminants is to conduct column experiments where conditions can be carefully controlled. There is concern, however, that many of the mechanisms affecting transport are scale dependent and cannot be extrapolated from small-scale, relatively quick experiments, to large-scale transport over extended distances and time.

Field experiments, on the other hand, involve substantial expenditures of time, labor, and equipment.

At the Borden Site in Ontario, Canada, a large-scale tracer test injected 12 m<sup>3</sup> of a uniform solution with known masses of two inorganic tracers and five halogenated organic compounds. With a three-dimensional array of over 5000 sampling points and over 19,900 samples collected over a three-year period, retardation factors were observed under in-situ field scale conditions in a relatively homogeneous sand aquifer (1,2,3). Despite high-caliber results, experiments, such as the work at Borden, are not economical for many ground water contamination investigations, and the injection of further contaminants may not be permitted in many investigations. Less elaborate field determinations of  $K_d$  have made assumptions that are not considered accurate. For example, Mehran et al. (4) used the TCE concentrations in the combined sediment and pore water to represent mass of TCE on the solid phase in the  $K_d$  equations without subtracting the TCE concentrations that would have been in the pore water. Thus, their  $K_d$  values may be high.

This study aims to demonstrate a simple, yet representative, field-based measurement of the  $K_d$ s and retardation factors derived from sediment and water samples taken during drilling and after completion of monitor wells. By establishing sampling protocols and refinements of standard EPA approved analytic methods, this study intends the measurement to be more accessible to small ground water investigations with a competent hydrogeologist in the field and access to EPA approved laboratories with capability for sediment and water analyses. Use of existing common technology and avoidance of contaminating tracers are considered prime benefits of this field-based measurement of  $K_d$ s and subsequent retardation factors.

### Background on the LLNL

The field site chosen for this study is located in a well-characterized PCE plume west of the Lawrence Livermore National Laboratory (LLNL) site (Fig. 1) (5,6,7). The isoconcentration maps of PCE in shallow and deeper ground water indicate the primary source of PCE may have been a storm drain discharge to Arroyo Seco (Fig. 2).

This storm drain was constructed in the early 1940s when the site was used as a U.S. Naval Air Station for pilot training and engine maintenance. The majority of the PCE originated with the Navy's operations. The plume has the potential to impact neighboring domestic and agricultural wells. A municipal supply well is located about one-half mile west of the leading edge of the plume.

A "depth sampling" technique to determine the VOC content of several water-bearing zones in a single borehole

is crucial to the methodology outlined below (8). The depth sampling technique (Fig. 3) enables a "section of the aquifer" sample to be retrieved while minimizing contamination from other depths.

A cluster of specially constructed wells was completed in 1989 to provide a suite of saturated sediment samples upon which to test and further develop the field-based retardation factor methodology. Fig. 2 shows the placement of these completions and the hypothesized boundary of a buried stream channel in which geologic logs suggest the wells are completed.

### Methodology

In this section, the calculational algorithm is presented as well as the laboratory and field analyses that were used to determine the main components of this algorithm.

#### Algorithm:

The algorithm to calculate the distribution coefficient,  $K_d$ , and the retardation factor,  $R$ , is given by the following equations:

$$K_d = \frac{\text{mass of solute on the solid phase per unit mass of solid phase}}{\text{concentration of solute in solution (ppm)}} \quad (\text{Eq. 1})$$

where the numerator equals:

$$\frac{M_{css} - M_{cw}}{M_s} = \frac{C_{ss} \cdot M_{ss} - (C_w \cdot V_w)}{M_s} \quad (\text{Eq. 2})$$

and, according to Freeze and Cherry (9):

$$R = 1 + \frac{\rho_b}{\eta} (K_d) \quad (\text{Eq. 3})$$

where:

- $M_{css}$  = Total mass of contaminant in saturated sediment sample ( $\mu\text{g}$ )
- $M_{cw}$  = Total mass of contaminant in water of saturated sample ( $\mu\text{g}$ )
- $M_{ss}$  = Total mass of saturated sample (g)
- $M_s$  = Total mass of solid phase of saturated sample (g)
- $C_{ss}$  = Concentration of contaminant in saturated sample ( $\mu\text{g/g}$ )
- $C_w$  = Concentration of contaminant in liquid phase ( $\mu\text{g/ml}$ )

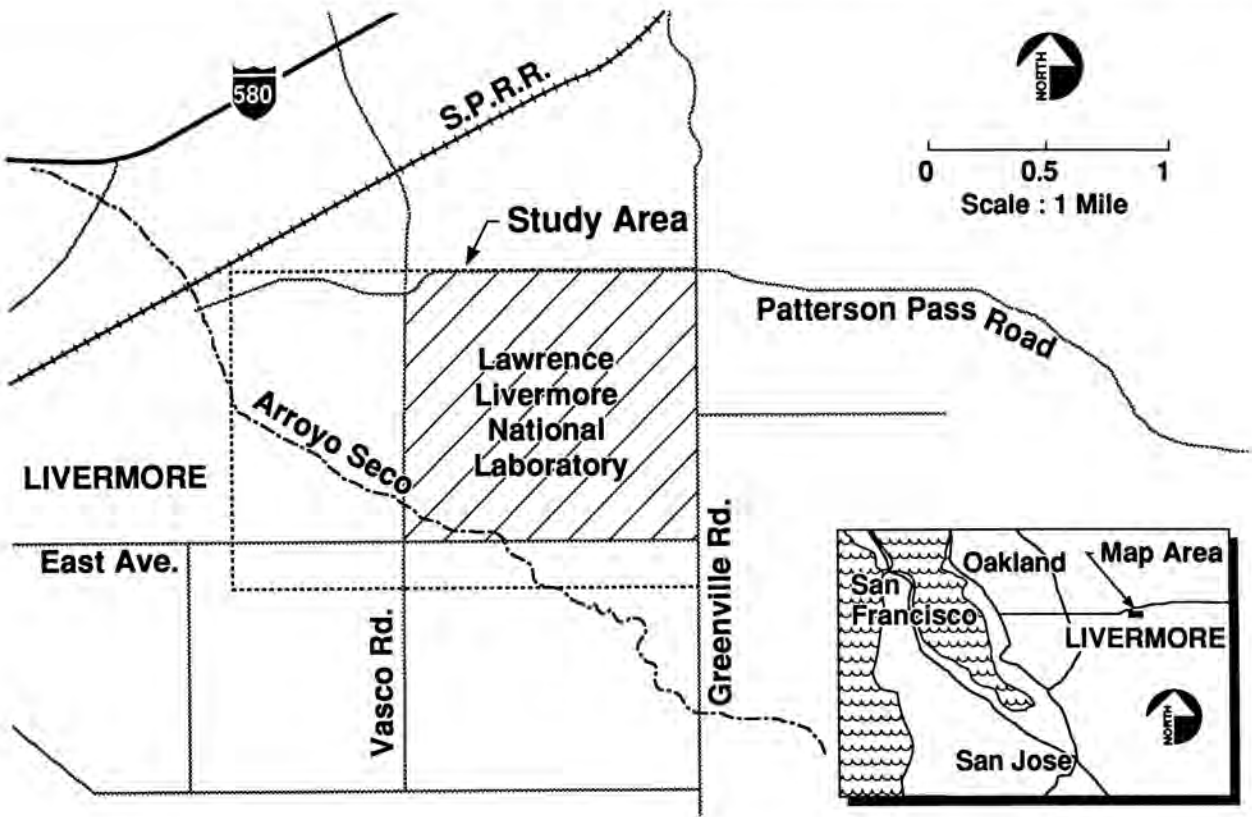


Fig. 1. Locations of LLNL and Study Area.

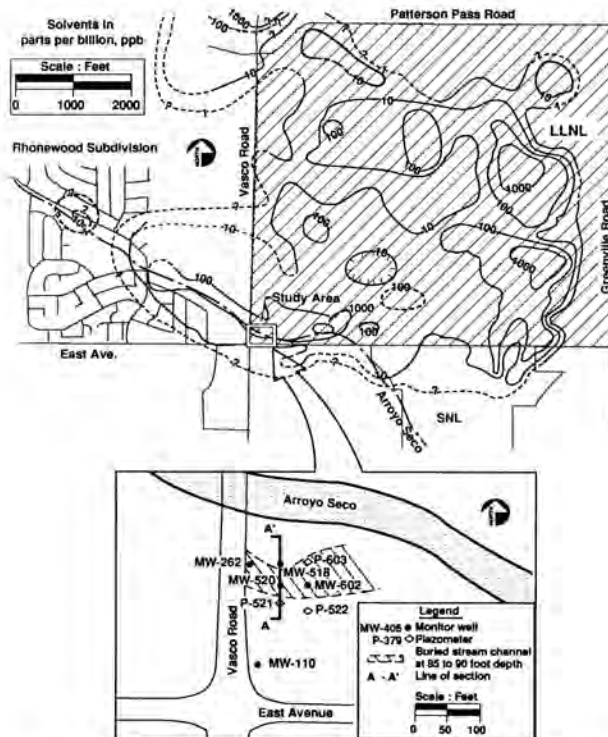


Fig. 2. Isoconcentrations of VOCs in Ground Water at LLNL. Insert Shows Detailed Well Locations.

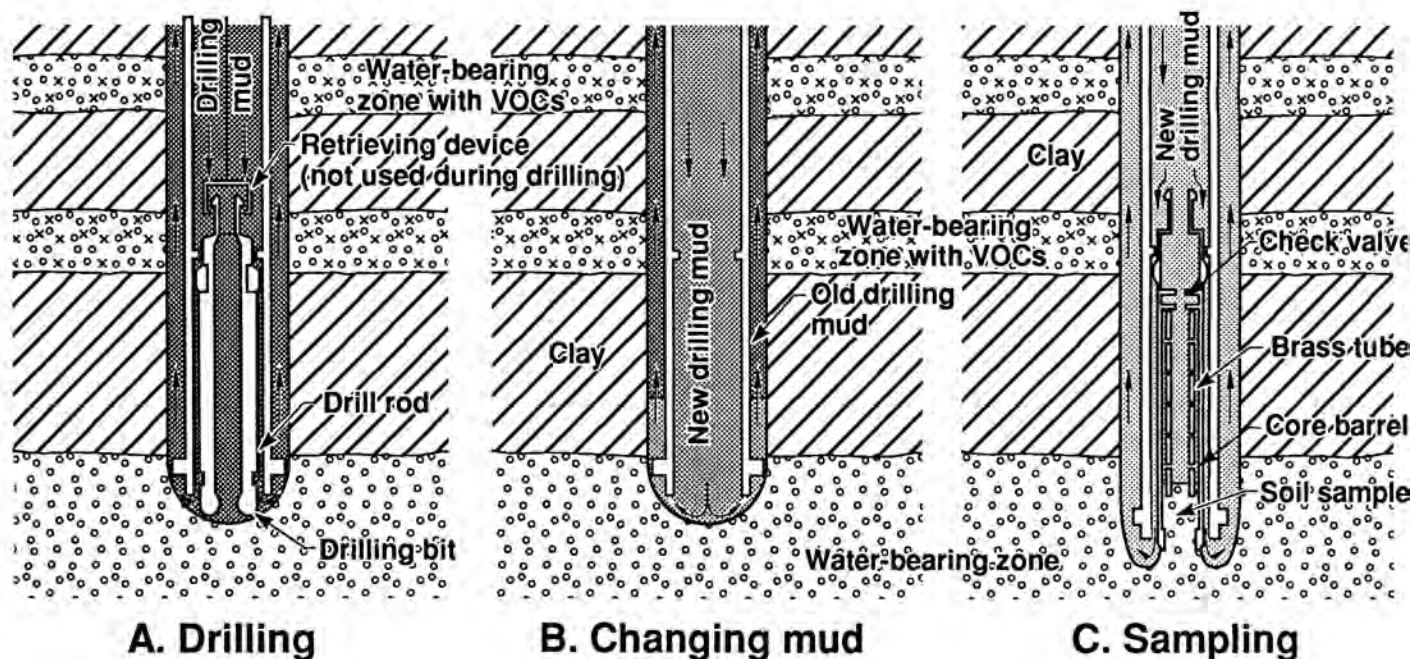


Fig. 3. Schematic Diagram of Punch-Coring. Arrows Indicate Direction of Drilling Mud Circulation.

- $V_w$  = Volume of water in saturated soil sample (ml)  
 $R$  = Retardation  
 $\rho_b$  = Bulk density of soil sample (g/cc)  
 $\eta$  = Porosity (dimensionless)

Determination of retardation using the algorithm begins with a measure of the total solute and sorbate in the saturated alluvial sample. The concentration of contaminant in the liquid phase is then measured. The liquid phase concentration is used to reduce the total contaminant concentration on both the solid and liquid phases to yield the concentration of the sorbate (contaminant) on the solid phase of the alluvial sample (Eq. 2). The distribution coefficient is defined as the ratio of concentration of the sorbate on the solid phase to concentration of the solute in the liquid phase (Eq. 1). The numerator is given in units of  $\mu\text{g/g}$ , and the denominator is given in units of  $\text{oml}$  resulting in the conventional  $K_d$  units of  $\mu\text{l/g}$ . Bulk density, porosity, and the distribution coefficient combine, according to Eq. 2, to calculate a field-based retardation factor.

Sensitivity studies indicate that to attain an accuracy in the distribution coefficients to within 1 to 5 percent, measurement of soil properties, such as skeletal density and bulk density, need to be more accurate than traditional volume displacement and wet weight/dry weight measurement pro-

cedures. Calculations were done on a series of hypothetical samples to observe the sensitivity of  $K_d$  and  $R$  to variations in parameters of the algorithm. These sensitivity studies suggest the level of detection for the VOC concentration measurements are adequate to attain a  $K_d$  accuracy to within 5 percent; however, the accuracy of the measurement of sediment properties could be improved upon. Calculations indicate the determined  $K_d$  was approximately three times more sensitive to variation in bulk density than variation in skeletal density (Fig. 4).

To attain an accuracy in the distribution coefficients in the 1- to 5-percent range, measurement of the skeletal density needs to be accurate to 0.05 g/cc. As the algorithm is more sensitive to the bulk density, measurement of this parameter is required to be accurate to 0.01 g/cc. Mercury porosimetry was chosen as a more accurate technique than traditional volume displacement and wet weight/dry weight measurement procedures because the accuracy is judged to be closer to 0.005 g/cc as opposed to 0.05 g/cc for traditional methods.

#### Laboratory and Field Measurements:

The three main components of the field-based method involve (1) measurement of the VOCs in saturated alluvial deposits, (2) measurement of sediment properties, and (3) measurement of VOCs in pore water. The design and

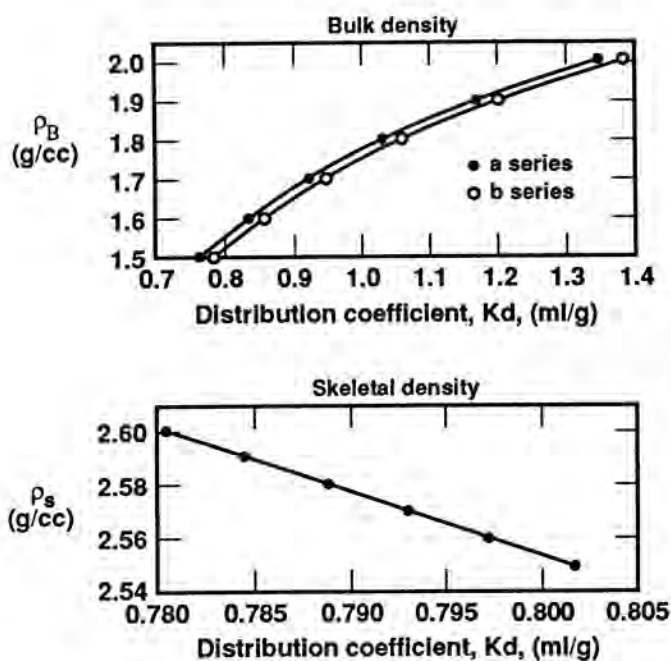


Fig. 4. Plot of Changing  $K_d$  With Variation of Density. Other Parameters for a Hypothetical Sample are Held Constant.

implementation of new measurement techniques and protocols is being compared to traditional measurement protocols. A brief overview of these new measurement protocols is presented here.

#### 1. Measurement of VOCs on Saturated Sediment

**Samples:** Two methods are being compared for their efficacy in VOC recovery from saturated sediment samples: (1) Modified EPA method 8010, using headspace extraction (EPA 3810); and (2) modified EPA method 8010, using a specially constructed bulk thermal desorption chamber (10).

The headspace method involves an aliquot of the 2.5-by-3-in. core sample. The bulk thermal desorption chamber analyzes the entire core sample. The headspace extraction has advantages of speed, ease of analysis, and a low detection limit. Potential disadvantages include the possibilities that (1) the desorption of VOCs during analytical extraction may be differential or incomplete and (2) the aliquot may not be representative of the heterogeneous core sample. The bulk thermal desorption chamber (BTDC) extraction provided a reference method against which the headspace extraction method could be compared. The BTDC extraction has the lower detection limit of the two methods.

The BTDC uses a more rigorous VOC extraction technique and a larger sample, approximately 500 g, than does the headspace technique (nominally 20 g). Its disadvantage

is that it is an experimental method, and its prototype would be more troublesome and expensive to reproduce. VOC extraction efficiencies of better than 94 percent were obtained for the BTDC. No significant difference in PCE concentration was found between headspace or the BTDC extraction techniques (10). For more detail on the methods, see Rice (11) and Rice et al. (10).

**2. Measurement of Sediment Properties:** Measurements of sediment properties of the saturated sample, bulk density, skeletal density and porosity are important for calculating retardation factors. In addition to employing more traditional methods, this study is pioneering protocols that combine freeze-drying techniques with high-pressure mercury porosimetry equipment. This minimizes the alteration of sediment structure upon the drying which must be accomplished in the determination of the volume of void space.

The mercury porosimetry methodology places a dried subcore of the 3-in. saturated sediment sample into a cylindrical glass vessel, which connects to the mercury porosimeter. Mercury surrounds the sample for an initial volume reading. Then, the pressure is increased until the mercury, which invades the sample, fills all possible pore spaces. The difference in these volumes determines the pore volume.

As in other conventional pore structure analysis techniques, such as helium pycnometry and nitrogen adsorption/condensation, samples must be completely dry before introduction to the mercury porosimeter. As drying is potentially damaging to the pore structure, two drying methods, freeze drying and normal vacuum oven drying, were compared. Visible volume reduction occurred in the oven-dried subsamples, but not in the freeze-dried subsamples.

Four samples were taken from each of two 2-1/2-in. (6.4 mm) diameter cores; one pair was freeze dried, and the adjacent pair was dried using a vacuum oven. The small sub-cores were each approximately 17 mm in diameter by 17 mm in length. They were placed in wire mesh baskets to maintain their general shape. After drying, mercury porosimetry was measured. The measured porosity was different for the two drying methods (Table I). The oven-dried samples showed less porosity. The porosimeter showed that the loss of porosity due to oven drying occurred mainly in the pores below 0.03 mm diameter. This suggested that while both methods produced internally consistent results, the initial volume measurement needed by the mercury porosimeter would be more accurate from freeze-dried samples as this method tended to preserve the fine pore structure of sediment samples.

It is also possible that the freezing process may change the pore structure. Therefore, nuclear magnetic resonance (NMR) imaging/relaxation techniques are being investigated as another method of comparison. A series of samples is being analyzed for spatially averaged pore size

distribution. Two samples will be measured before and after freezing. These two samples as well as two others will be dried at 100°K and subsequently resaturated. Another series of NMR experiments will be performed to assess what stage of the drying process (if any) results in pore structure changes.

TABLE I

Comparison of Mercury Porosimetry Results from Freeze-Dried and Oven-Dried Cores

Source and depth of sample duplicates	Freeze-dried	Oven-dried
MW-570 162.5 feet	40.0% ±5%	31.00% ±2%
MW-518 89.0 feet	31.2% ±3%	27.50% ±.7%

3. Measurement of VOCs in pore water: This investigation involves a traditional sampling of well water for the VOC concentration in the pore water. The traditional methodology of sampling water from a

monitor well yields a representative aquifer sample from a relatively large area around the well. The water sample is thus integrated over the vertical extent of the well completion zone and a significant horizontal distance into the completion zone. The degree of horizontal distance integration is dependent on such parameters as duration of pumping before sampling and hydraulic conductivity of the completion zone. It should be noted that the VOC measurement from the saturated sediment sample is a "snapshot in time" or temporally synoptic picture of the partitioning. A water sample must be taken after well completion and development and is thus taken a minimum of several days after the saturated sample is taken. As contaminant transport is not static, subsequent well water samples potentially introduce the temporal error of being taken at a later time. A smaller scale pore water sample should represent a significant improvement on the accuracy of a field-based retardation factor algorithm that utilizes a VOC concentration in the water. The smaller scale pore water sample would be on the

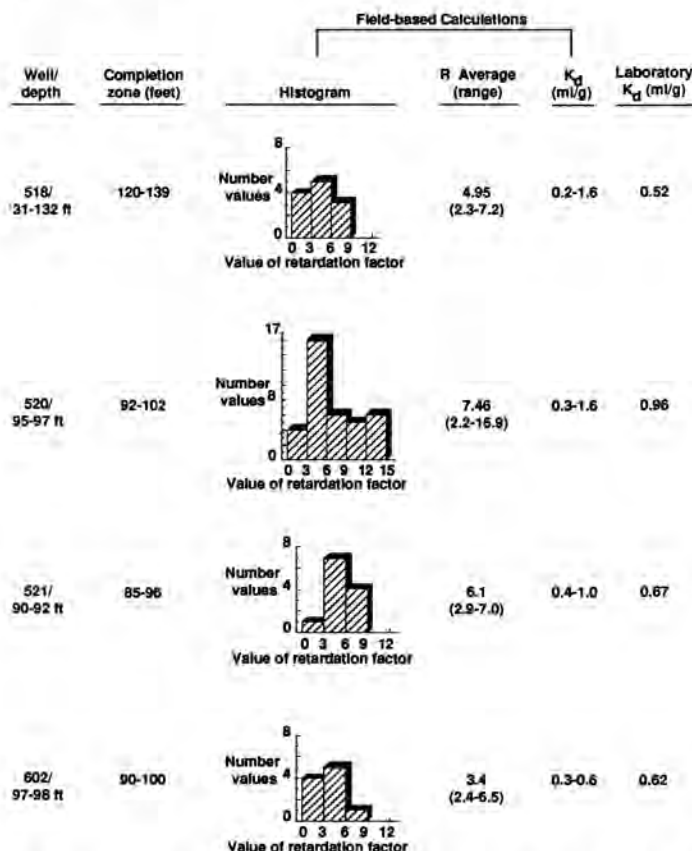


Fig. 5. Initial Results: Field-Based Retardation Factors From Completion Zone Data.

same spatial and temporal scale as the measurement of VOCs on the saturated samples.

Another limitation of the traditional water sample is that it constrains the field-based retardation factor determination to saturated sediment samples taken within the completion zone. The measurements of sediment properties and VOC content of saturated sediment samples were profiled between the water table depth, approximately 70 feet, and the lower vertical extent of contamination, approximately 150 feet. However, the traditional well water sample should only be used as a measurement of VOCs in pore water at the vertical horizon of the well-completion zone. Developmental work is in progress to measure the smaller scale pore water concentration by centrifuging a saturated sediment sample. The current experimental chamber for the water in the catchment volume is pulled out through the septum and injected directly into the gas chromatography apparatus.

## RESULTS

The range in retardation factors shown in Fig. 5 resulted primarily from using various combinations of available porosimetry and well water data in the algorithm. Initial results from analyses of completion zone samples for wells MW-518, MW-520, MW-521, and MW-602 have shown a range of retardation factors between 1 and 15 with the average values for well-completion zones being 4.9, 7.5, 6.1, and 3.4 respectively (Fig. 5).

Distribution histograms of the range of values shows the majority of retardation factors lie between 3 and 6. Laboratory  $K_d$  values calculated from equilibrium batch experiments (12) on sediments from these completion zones compared well with the field-based  $K_d$  values (13). The field-based range of  $K_d$  for the 131- to 132-foot depth in MW-518 was 0.2 to 1.6 ml/g as compared to 0.52 ml/g for the laboratory  $K_d$ . The field-based range of  $K_d$  for the 95- to 97- foot depth in MW-520 was 0.3 to 1.6 ml/g as compared to 0.96 ml/g for the laboratory  $K_d$ . The field-based range of  $K_d$  for the 97- to 98- foot depth in MW-602 was 0.3 to 0.6 ml/g as compared to 0.6 ml/g for the laboratory  $K_d$ . The laboratory  $K_d$  for the 90- to 92-foot depth in MW-521 was 0.67 ml/g as compared to the range of 0.4 to 1.0 ml/g resulting from field-based calculations. MW-521 was completed in a less permeable unit, which may not produce a representative well water sample upon which these calculations were dependent. However, the field and laboratory results still correlated.

Figure 6 overlays the geologic logs and vertical PCE profile of these four wells. The PCE profiles are confined to the zones of higher conductivity, approximately 90 to 100 feet and 130 to 140 feet in most of the wells (10). However, more conductive zones exist in between the aforementioned zones that do not display contamination. This suggests that

contaminant transport is primarily horizontal in this area.

## SUMMARY

Accurate characterization of contamination and effective remediation require adequate understanding of the degree to which contaminants interact with the solid phase of the aquifer system. Failure to consider, as accurately as possible, the degree of contaminant retardation can lead to serious miscalculations of the magnitude of contamination and the difficulty of remediation. This project aims to demonstrate field-based measurement of the distribution of solutes between the solid and liquid phase ( $K_d$ S) and derived retardation factors in a heterogeneous geologic setting of the well-characterized Superfund site at LLNL.

Specially constructed monitor wells have been completed to provide optimal saturated sediment samples for the technology demonstration. Field and laboratory procedures for handling saturated sediment samples have been refined to minimize loss of VOCs. An algorithm was developed to calculate the field-based retardation factors, and sensitivity analyses were performed to establish required accuracy of the components of the algorithm.

Design and implementation of new methods and protocols has proceeded in measurement of (1) VOCs in saturated sediment samples, (2) sediment properties, and (3) VOCs in pore water. Two extraction methods have been compared for their efficacy in VOC recovery from saturated sediment samples. This study is pioneering protocol that combines freeze-drying techniques with high-pressure mercury porosimetry equipment to determine sediment properties such as bulk density, skeletal density, and porosity with increased accuracy. Centrifuge techniques are being explored to develop protocol for measurement of VOCs in pore water on the same spatial and temporal scale as the VOC measurements on the 3-in. saturated soil core sample. The various components of the algorithm are then used in the calculations for field-based retardation factors, which compare favorably against linear sorption isotherms from laboratory batch sorption experiments. Future work will focus on methodology refinement, correlation of hydraulic conductivity with transport parameters, characterization of the spatial variability of the field site and its impact on VOC transport, and incorporation of retardation factors into solute transport and remediation modeling.

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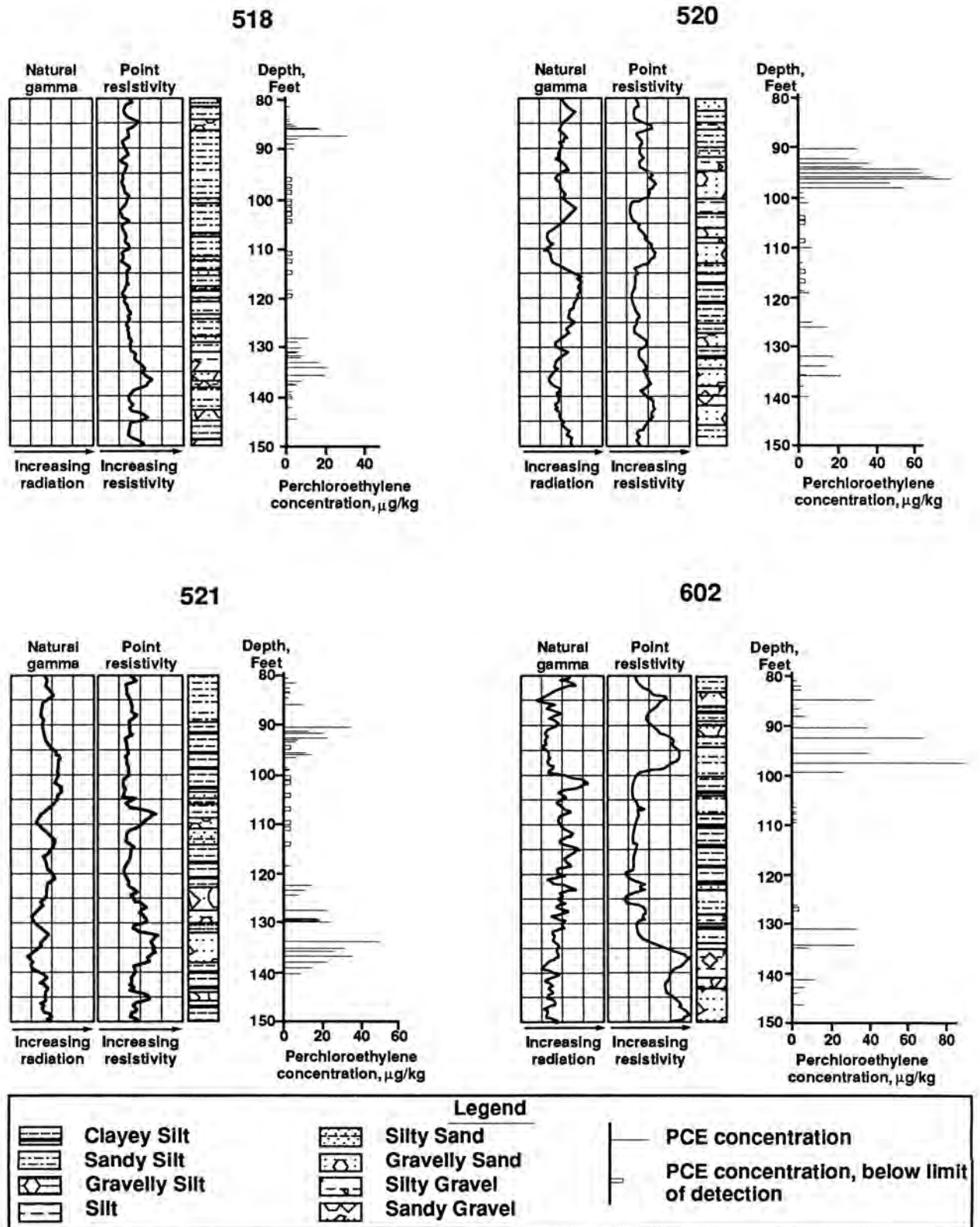


Fig. 6. Saturated Sediment Sample Results MW-518, MW-520, P-521, and MW-602.



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