

**COOPERATIVE LLNL/HAZWRAP PROJECT TO DEMONSTRATE  
DETERMINATION OF FIELD-BASED RETARDATION FACTORS:  
DETERMINATION OF SORPTION CONSTANTS**

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**ABSTRACT**

In a demonstration of methods to measure field-based retardation factors, a number of investigations are underway to determine the relationship between field-based measurements for calculating sorption constants ( $K_{ds}$ ) and those determined from batch sorption experiments in the laboratory. The  $K_d$  of a compound in a porous medium is an important component for determining its retardation factor ( $R_f$ ), which is the average rate of movement of a chemical through the sediment compared to the rate of flow of water. Field-based  $K_{ds}$  are site or sediment specific, and laboratory  $K_{ds}$  provide an upper boundary for sorption capacity.

Studies have been initiated to predict the rate and extent of lateral and vertical migration of volatile organic compounds (VOCs) in ground water beneath and in the vicinity of the Lawrence Livermore National Laboratory (LLNL) site in Livermore, California. A ground water study of this area indicated the presence of VOCs, primarily perchloroethylene (PCE) and trichloroethylene (TCE), generally in the tens of parts-per-billion range and in a few areas exceeding a part-per-million. Cores from the completion zone of approximately 50 different LLNL monitor wells were selected for analysis for a number of physical and chemical properties including organic carbon content, cation exchange capacity, and grain size distribution. Additionally, cores from the saturated and unsaturated zones of four HAZWRAP-sponsored boreholes were studied to ascertain the vertical profile of these physical and chemical properties.  $K_{ds}$  were determined from sorption experiments performed on samples from each of the cores. A pooled group of cores from one borehole was separated into sand, silt, and clay fractions that were individually analyzed.

In general, sorption of the VOCs to LLNL aquifer material is low. Laboratory-derived  $K_{ds}$  for TCE ranged from 0.1 to 1.6 and PCE, which is the most highly chlorinated and least soluble of the chemicals studied, was sorbed the most, usually a factor of two or three times the sorption of TCE to the same material. When core samples were separated into sand, silt, and clay fractions, the VOCs sorbed most to the clay-sized fractions and least to the sand fractions. Sorption of these chemicals appears to be correlated to the clay content and cation exchange capacity of the soil.  $K_d$  values calculated from field-based measurements are in close agreement with  $K_{ds}$  determined from laboratory batch experiments.

**INTRODUCTION**

This report is part of a larger ground water study initiated in 1983 to investigate volatile organic compound (VOC) contamination in ground water beneath and in the vicinity of Lawrence Livermore National Laboratory (LLNL) at Livermore, California. Extensive studies have been initiated to predict the rate and extent of lateral and vertical migration of VOCs that resulted from releases primarily in the 1940s and 1950s. Findings from a preliminary ground water study of this area indicated the presence of VOCs in the tens of parts-per-billion range and three areas where parts-per-million concentrations were detected (1, 2, 3). The VOCs consist principally of tetrachloroethylene (PCE), trichloroethylene (TCE), and smaller amounts of the dichloroethanes and dichloroethylenes.

To plan adequately for remediation strategies of the contaminated area, the rate and extent of movement of the VOCs in the ground water must be predicted. Therefore, the sorptive properties of these compounds should be understood in relation to the subsurface sediments that exist

at the LLNL site. When sorption constants ( $K_{ds}$ ) are determined, retardation of the chemicals of concern can be calculated from the following equation suggested by Bear (4):

$$R = 1 + \frac{\rho_b}{\eta} + (K_d)$$

where

$R$  = retardation of the chemical

$\eta$  = porosity

$\rho_b$  = bulk density

$K_d$  = sorption constant.

Sorption constants can be calculated from a combination of measurements including (1) total VOCs in the saturated alluvial deposits, (2) VOCs in the pore water, and (3) sediment properties, such as porosity and bulk density as described by Rogers et al. (5) and Rice et al. (6). Core samples are recovered from the subsurface using a punch-core depth technique developed at LLNL (7), which involves frequent drilling mud changes to prevent cross

contamination of core samples. Analyses are then performed on the water and the sediment from the cores without modification or addition of chemicals; hence they are labeled "field-based" measurements. Batch isotherm experiments are performed to determine laboratory sorption constants and to verify the calculated field-based values. Additionally, the batch isotherm approach provides an upper limit of anticipated sorption due to the nature of the procedure where the solution to sediment ratio is at least forty-to-one.

The objectives of this study are to (1) determine the sorption constants for cores from completion zones at more than 50 monitoring wells at LLNL, (2) establish vertical profiles of chemical and physical properties in cores representing both permeable and confining material from four wells, and (3) compare sorption constants determined from laboratory experiments and field-based measurements.

### Methods

The determination of laboratory sorption constants are based on batch isotherm experiments using carbon-14 radio-labeled chemicals described in Bishop et al. (8). The sorbent-sorbate combinations were prepared in triplicate using a 0.5 to 1 g/40 mL solid-to-solution ratio. Concentrations of test chemical in the solution phase were compared to solutions that were treated in an identical manner but contained no sorbent. The amount of chemical sorbed to the solid phase was determined by difference. In preliminary experiments, a series of sorption experiments performed in the concentration range of 1 ppb to 1 ppm resulted in linear isotherms. Subsequently, most of the sorption experiments conducted on the core material were performed at one concentration point within the 1 ppb to 1 ppm range.

Sorption experiments were performed on samples of cores that had been pre-screened to < 2mm to remove the gravel component. The gravel fraction was assumed to have no sorption; therefore, resulting sorption data were normalized by the percentage of gravel in the core to obtain reported  $K_d$  values. Additionally, combined cores from one of the wells were separated into sand, silt, and clay fractions,

and each fraction was subjected to sorption analysis. Most of the cores studied for sorption characteristics were also analyzed for several physical and chemical properties including particle size, organic carbon content (org C), and cation exchange capacity (CEC) by Nelson Laboratories, Stockton, California. Particle fractionation of sand, silt, and clay was performed by the sieve and siphon method of Black (9); CEC was determined by the ammonium acetate procedure described in Hesse (10); and org C was analyzed by the wet digestion method of Walkley-Black (10).

### Results and Discussion

Results of an early study of cores from wells in this area showed very little correlation between the org C content of the subsurface material and the sorption constants for TCE and PCE (8). This is not surprising since the org C content of the local aquifer material is very low, usually less than 0.1 percent. According to a model by Karickhoff (11), chemicals, such as TCE and PCE, with low octanol water values ( $\leq 3.5 \log K_{ow}$ ) do not sorb linearly to low-organic sediments. Formulas available in the literature for predicting sorption constants based on org C values of the sediment and solubility characteristics of the chemical underestimated measured  $K_d$  values (12,13).

Because org C plays a minor role in sorption of VOCs to this low organic aquifer material, it is important to look at other sediment characteristics driving the sorption of VOCs. Sand, silt, and clay fractions of combined cores were analyzed for CEC and organic matter. Samples of these fractions were also subjected to batch isotherm experiments with PCE, TCE, and 1,2-dichloroethane (DCA). Data appear in Table I along with the percentage of each fraction in the composite. Results showed an order of magnitude of more sorption to clay-sized particles than to sand particles and silt sorbed an intermediate amount. Of the three chemicals studied, PCE sorbed most and DCA least. Sorption isotherms of the three chemicals on each fraction appear in Fig. 1.

The sorptive properties of core material to TCE and PCE with depth in one of the monitor wells (MW-518) appear in Table II along with org C content, CEC, and

TABLE I  
Characteristics and Sorption Constants for Particle-Size Fractions

Fraction	% of Total	% Org	CEC (meg/100g)	PCE	$K_d$ S		
					TCE	DCA	
Gravel	15.8	---	---	---	---	---	---
Sand	30.9	0.12	2.5	1.2	0.7	0.4	
Silt	31.9	0.16	6.0	2.8	2.0	1.2	
Clay	21.6	0.05	18.2	10.0	6.5	1.6	

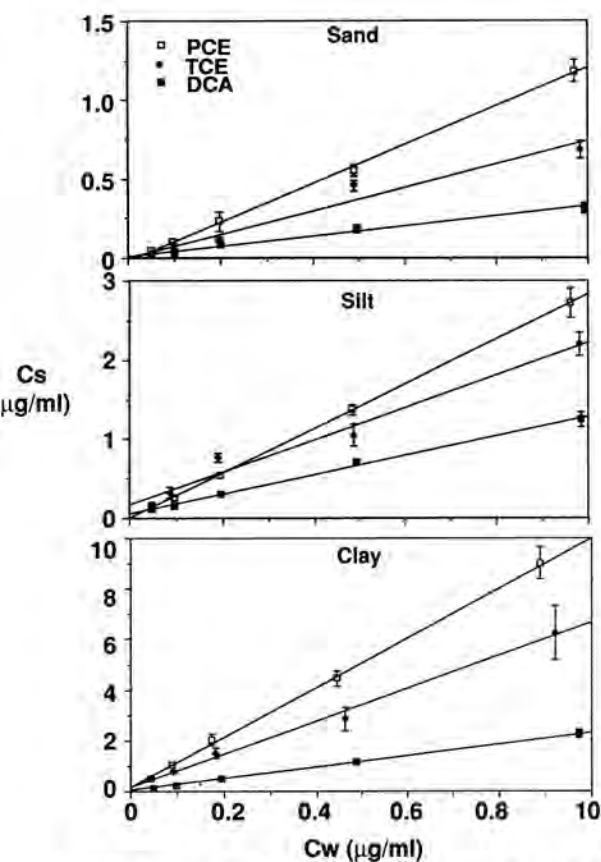


Fig. 1. Sorption Isotherms for Sand, Silt and Clay.

percent clay in each core. The screened interval in the well is in a permeable zone at a depth of approximately 135 feet and is composed primarily of gravelly sand. In the permeable zone, the sorption capacity of the aquifer material for the chemicals is low. This aquifer material is also very low in clay content and cation exchange capacity. Sorption of TCE appears to be moderately correlated to clay content and CEC of aquifer material in the depth profile study in three wells since correlation coefficients of approximately 0.8 or higher are achieved (Fig. 2).

In general, the PCE- $K_{ds}$  are two to three times higher than TCE- $K_{ds}$ .

A frequency distribution of all the TCE- $K_{ds}$  from cores of more than 50 wells appears in Fig. 3.

The range of TCE- $K_d$  values is 0.1 to 1.6 with a mean of 0.77. These values are consistent with those observed in the literature for soils low in organic carbon (14,15).

Field-based measurements of sediment properties and VOC analyses of saturated sediment samples and pore water were used to calculate  $K_d$  values. These calculated  $K_d$  values are in fairly close agreement with the laboratory determined  $K_{ds}$  from batch isotherm experiments on cores from the screened interval of the four wells subjected to

TABLE II  
Depth Profile of MW 518

Depth	% Clay	CEC (meq/100g)	%Org C	TCE $k_d$	PCE $K_d$
18.3	9	9.3	0.05	0.05	1.58
34.7	25	23.8	0.05	0.72	1.70
48.0	10	7.0	0.04	0.31	2.15
92.5	44	27.8	0.10	1.21	2.48
102.5	38	29.8	0.06	1.18	3.28
111.5	25	25.9	0.04	0.87	2.20
121.5	24	21.4	0.02	1.15	2.59
135.0	5	4.5	0.01	0.11	0.52
146.5	14	18.9	0.04	0.89	2.92
154.5	21	13.2	0.03	0.86	1.94

depth profile studies. These comparisons appear in Table III.

In summary,  $K_{ds}$  for TCE were established in core material from more than 50 wells. The range of TCE- $K_{ds}$  was 0.1 to 1.6 with a mean of 0.77. For the materials studied, this  $K_d$  corresponds to a range of retardation factors of from 2.9 to 6.2. Sorption constants for PCE are two or three times higher than those for TCE on the same core material. Sorption constants for TCE with core-samples from the four extensively sampled wells correlated with CEC and clay content. Finally, sorption constants determined in the laboratory fell within the range of those calculated from

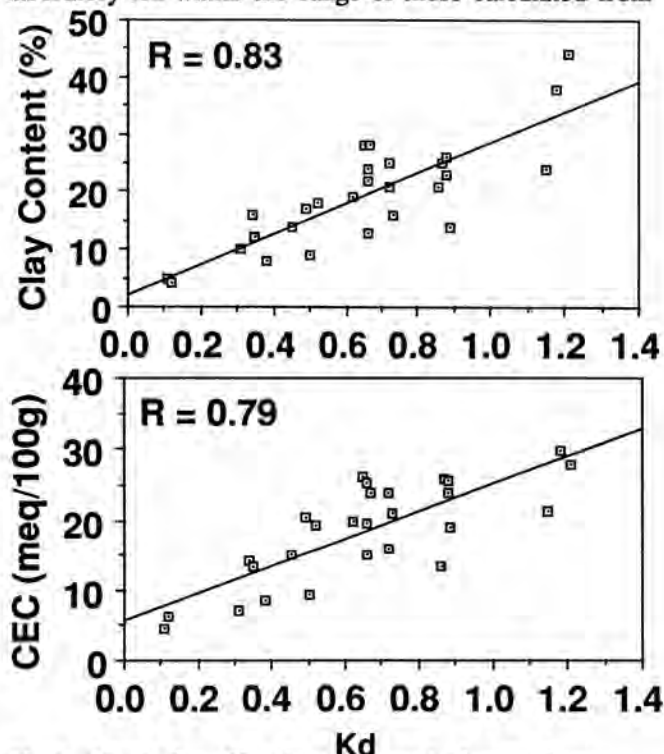


Fig. 2. TCE  $K_d$  vs. Clay Content and Cation Exchange Capacity (CEC) in Cores From Vertical Profile Study.

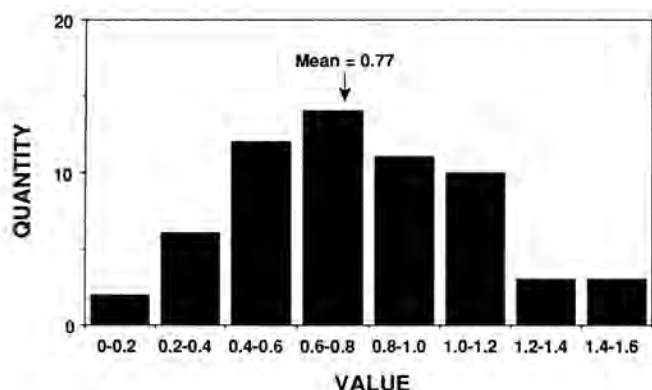


Fig. 3. Frequency Distribution of TCE K<sub>d</sub> Values Obtained From Sub-Samples of Cores From Monitoring Wells at LLNL.

TABLE III

Comparison of Laboratory and Field-Derived Sorption Constants for PCE

Well	Depth	Lab. K <sub>d</sub>	Field K <sub>d</sub>
518	131.3	---	0.2 - 1.6
518	135.0	0.52	---
520	92.5	0.96	---
520	96.3	---	0.3 - 1.6
521	91.3	---	0.4 - 1.0
521	91.8	0.67	---
602	97.5	---	0.3 - 0.6
602	98.0	0.62	---

field-derived measurements where depth profile studies were performed.

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