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**Title and Subtitle**
Flush of Organic Contaminants From a Groundwater Plume at the Rocky Mountain Arsenal.

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**Summary**
During the summer of 1988, UCLA conducted a field experiment on flushing of organic contaminants from a contaminated aquifer in the western tier of RMA. The objectives of the study were to:

1. Estimate the hydraulic conductivity of the aquifer.
2. Estimate the degree to which TCE and 111TCE are retarded in their mobility due to sorption by the aquifer media.
3. Determine the effects of spatial variability of aquifer properties on water flow and TCE and 111TCE flushing rates.
4. Compare results of field and laboratory investigations.

The laboratory analyses of coring samples indicated that both the hydraulic conductivity of the aquifer and the TCE mobility are likely to vary significantly with depth. The field experiment consisted of 1) air stripping extracted water, 2) spiking it with a tracer, and 3) reinjecting it. The field data show that flushing will be very efficient in the highly permeable strata.

**Subject Terms**
Laboratory studies, well construction, hydraulic conductivity estimates.

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**Standards Used**
FLUSHING OF ORGANIC CONTAMINANTS
FROM A GROUND WATER PLUME AT THE
ROCKY MOUNTAIN ARSENAL:
VOLUME I. FIELD AND LABORATORY STUDIES

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1.0 EXECUTIVE SUMMARY

During Summer 1988 a field experiment on flushing of organic contaminants from a contaminated aquifer in the Western Tier of the Rocky Mountain Arsenal (RMA) was conducted by UCLA in collaboration with R.L. Stollar and Associates (RLSA, Lakewood, Colorado) and representatives of the U.S. Army Office of the Program Manager (PMO) for Rocky Mountain Arsenal Cleanup. Preparatory drilling, coring and field tests were conducted during Summer and Fall 1987 in collaboration with Ebasco Services, Inc. (Lakewood, Colorado).

The goals of the field experiment were to test and refine a field method for determining key parameters required for the design of ground water cleanup programs, namely those describing ground water flow and contaminant flushing rates. Rarely are these phenomena well understood, despite their obvious importance. The specific goals of this work were: estimation of the hydraulic conductivity of the aquifer, estimation of the degree to which trichloroethylene (TCE) and 1,1,1 trichloroethane (TCA) are retarded in their mobility with respect to the flow of the ground water due to their sorption by the aquifer media, determination of the effects of spatial variability of aquifer properties on water flow and TCE and TCA flushing rate, and a comparison of the results of investigations conducted in the field and the laboratory.

Using a special apparatus, nearly continuous core samples were collected from the 30 foot thick confined aquifer (approximately 60 to 90 feet below ground surface). Laboratory analyses of the cores yielded a detailed profile of particle size distribution and TCE sorption distribution coefficient; both were found to vary significantly. These results indicate that both the hydraulic conductivity of the aquifer and the TCE mobility are likely to vary significantly.

The laboratory sorption measurements suggest that the TCE could be retarded in its mobility with respect to the flow of the water. That is, approximately 2:1 in some cases, but not be retarded.

A field experiment was conducted to make direct observations of organic contaminant flushing from within the plume. The field experimental setup, proceeding downgradient, consisted of a fully penetrating injection well, four drive point monitoring wells (6" screen length), one fully penetrating monitoring well, and one fully penetrating injection well. The distance between the injection and extraction wells was 27.6 feet (8.4 m). The drive points were placed to sample within layers of varying hydraulic characteristics. Ground water extracted at a rate of approximately 14 gpm was air-stripped to remove organic contaminants, spiked with a pulse of conservative tracer (potassium ferricyanide) and reinjected. Monitoring of the drive points resulted in data that breakthrough curves for the injected tracer and elution curves for the organic contaminants and clearly illustrate the importance of layering within the sand and gravel aquifer.
Interpretation of the field data has yielded estimates of the relative and absolute hydraulic conductivity of the aquifer at 3 depths, and estimates of the retardation of the TCE and TCA during flushing from the 3 depths. None of these estimates were available prior to this work. The absolute hydraulic conductivities, which must be considered rough estimates, are all significantly lower than the value assumed in previous work by Army consultants. The retardation of the organics was found to be insignificant in one stratum, slight in another, and relatively significant in the deepest stratum.

The laboratory estimates of hydraulic conductivity compared relatively well with the previous estimates from pump tests near the site, but do not compare well in absolute value with the estimates derived from this field work, nor do they adequately characterize the relative permeability changes in the vertical direction at the site. The laboratory estimates of contaminant sorption yield estimates of retardation which compare favorably with the field results in individual strata. However, the vertical variability of both hydraulic conductivity and sorption capacity in the aquifer suggests that normal core sample collection processes (a 6-12" section every 5 feet) would be insufficient to allow characterization of the important features of the aquifer or prediction of the contaminant elution in the fully penetrating monitoring well. In fact, normal coring in flowing sands such as the Western Tier aquifer would probably not yield any sample, so improved techniques such as that applied in this work would be required to acquire continuous core samples, subsections of which could be subjected to laboratory analyses.

Overall the field data graphically illustrate that flushing of the contaminants from the aquifer will be very efficient in the highly permeable strata, but very slow in the less permeable strata, both due to lower flow rates and in some strata to retardation. Thus, if these results apply to significant volumes of the aquifer, which is likely, remediation of the aquifer by flushing (i.e., ground water extraction such as not underway at the boundary containment system in the Western Tier of RMA) will be considerably slower than predicted by models assuming a homogeneous aquifer and no contaminant retardation.

Understanding of the heterogeneities of aquifers, such as provided by this work, should be useful in designing extraction well networks and pumping regimes that could accelerate contaminant removal and aquifer cleanup. Presumably this could lead to significant savings in remediation costs. Furthermore, the success of the first experiment in the Western Tier of RMA suggests that the field method has general applicability. Future goals are to apply the method to the estimation of ground water cleanup rates for more highly retarded contaminants and for aquifers impacted by mixtures of contaminants.

Needed for evaluation of G.W. Alternative. Especially for evaluation of effectiveness (identified in EPA guidance) for deeper water bearing zones.
2.0 BACKGROUND

To design efficient remediation schemes for contaminated ground water, it is necessary to have reliable methods for simulating the transport of the contaminants and any agents added as part of the remediation program (e.g. nutrients, substrates, etc. during in-situ bioremediation). Although computer modeling capabilities are advanced in theory, good estimates of some of the key parameters required for modeling ground water cleanup are rarely available in practice. In particular, estimates of hydraulic conductivity are generally sparse and often of questionable accuracy. Furthermore, there is no reliable method for estimating the degree to which the contaminants are retarded in their mobility with respect to the flow of the ground water in typical aquifers. Lacking good estimates of these crucial parameters, predictions of cleanup rates and efficiencies are at best very crude and at worst misleading.

There are numerous theories and corresponding computer models of flow and contaminant behavior in ground water. Many of these have been developed and some have been tested through small-scale laboratory experiments. A few field-scale experiments have been conducted on tracer dispersion (Pickens and Grisak, 1981; Guven et al., 1985; Molz et al., 1986a,b; Palmer and Nadon, 1986; etc.) and even fewer on contaminant transport (Pickens et al., 1981; Roberts et al., 1982; Whiffin and Bahr, 1985; and Mackay et al., 1986a). The results of the field experiments have often not fit the expectations of the relatively simple modeling approaches applied in practice (see for example Mackay et al., 1986a, Roberts et al., 1986, Bahr, 1989). The generally accepted reasons for the discrepancies between theoretical expectations and the field results are an oversimplification of the physical characteristics of the aquifer in most models (assuming homogeneity for spatially variable media), and the assumption that the modeled transport processes are time-invariant (e.g. steady state flow field or equilibrium sorption of the contaminant by the aquifer media), and omission of important processes from the models (e.g. biotransformation, etc.).

Furthermore, even if the model formulation is adequate, it is widely acknowledged that the parameters describing the processes are difficult to estimate. The problem is exacerbated because aquifers are not homogeneous. Pickens and Grisak (1981), Guven et al. (1985), Molz et al. (1986a,b) and others have shown that the hydraulic conductivity of aquifers is not uniform, especially very near Mackay et al. (1986b) and Durant (1986) have shown that the sorption capacity of aquifer media may have significant spatial variability. Considering the inevitable heterogeneity of real geologic media, there is a very significant problem in collecting a "representative" sample of an aquifer for laboratory analysis and process parameter estimation. It is possible, for example, that laboratory analysis of a few core samples would yield detailed understanding of the water flow and contaminant transport within a few regions of the medium. However, this might not contribute significantly to the understanding of the flow and
contaminant transport in the medium as a whole, or might miss strata that completely dominate flow and transport.

For such reasons, it is common to conduct aquifer tests in the field rather than to analyze core samples for estimating hydraulic characteristics of aquifers. For similar reasons, we expect that a properly designed and interpreted field test of contaminant elution from a within ground water plume would be the most reliable way to estimate contaminant transport characteristics (i.e. retardation) of aquifers at scales of practical interest.

The overall goal of the work reported herein is the implementation and evaluation of various scales and designs of field tests in order to determine the optimal approach for estimation of both hydraulic and contaminant transport parameters in contaminated aquifers, especially those applicable to remediation processes. In this report, we describe the results of a two-well forced gradient test of contaminant elution.
3.0 EXPERIMENTAL SITE

The experiment was conducted in a 30 foot thick confined alluvial sand and gravel aquifer in the "Western Tier" of the Rocky Mountain Arsenal (RMA), Denver, Colorado. As shown in Figure 1, the experimental site is within a contaminant plume at least 1 km northwest of the possible source(s) of the plume; Figure 1 was prepared from data presented by Ebasco (1989b). As part of our early characterization work, ground water samples from the experimental site were analyzed by gas chromatography coupled with mass spectrometry (GC/MS) using EPA method 524.2. The only detected compounds were 1,1-dichloroethene (1,1,DCE), 1,1,1-trichloroethane (TCA) and trichloroethylene (TCE). The concentrations of 1,1-DCE were very low (few ppb) and were not detectable using the analytical procedures applied to the ground water samples collected during the field experiment (GC with electron capture detector as described below).

Based on quarterly head measurements from a large number of wells, the regional gradient in the Western Tier aquifer has been estimated as approximately 0.003 (Ebascos, 1989a). Water level contours we plotted using data provided by Ebascos indicated that the gradient in the vicinity of the site (i.e. estimated over a relatively short distance of one to two thousand feet) ranged from 0.0023 to 0.0039 in seven sets of monitoring data we examined (8/86, 9/86, 10/86, 11/86, 12/86, 2/87, 11/87); the average of the values was approximately 0.0029, quite consistent with the regional gradient estimate. Ebasco (1989a) reviewed the past efforts to characterize the aquifer properties in the Western Tier, and listed the results of several pump tests conducted near the site of this experimental work (see Figure 1). Ebasco (1989a) reported the hydraulic conductivities estimated by the three pump tests to be as follows: 1) 386 f/day (0.14 cm/s), 2) 231-3921 f/day (0.08-1.4 cm/s), and 3) 345-462 f/day (0.12-0.16 cm/s). After a discussion of the sources of uncertainty in these estimates, Ebasco (1989a) stated that the results of pump test #1 should be considered most representative of the alluvial aquifer impacted by the organic contamination.

Prior to the work reported herein, there were no estimates of the porosity of the aquifer, other than those drawn from tabulations of typical values for various aquifer media (e.g. Freeze and Cherry, 1979), i.e. 0.25 to 0.5 for unconsolidated sands. Using these estimates and the hydraulic conductivity estimated by pump test #1, the average linear ground water flow rate may be calculated from Darcy's law to fall in the range 6 to 12 f/d. This range appears unrealistically high, presumably because the hydraulic conductivity estimate is too high (R.L. Stollar, R. L. Stollar and Associates, personal communication, 1989).

Figure 2 is a vertical section at the site, showing that the aquifer lies from approximately 60-90 feet below the surface and is confined above by a 10 foot thick clay aquitard and below by the Denver Formation, a Cretaceous-Tertiary siltstone. Monitoring during this work showed that the plume extends vertically through-
Figure 1. Map of Western Tier of Rocky Mountain Arsenal showing contaminant plumes, the experimental site (*) and previous pump tests. Plumes contours are 5 ppb TCE (Ebasco, 1989b).
Figure 2. Vertical section at experimental site, illustrating the aquifer and confining units. Depths below ground surface use the elevation 5176 ft above mean sea level as datum.
out the entire thickness of the sand/gravel aquifer, but the TCE and TCA concentrations decrease with depth in the aquifer from about 43 ppb (TCE) and 35 ppb (TCA) just below the water table to about 25 ppb (TCE) and 16 ppb (TCA) just above the Denver Formation. Based on analyses conducted several months apart, the concentrations of contaminants within the plume do not appear to fluctuate significantly over such time periods.
4.0 OBJECTIVES

The overall goal of our work is the implementation and evaluation of various scales and designs of field tests in order to determine the optimal approach for estimation of both hydraulic and contaminant transport parameters in contaminated aquifers, especially those applicable to remediation processes. In the work reported herein, our goal was to evaluate the effectiveness of a forced-gradient field method. Such a test is, in essence, a pilot scale remediation program, involving the injection of contaminant-free water into a plume to flush out (elute) the contaminants.

In particular we sought answers to the following specific questions:

1) Can a forced-gradient test yield reliable estimates of hydraulic conductivity and contaminant retardation for moderately hydrophobic contaminants in a sand/gravel aquifer?

2) How important is stratification within the aquifer in controlling contaminant removal rate and therefore cleanup time?

3) Can new coring techniques be successfully applied to collect undisturbed samples of the unconsolidated sands for visual inspection and laboratory analysis?

4) How well do laboratory analyses of core samples estimate the hydraulic conductivity of the aquifer, i.e. how do the laboratory estimates compare to the field observations?

5) How well do laboratory analyses of core samples estimate the contaminant retardation during groundwater transport through the aquifer, i.e. how do the laboratory estimates compare to the field observations?

6) Can the contaminant retardation be accurately predicted from measurements of the solid organic carbon content of the aquifer media?
5.0 ACQUISITION AND ANALYSIS OF CORE SAMPLES

5.1 CORING METHOD

Scant information was available at the start of this work on the structure of the aquifer in the Western Tier. This results in part because the coring techniques commonly used at the Arsenal had very low recovery when applied to the unconsolidated "flowing" sands and gravels of which the Western Tier aquifer was composed (i.e. the core barrels would be nearly empty when brought to the surface).

For this reason, a relatively new coring technique called a wireline piston core barrel sampler (Zapico et al., 1987) was employed in this study. This coring method has been used with success by the University of Waterloo and the U.S. Geological Survey to collect relatively undisturbed samples, preserving much of the fine stratigraphy, from unconsolidated sands and gravels. Using this device, we were able to collect nearly continuous core samples from just above the water table to a foot or so into the underlying Denver Formation. Three boring sessions were conducted through a hollow stem auger. Core #1 was collected during drilling of the injection well borehole. Core recovery was excellent for most of the bore (generally 90+% for each 5 foot core sleeve), though no core was recovered from the 64 feet to 69 feet interval and partial recovery in one core suggested loss of materials from the 72 feet to 74 feet interval. For this reason an additional core sample (Core 2) was collected from a boring 5 feet to the west of the injection well, covering only the vertical interval of 64 feet to 68.3 feet below ground surface. Core 3 was taken in the extraction well borehole.

5.2 INSPECTION, SPLITTING AND PHYSICAL ANALYSES OF THE CORES

The coring device yielded five foot samples encased in a clear plastic sleeve (2" ID). Visual inspection of the intact cores indicated that the aquifer consists of an interbedded sequence of alluvial sediments ranging in size from moderately sorted medium to coarse grained sand to poorly sorted sandy gravel. Individual layers are generally massive without observable lamination or structure and apparently extend horizontally for the entire strike distance of the tested section. Contacts between layers are gradational over a vertical distance of a few inches, although the contact between the alluvium and the underlying Denver Formation is sharp.

Bulk Density, Solid Density and Porosity

After shipment to the UCLA laboratory, the cores were cut into approximately one foot vertical intervals, taking care to cut, whenever possible, at the contacts between observable layers. The solids within each interval were dried at room temperature under a fume hood for several days. For four of the intervals, the bulk density of the aquifer media was determined as the ratio of the dry mass of solids to the calculated internal volume of the core
sleeve. The estimated values of the bulk density thus determined are listed in Table I.

Table I. Bulk density and porosity for intervals from Core 1.

<table>
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<tr>
<th>Depth interval (ft below ground surface)</th>
<th>Bulk density (g/cm³)</th>
<th>Porosity (-)</th>
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<tr>
<td>61.0 - 62.0</td>
<td>1.78</td>
<td>0.30</td>
</tr>
<tr>
<td>70.2 - 71.25</td>
<td>1.71</td>
<td>0.33</td>
</tr>
<tr>
<td>75.0 - 76.0</td>
<td>1.76</td>
<td>0.31</td>
</tr>
<tr>
<td>79.0 - 80.0</td>
<td>1.55</td>
<td>0.39</td>
</tr>
<tr>
<td>87.25 - 88.5</td>
<td>1.88</td>
<td>0.27</td>
</tr>
</tbody>
</table>

The deepest sample in Table I represents the top of the Denver Formation, which has the highest bulk density measured (1.88 g/cm³). The bulk density of the aquifer media was found to vary between 1.55 and 1.78 g/cm³, with three of the four strata falling in the narrower range of 1.71 to 1.78 g/cm³.

The dry material from each sampled interval was homogenized manually and split into subsamples for physical and chemical analyses using a riffle splitter. When subsamples of only a few to a few tens of grams were required, the larger subsamples were split using a rotary micro riffle splitter (Quantachrome Corporation).

The solid density of the media was determined for 20 subsamples by water displacement (method described in more detail later). The measured solid densities varied little, with a mean of 2.56 g/cm³ and a standard deviation of only 0.02 g/cm³ (standard error of only 0.8%). This value is consistent with the range reported for alkali feldspars (2.54-2.57 g/cm³) which are a major component of the petrology of the sands. However, this range is somewhat lower than the solid density of pure quartz (2.65 g/cm³), the value normally assumed in the absence of specific measurements.

Given the bulk and solid densities (p_b and p_s), the porosity (θ) of the aquifer may be calculated as

\[ θ = 1 - \frac{p_b}{p_s} \]

Calculated values for porosity are listed in Table I. For three of the aquifer samples the porosity falls in the range of 0.30 to 0.33; for one of the samples the estimate is considerably higher (0.39). It is possible that this discrepancy results from an error in the bulk density measurement; the low bulk density of 1.55 g/cm³ could have resulted from slight expansion of the core contents due
to less than perfect core recovery. On the other hand, the bulk density and porosity of that sample are not outside the range of values found for unconsolidated sands and gravels (Freeze and Cherry, 1979). Nevertheless, because of the real possibility of error in the bulk density measurement of the lowest value and the uniformity of the other three estimates, we take as the best estimates of bulk density and porosity of the aquifer the averages of the values for the first three samples, namely 1.75 g/cm³ and 0.31, respectively.

**Particle Size Distributions**

Particle size distributions of the subsamples were obtained by standard sieve analysis, i.e. mechanical sorting for fifteen minutes through a ten pan set of ASTM standard sieves with mesh sizes ranging from 8 to 230, i.e. screen openings of 4 mm to 63 microns. Collected fractions were weighed and the data used to develop particle size distributions (Volume II, Appendix A).

The mean grain sizes for a set of 27 subsamples taken from the cores range from 0.39 to 3.23 mm, corresponding to medium sands to gravel. Figure 3 shows the variation of mean grain size with depth and indicates that a coarse layer of about 2-3 feet thickness is present in the upper part of the aquifer, perhaps adjacent to other relatively coarse layers, while the mean grain size is relatively uniform and fine grained below 70 to 75 feet. Sorting (based on the standard deviations of the grain size distributions) ranged from extremely poorly to moderately sorted. Throughout the aquifer, the combined silt and clay fraction of these sands was very low. By weight, the fine fraction (< .0625 mm) of the alluvial aquifer comprised between 0.34% and 2.4% of the mass of the samples. The Denver Formation has a higher fine fraction ranging from 6.8% to 8.7%. Visual inspection of the sieved material indicated that the aquifer sands and gravels are composed of subangular to subrounded feldspar and quartz mineral grains, lithic fragments and minor amounts of clay and altered mica.

**Hydraulic Conductivity Estimates**

Thirteen samples from Core 1 were sent to the Institute for Ground Water Research, University of Waterloo for analysis of hydraulic conductivity by falling head permeametry. The permeameter tests were performed at an average room temperature of approximately 22°C. Because the in-situ ground water temperature at depths corresponding to the cored interval is approximately 10°C, a field value for hydraulic conductivity will be a factor of 1.36 less than a measured value based on viscosity and density corrections.

Temperature-corrected hydraulic conductivity (K) measurements for these 13 samples are shown graphically in Figure 4. The K values obtained range from 0.77 x 10⁻² to 3.75 x 10⁻² cm/s for the aquifer media; a value of 0.01 x 10⁻² cm/s was obtained for the top of the Denver Formation. The data suggest that the hydraulic conductivity does not vary widely in the depth interval 75 to 85
Figure 3. Variation of mean grain size of aquifer media with depth.
feet. Although the data are sparse above that interval, there is some indication that a higher hydraulic conductivity layer or layers may exist from 60 to 70 feet.

Hydraulic conductivities were also estimated for the core samples using three published methods relying on correlations with data from grain size distributions (Hazen, 1893; Masch and Denny, 1966; Summers and Weber, 1984) (Volume II, Appendix B). The results are presented in Figures 5, 6 and 7. Hazen's method, which is based on the amount of fines present, yielded estimates of hydraulic conductivity for the permeable sands and gravels which ranged from $1.7 \times 10^{-2}$ to $43.6 \times 10^{-2}$ cm/s; the conductivity of the top of the Denver Formation was estimated as $0.5$ to $0.6 \times 10^{-2}$ cm/s. The technique of Masch and Denny, which is based on the median and standard deviation of the grain size distribution, yielded estimates for the sands and gravels which ranged from $0.1 \times 10^{-2}$ to $4.7 \times 10^{-2}$ cm/s. The newer method proposed by Summers and Weber (1984), which is based on the percentages of fines, sands, and gravels, yielded estimates for the aquifer media which ranged from $0.7 \times 10^{-2}$ to $17.6 \times 10^{-2}$ cm/s.

Visual inspection of Figures 4 through 7 indicates that the technique of Masch and Denny yields a profile which differs substantially in form from that of the other methods, which are reasonably similar and clearly indicate a higher conductivity zone in the upper third of the aquifer. Figure 8 facilitates the comparison of the techniques based on grain size analyses by plotting the estimates against one another. The straight line in each of the frames indicates a perfect correlation. Although the techniques of Hazen and Summers/Weber yield different hydraulic conductivity estimates, they appear to be relatively strongly correlated. The results from both of the latter techniques indicate that the aquifer is stratified, with a relatively high conductivity stratum in the vertical interval of approximately 60 to 70 feet below ground surface (or perhaps two relatively high conductivity strata in that interval with a thin, relatively lower conductivity stratum in between at a depth of about 65 feet). The results suggest that the hydraulic conductivity in the lower portion of the aquifer is variable, perhaps increasing somewhat at the bottom, just above the Denver Formation.

Examination of Figures 4 through 7 indicates that most of the estimated hydraulic conductivities fall below the previously available estimate of $14 \times 10^{-2}$ cm/s (386 f/day), which was assumed to apply to the aquifer as a whole (Ebasco, 1989a). Data in Figures 4 through 7 do indicate some strata may have higher hydraulic conductivities ($10 \times 10^{-2}$ to $50 \times 10^{-2}$) in the range of the previous estimate, but the conductivity of the bulk of the aquifer material, at least at the experimental site, appears likely to be lower.
Hydraulic Conductivity Estimated From Permeameter Method

Figure 4. Profile of hydraulic conductivity estimated by falling head permeametry of subsamples from core 1.
From Grain Size (Hazen's Method)
Hydraulic Conductivity Estimated
Figure 7: Profile of hydraulic conductivity estimated by the technique of Summers and Weber (1984) from particle size distribution data.
Comparison of Grain Size K Estimates
\( (K = 10^{-2} \text{ cm/sec}) \)

Figure 8. Comparison of hydraulic conductivity estimates from techniques based on particle size distribution data.
5.3 ANALYSES OF SORPTION OF TCE BY THE AQUIFER MEDIA

This work assessed the capacity of the aquifer media to sorb TCE from solution, and therefore retard its mobility relative to the flow of ground water. Our goals initially were to determine the magnitude of the effect and its variability with depth. Small batch experiments were conducted with representative subsamples from the cores. The following is a summary drawn from Becker (1990).

Method of analysis

The sorption coefficient \( K_d \) for TCE was determined using a modification of the method proposed by Garbarini and Lion (1985). In this method, the sorption coefficient, \( K_d \), is determined from a comparison of TCE headspace concentration in a three phase system (air, water, sand) with TCE headspace concentration for a control containing air, water and the same amount of injected TCE. If the sands sorb TCE, the headspace concentrations of TCE in the three phase system should be less than expected on the basis of the results from the two phase system. Analyses are run with 25 gram subsamples from the core intervals, prepared using a rotary microriffle splitter. The water used in the experiments was groundwater from the site, amended to 0.01 M CaCl₂, to ensure a constant ionic strength from bottle to bottle, i.e. to swamp out any effects of the sorbent on ionic strength (Garbarini and Lion, 1985). After addition by microsyringe of appropriate masses of TCE, the bottles were then vigorously shaken by hand for 40 seconds and tumbled in the dark at 12 rpm for approximately 3 to 5 days at room temperature (approximately 23°C). The concentration of TCE in the headspace of each bottle was determined using a gas chromatograph equipped with an electron capture detector. Each bottle was analyzed twice or until the measured concentrations varied less than 10%. Distribution coefficients \( (K_s) \) for the samples were calculated from these data using modified forms of the equations provided by Garbarini and Lion (1985). Additional detail is provided by Becker (1990).

Sorption results

Table II lists the measured \( K_d \) values. Figure 9 presents a profile of the sorption distribution coefficients for TCE determined in sorption analyses of samples from Core 1 (injection well bore) and Core 3 (extraction well bore). The sorption capacity of the aquifer clearly varies with depth, with values of \( K_d \) ranging from essentially zero (i.e., below detection limit of the method used in the analyses) to 0.21 cm³/g. The results indicate that there may be layering of the sorption capacity of the aquifer media, with some strata having near zero sorption capacity while the rest have relatively similar sorption capacities. In the strata with near zero sorption capacity, the TCE would be expected to migrate with no retardation, i.e., at the same rate as the ground water. In the other strata, the TCE would be expected to migrate at a velocity lower than that of the ground water.
Table II. Solid organic carbon content \( (f_{oc}) \) and sorption distribution coefficient \( (K_d) \) measured in strata from core samples. The retardation factor \( (R) \) estimated from the measured \( K_d \) is also listed.

<table>
<thead>
<tr>
<th>Core no.</th>
<th>Depth interval* (ft)</th>
<th>( f_{oc} ) (g)</th>
<th>( K_d ** ) (cm$^3$/g)</th>
<th>( R ** * )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>59.50-61.00</td>
<td>0.005</td>
<td>0.08</td>
<td>1.5</td>
</tr>
<tr>
<td>1</td>
<td>62.00-65.50</td>
<td>--</td>
<td>0.14</td>
<td>1.8</td>
</tr>
<tr>
<td>2</td>
<td>64.00-65.00</td>
<td>--</td>
<td>0.07</td>
<td>1.4</td>
</tr>
<tr>
<td>2</td>
<td>65.00-66.00</td>
<td>--</td>
<td>0.13</td>
<td>1.7</td>
</tr>
<tr>
<td>2</td>
<td>66.00-67.00</td>
<td>--</td>
<td>0.00</td>
<td>1.0</td>
</tr>
<tr>
<td>2</td>
<td>67.00-68.00</td>
<td>--</td>
<td>0.00</td>
<td>1.0</td>
</tr>
<tr>
<td>1</td>
<td>69.25-70.25</td>
<td>0.003</td>
<td>0.14</td>
<td>1.8</td>
</tr>
<tr>
<td>1</td>
<td>71.25-72.00</td>
<td>0.004</td>
<td>0.17</td>
<td>2.0</td>
</tr>
<tr>
<td>1</td>
<td>74.00-75.00</td>
<td>0.003</td>
<td>0.11</td>
<td>1.6</td>
</tr>
<tr>
<td>1</td>
<td>75.00-76.00</td>
<td>0.003</td>
<td>0.16</td>
<td>1.9</td>
</tr>
<tr>
<td>1</td>
<td>76.00-77.00</td>
<td>--</td>
<td>0.00</td>
<td>1.0</td>
</tr>
<tr>
<td>1</td>
<td>77.00-78.00</td>
<td>--</td>
<td>0.00</td>
<td>1.0</td>
</tr>
<tr>
<td>1</td>
<td>78.00-79.00</td>
<td>0.003</td>
<td>0.00</td>
<td>1.0</td>
</tr>
<tr>
<td>1</td>
<td>79.00-80.00</td>
<td>--</td>
<td>0.00</td>
<td>1.0</td>
</tr>
<tr>
<td>1</td>
<td>80.00-81.00</td>
<td>--</td>
<td>0.00</td>
<td>1.0</td>
</tr>
<tr>
<td>1</td>
<td>81.00-81.75</td>
<td>--</td>
<td>0.10</td>
<td>1.6</td>
</tr>
<tr>
<td>1</td>
<td>81.75-82.75</td>
<td>--</td>
<td>0.08</td>
<td>1.5</td>
</tr>
<tr>
<td>1</td>
<td>82.75-83.75</td>
<td>0.11</td>
<td>0.00</td>
<td>1.0</td>
</tr>
<tr>
<td>1</td>
<td>84.00-85.25</td>
<td>0.003</td>
<td>0.20</td>
<td>2.1</td>
</tr>
<tr>
<td>1</td>
<td>85.25-86.25</td>
<td>--</td>
<td>0.21</td>
<td>2.2</td>
</tr>
<tr>
<td>1</td>
<td>86.25-87.25</td>
<td>--</td>
<td>0.14</td>
<td>1.8</td>
</tr>
<tr>
<td>1</td>
<td>87.25-88.50</td>
<td>--</td>
<td>0.00</td>
<td>1.0</td>
</tr>
<tr>
<td>3</td>
<td>74.80-75.80</td>
<td>0.011</td>
<td>0.00</td>
<td>1.0</td>
</tr>
<tr>
<td>3</td>
<td>75.80-76.80</td>
<td>0.007</td>
<td>0.12</td>
<td>1.7</td>
</tr>
<tr>
<td>3</td>
<td>76.80-77.80</td>
<td>0.009</td>
<td>0.00</td>
<td>1.0</td>
</tr>
<tr>
<td>3</td>
<td>77.80-78.80</td>
<td>0.004</td>
<td>0.00</td>
<td>1.0</td>
</tr>
<tr>
<td>3</td>
<td>79.80-80.80</td>
<td>0.003</td>
<td>0.06</td>
<td>1.3</td>
</tr>
<tr>
<td>3</td>
<td>80.80-81.80</td>
<td>0.006</td>
<td>0.16</td>
<td>1.9</td>
</tr>
<tr>
<td>3</td>
<td>81.80-82.80</td>
<td>0.006</td>
<td>0.08</td>
<td>1.5</td>
</tr>
<tr>
<td>3</td>
<td>82.80-83.80</td>
<td>0.007</td>
<td>0.09</td>
<td>1.5</td>
</tr>
<tr>
<td>3</td>
<td>83.80-84.80</td>
<td>0.005</td>
<td>0.00</td>
<td>1.0</td>
</tr>
<tr>
<td>3</td>
<td>84.80-86.05</td>
<td>0.005</td>
<td>0.00</td>
<td>1.0</td>
</tr>
<tr>
<td>3</td>
<td>86.30-87.40</td>
<td>0.002</td>
<td>0.19</td>
<td>2.1</td>
</tr>
</tbody>
</table>

* All depths relative to a ground elevation of 5176.4 ft

** Values listed as zero include measurements whose mean values were zero or slightly negative; in the latter case, the results were statistically indistinguishable from zero.

*** Calculated from the measured \( K_d \), porosity and bulk density, as described in the text.
Figure 9. Measured sorption distribution coefficient, $K_d$ (mean \pm std. dev.), for trichloroethylene versus depth at injection well boring (cores 1 and 2) and extraction well boring (core 3).
Table II lists the retardation factors (R) that would be predicted for ground water transport in the depth intervals analyzed. The retardation factor is equal to the average velocity of the ground water divided by the average velocity of the TCE, assuming that sorption is linear, reversible and at equilibrium. Under these conditions, R may be calculated as follows (Freeze and Cherry, 1979):

\[ R = 1 + \left( \frac{p_b}{\theta} \right) K_d \]

where \( p_b = \) bulk density = 1.75 g/cm\(^3\)
\( \theta = \) porosity = 0.31

The mean values of the measured \( K_d \)s were used in this calculation. On the basis of the laboratory analyses, the TCE is predicted to migrate with a retardation factor that varies from 1.0 to 2.2 in the various strata analyzed.

**Correlation of sorption capacity with organic carbon content**

To test whether the sorption was dominated by the solid organic carbon content \( (f_{oc}) \) of the aquifer media, as is commonly assumed (Lyman et al., 1982; Karickhoff, 1984), we measured the \( f_{oc} \) of some of the samples for which the \( K_d \) had been determined. Using a newly refined protocol (Ball et al., 1990) designed for application to low carbon content sands, we found that the \( f_{oc} \) of the aquifer media varied somewhat with depth (Figure 10), but most values were extremely low, less than 0.01%.

It is generally assumed that the solid organic carbon content of geologic media will dominate sorption of hydrophobic organic chemicals only if \( f_{oc} \) is greater than approximately 0.1% (Schwarzenbach and Westall, 1982; Karickhoff, 1984). Since the values in the RMA aquifer are all significantly less than this generally accepted threshold limit, we would not expect the sorption of TCE to be well predicted solely on the basis of the organic carbon content of the strata. This is in fact the case, as evident in Figure 10. There is no correlation between \( f_{oc} \) and \( K_d \) for TCE. Nevertheless we attempted to estimate the sorption capacity for TCE assuming that sorption was organic-carbon-dominated, i.e. that

\[ K_d = f_{oc} \times K_{oc} \]

where \( K_{oc} \) is the organic-carbon-normalized sorption coefficient. Many semi-empirical methods have been proposed to estimate \( K_{oc} \) from properties of the sorbing chemical (Lyman et al., 1982). Many of the methods estimate \( K_{oc} \) (cm\(^3\)/g) from the octanol-water partition coefficient \( (K_{ow}) \) of the sorbing chemical. We chose to apply one of the most commonly used (Schwarzenbach et al., 1981):

\[ \log K_{oc} = 0.72 \log K_{ow} + 0.49 \]

The octanol-water partition coefficient of TCE is approximately 195 (Lyman et al., 1982), thus the \( K_{oc} \) estimated by the correlation is approximately 138 (cm\(^3\)/g). Given the range of measured
Figure 10. Plot of organic carbon content ($f_{oc}$) vs TCE sorption distribution coefficient ($K_d$) measured for various depth intervals in core samples of the aquifer media.
values of \( f_{oc} \) from Table II (0.002% to 0.011%), we would thus estimate the sorption capacity for TCE to range from 0.003 to 0.015 cm\(^3\)/g. These estimates of TCE sorption distribution coefficient are significantly lower than the range of non-zero measured sorption capacities.

As a further test of the semi-empirical estimation techniques, we had organic carbon analyses conducted on subsamples from two strata by a commercial analytical laboratory that is used widely by consulting engineering and hydrogeological firms. Despite the fact that we made it quite clear that the samples were likely to have very low organic carbon content and thus may have required special handling, the analytical laboratory reported the results noted in Table II, i.e. 0.11% and 0.23%, for depth intervals 82.75-83.75 and 84.00-85.25 in Core 1. Both values were considerably higher than the range obtained in our laboratory, most likely because the commercial facility failed to remove all of the inorganic carbon prior to the determination of organic carbon, a very crucial step in analyses of such low organic carbon materials (Ball et al., 1990). In particular, the value of 0.23% was approximately 75 times higher than the corresponding value obtained during analysis of the same stratum at UCLA.

Although the commercially measured \( f_{oc} \) values are almost certainly incorrect, it is interesting to determine what the semi-empirical estimation methods would yield if the values were taken to be correct, as might often be the case in practice (i.e. by practitioners unaware of the limitations of the estimation method and the likelihood of incorrect \( f_{oc} \) values). Using the same estimation method described above, the sorption distribution coefficients (K\(_d\)) for TCE for the two strata were estimated as shown in Table III. For the 82.75-83.75 ft stratum, which was determined not to sorb TCE significantly in our laboratory sorption experiments (i.e. K\(_d\) = 0), the semi-empirical technique coupled with the commercial lab \( f_{oc} \) values estimated significant sorption should have occurred. For the 84.00-85.25 ft stratum, the semi-empirical technique coupled with the commercial lab \( f_{oc} \) values estimated a K\(_d\) value on the order of 0.3 cm\(^3\)/g, approximately 1.5 times the measured value. Clearly significant error is associated with estimation of sorption capacity of the two strata using the commercial laboratory estimates of \( f_{oc} \).

In summary, our results indicate that neither the magnitude nor the variability of TCE sorption distribution coefficient can be reliably estimated from the organic carbon content of the aquifer solids using semi-empirical estimation methods. Considering the difficult of the \( f_{oc} \) analytical method, and the very real danger of obtaining incorrect \( f_{oc} \) data from poorly controlled analyses, the practical utility of the sorption estimation methods based on measurement of \( f_{oc} \) is very limited. Such semi-empirical methods will not work and should not be used for estimating sorption capacities for low organic carbon content, sandy aquifer media. Unfortunately, as reviewed by Mackay (1990), nearly all of the sandy aquifers for which reliable estimates of organic carbon
Table III. Comparison of measured $K_d$ values with estimates based on commercial organic carbon ($f_{oc}$) analyses of the aquifer media (Core #1).

<table>
<thead>
<tr>
<th>Depth interval (ft)</th>
<th>82.75-83.75</th>
<th>84.00-85.25</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f_{oc}$ (% commercial lab)</td>
<td>0.11</td>
<td>0.23</td>
</tr>
<tr>
<td>$K_d$ estimates (cm$^3$/g)*</td>
<td>0.15</td>
<td>0.31</td>
</tr>
<tr>
<td>$K_d$ measurements (cm$^3$/g)</td>
<td>0.0</td>
<td>0.2</td>
</tr>
</tbody>
</table>

*using $K_{qc}$ correlation equation of Schwarzenbach et al. (1981), as described in text.

Content are available have very low organic carbon contents, generally well below 0.1%. Thus in the absence of reliable evidence to the contrary, it should be assumed that the semi-empirical techniques for estimating sorption distribution coefficients are inappropriate for sandy aquifers in general.
6.0 IMPLEMENTATION AND MONITORING OF THE FIELD EXPERIMENT

During the field test, water was pumped from a fully penetrating extraction well, air stripped to remove organic contaminants, spiked with a tracer and reinjected into the aquifer via a fully penetrating injection well. The migration of the injected tracer and the flushing (elution) of the organic contaminants from the aquifer by the injected organic-free water were monitored via four short screen drive point samplers and one fully penetrating monitoring well installed between the injection and extraction wells. The locations of the wells and drive points are shown in Figure 11. Details of the experimental setup and operation are described below.

6.1 EXPERIMENTAL EQUIPMENT AND METHODS

Injection and Extraction Wells

Both the extraction and injection wells were constructed of 4" ID PVC casing and screened sections (0.020" slot size). The wells were installed through a hollow stem auger drilled approximately 0.5 ft into the Denver Formation (a total depth of 86.25 feet below ground surface at the injection well location). As the auger flights were pulled up, the annulus around the well was backfilled in the saturated zone with gravel, sealed with bentonite for several feet into the overlying clay confining layer, and grouted with a bentonite/cement slurry to the surface. The extraction well was installed 27.6 feet downgradient of the injection well. Both wells were developed by pumping until the extracted water was relatively free of fines.

Drive Point Samplers and Monitoring Well

The groundwater was monitored with four 2" stainless steel/PVC drive points (wells A, B, C, D) and one 2" PVC fully penetrating well (well M). The locations of and intervals sampled by these devices are shown in Figure 11. Screening depths, spacing and logs of all wells are listed in Volume II, Appendix C.

Figure 12 is a schematic diagram of the construction of the stainless steel drive point samplers, which were custom-built for this experiment. Each sampler consisted of a 6" screen (wire-wound, 0.020 inch slot size) separated from a standard iron drive point by a stainless steel end plate either thick enough (1/2") to withstand the pounding described below or backed with an equivalent steel plate. Above the screened section was sufficient flush thread stainless steel casing to extend to or near the water table, with flush thread PVC casing continuing to the ground surface. The drive points were installed by augering to the top of the saturated zone and then driving the points out the bottom of the hollow stem augers using drill rods placed inside the 2" casing (seated on the bottom of the screened section). The points were driven to their respective sampling horizons (Figure 11 and Table IV) by pounding on the top of the drill rods. Above the water table the wells were grouted to the surface.

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Figure 11. Vertical schematic of the site illustrating the location and screened intervals of the wells and drive point samplers. The diameters of the wells are exaggerated for clarity.
Figure 12. Schematic diagram of a drive point sampling system.
Note that wells B, C, D were installed as a cluster during augering at a location approximately 9.1 feet from the injection well, while drive point A was placed approximately 2.6 feet farther from the injection well during a separate drilling operation.

The sampling intervals for the drive points were selected to represent four apparently different strata within the aquifer which had been identified by analyses of the core samples from the site. In particular, we hoped to sample strata representing the extremes of both hydraulic conductivity and TCE sorption capacity, and various combinations thereof. Figure 13 presents depth profiles at the injection well of both hydraulic conductivity (K) and TCE sorption distribution coefficient (K_d). The drive points sample the vertical intervals indicated by the boxes in the figure.

Figure 13. Profiles of hydraulic conductivity (K) and TCE sorption distribution coefficient (K_d) at the injection well (Cores 1 and 2).
As is clear from the figure, the characteristics of the aquifer media sampled by the drive points were anticipated on the basis of the laboratory analyses to be as indicated in Table IV.

Table IV. General hydraulic and sorption characteristics of the depth intervals sampled by the drive points.

<table>
<thead>
<tr>
<th>Point</th>
<th>Depth Interval (feet)</th>
<th>Relative Hydraulic Conductivity</th>
<th>Relative TCE Sorption Capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>65.5 - 66.0</td>
<td>High</td>
<td>Medium-Low</td>
</tr>
<tr>
<td>B</td>
<td>69.0 - 69.5</td>
<td>Low</td>
<td>Medium-Low</td>
</tr>
<tr>
<td>C</td>
<td>78.0 - 78.5</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td>D</td>
<td>84.0 - 84.5</td>
<td>Low-Medium</td>
<td>High</td>
</tr>
</tbody>
</table>

The fully penetrating monitoring well (well M) was constructed of standard 2" PVC flush thread blank and screen sections. Thirty feet of screen (0.020" slot size) was used to provide full penetration and sampling of the confined aquifer; blank PVC casing extended to the ground surface. The well was installed approximately 17 ft from the injection well with a hollow stem auger; the borehole was backfilled with gravel in the saturated zone, sealed with bentonite into the confining layer and grouted to the surface.

Injection-Extraction System

The purpose of the injection system was to deliver to the injection well a constant flow of water, free of organic contaminants, and spiked for various intervals with a constant concentration of tracer. Potassium iodide was chosen as the tracer because 1) the iodide ion has been found to travel conservatively in ground water, i.e. without retardation or reaction, 2) potassium iodide is nontoxic at the low concentrations used (in fact is added to table salt for nutritional purposes) and thus the amount remaining in the aquifer after the experiment would pose no health risk, and 3) iodide ion is relatively easy to analyze by specific ion electrode.

A schematic of the injection system is shown in Figure 14. The injection system was assembled over a period of about 10 days following development of the wells. A few days before the tracer injection, approximately 50 gallons of air-stripped ground water was pumped from the constant head reservoir into the spike tank. Fifteen kilograms of potassium iodide was added to the spike tank (55 gal plastic drum), which was mixed to insure uniformity of the spike solution before and throughout the tracer injection. The
spike solution thus had an iodide concentration of approximately 56,000 ppm.

Water was pumped at 14 gpm from the extraction well by a stainless steel submersible pump to the top of the air stripper. After passing through the stripping tower the water was collected in a constant head reservoir (approximately 0.6 m³ capacity). The air stripper was constructed of 10 feet of 12" diameter galvanized steel ducting, the top of which was connected to the inlet of a 1 hp blower. The stripping tower was filled with eight cubic feet of 5/8" diameter polyethylene rashing rings held in place by galvanized wire mesh at the top and bottom.

The air-stripped water was drawn from the reservoir at 14 gpm by a 1/2 hp electrically driven centrifugal pump, passed through a combined flowmeter and accumulator, spiked with a tracer solu- tion, and distributed via a manifold into the injection well. The spike solution was drawn from the bottom of the drum via a peris- taltic pump, passed through a flowmeter at approximately 60 ml/min and introduced into the injection line via a tee fitting. Approx- imately 10 feet of the 1" ID flexible PVC injection line downstream of the spike inlet was coiled to provide some mixing of the spike solution with the organic-free water prior to injection. Downstream of the mixing coil, the injection solution was split into three equal flows (monitored by individual flowmeters) which were delivered to the top 10 feet, middle 10 feet and bottom 10 feet of the injection well by three pipes (3/4" PVC with threaded, glueless joints), each slotted in its bottommost 10 feet.

Sampling equipment and sampling procedures

As shown in Figure 12, the drive point monitoring wells were sampled by dedicated compressed-air-driven teflon bladder pumps (American Sigma). The water was delivered to the surface via 3/8" ID teflon-lined or teflon tubing. The inlet to each pump con- sisted of a 6" long, 3/4" i.d. stainless steel pipe perforated with numerous 1/4" holes and covered with fine stainless steel wire mesh. The inlets were connected to the pumps via inflatable packers (Baski and American Sigma) with a single pass through central conduit. The pumps were positioned such that their inlets were within the 6" screened section of the drive points. They were held in place by the packers, which were inflated via 1/4" poly- ethylene tubing to 65 to 80 psi to form a positive seal with the inside of the casing. Packer pressure was monitored continuously with dedicated gages and adjusted when required. This system insured that the bladder pumps sampled water from the screened section alone, which was isolated from the water standing above the packer within the casing. Thus a purge volume of only three liters was required to flush the well with over 3 times the internal volume of the sampling point, pump and tubing prior to sampling.

Well M was sampled by a dedicated air-driven submersible piston pump (Bennett) fitted with 3/8" ID teflon tubing and positioned in the middle of the screened section of the well. A packer was not necessary since there was very little, if any, water
Figure 14. Schematic diagram of the injection system.
standing above the screened section. To allow for adequate flushing of the well, a purge volume of 15 liters was extracted prior to sampling.

The water pumped from the extraction well was sampled via a stopcock installed in the discharge pipe prior to the inlet to the air stripper. The injection water was sampled after spiking and mixing but before delivery to the injection well via another stopcock. Samples of the extracted water and injection solution were collected after brief purging (200-500 ml) to flush the relatively small dead volumes in the sampling ports.

After purging of the various sampling locations, two 100 ml plastic sample bottles were filled (for iodide analysis), followed by two precleaned 40 ml glass VOA bottles (for organics analysis). Immediately after the latter were filled, they were sealed headspace-free with a teflon-lined screwcap. The VOA bottles were stored in an ice chest, including during airfreighting to UCLA. The plastic bottles were stored at ambient temperature.

The wells and sample ports of the injection system were sampled frequently (every 1-4 hours) during the initial days of the field test. With time, as the organic contaminants eluted and the injected iodide pulse passed by the monitoring wells, the frequency of sampling was reduced.

Analytical Procedures

Iodide analysis. Iodide was measured in the field and laboratory with a solid state iodide selective electrode coupled to a Fisher Accumet Model 950 meter. The electrode (Orion 94-53) is advertised as having a linear response to iodide ions down to 0.002 ppm; in this work, with various difficulties and interferences encountered during field analyses (e.g. temperature fluctuations), the practical detection limit was approximately 0.1 ppm. The electrode is also known to be very selective for iodide, with insignificant interference from other major anions such as chloride and bromide.

Samples and standards were prepared for analysis as specified in the electrode manual (addition of 2 ml of Orion ionic strength adjustor solution to a 100 ml water sample). The meter allowed for the automatic storage or revision of the calibration curve, which was necessary for each analytical session primarily because of wide temperature fluctuations within the camper used as the laboratory at the site. After calibration, the iodide concentration in ppm could be read directly for the sample under analysis.

Organic analysis. Upon receipt of the VOA bottles at UCLA, they were transferred from the ice chests to an explosion proof refrigerator. Samples were prepared for analysis by a hexane extraction method similar to EPA method 625 (liquid/liquid extraction). Dibromopropane (DBP) was added to the hexane extractant to serve as an internal standard; final DBP concentration ranged between 100 and 300 ug/l. The extractant solution was stored in
a repipeter bottle and kept in a freezer to avoid volatilization losses or contamination. Hexane extraction was conducted by removing 10 ml of the water sample to be analyzed from the 40 ml VOA sample vial and immediately adding 3 ml of the DBP/hexane solution to the same vial. After recapping, the bottles were shaken on a table shaker for 10 minutes.

After phase separation, the hexane layer was transferred into autosampler vials, capped and loaded into the autosampler unit of Perkin Elmer 8500 gas chromatograph equipped with a capillary column (J & W Scientific #DB624) and an electron capture detector. As many as 75 samples were run sequentially to reduce the effect of variations in the performance of the instrument which were encountered from day to day. Standards were prepared throughout the analysis period from a single stock solution of TCE/TCA in methanol. A five point calibration curve was constructed as a part of each analytical session (standards with TCE and TCA concentrations of 0, 12.5, 25, 37.5, 50.0 µg/l each). The method detection limit (MDL) was determined for TCA and TCE as 0.07 ppb and 0.10 ppb respectively, with a 2% method error (Glaser et al., 1981).

6.2 IMPLEMENTATION OF THE FIELD EXPERIMENT

Ground water extraction, injection and iodide tracer spiking began on June 23, 1988, at 9:45 a.m. In other tracer injection experiments it is common to allow the flow field to reach steady state prior to tracer injection. In this case, however, such an approach was inappropriate because the flushing of the organics would begin immediately; to allow the least ambiguous comparison of the behavior of the tracer and organics, it was therefore necessary to begin the iodide injection immediately. The iodide injection ceased after 27.5 hours, earlier than planned, because of a pump failure. The flow rate for both the injection and extraction wells was held relatively constant throughout the experiment at approximately 14 gpm; the spike flow rate was held relatively constant at approximately 60 ml/min during the 27.5 hours of tracer injection. A drawdown of 3.15 ft was observed in the extraction well within minutes after pumping started. The corresponding buildup in the injection well was similar (3.29 feet). Small head changes (few inches) were recorded for the sampling wells, but were felt to be unreliable since their measurement was confounded by the tubing running down the casing to the sampling pumps. After the iodide spike was ceased, the ground water extraction and injection of organic-free water continued until 4:17 p.m. on August 16, for a total injection time of approximately 54.2 days (1300 hours). During this time, however, the injection was interrupted twice: event 1 was a brief interruption of injection (from approximately 290-293 hours) caused by a pump overheating; event 2 was a more prolonged interruption of injection which occurred over a weekend due to generator failure (the exact duration is unknown, thus the duration is assumed to be the entire time between observations, i.e. from approximately 560 to 610 hours). Over its duration, the field experiment resulted in the extraction, cleanup and reinjection of approximately 1,100,000 gallons of ground water.
6.3 MONITORING OF THE EXTRACTED AND INJECTED WATER

Figure 15 plots the results of organic analyses of samples of the extracted groundwater before and after passage through the air stripper. The concentration of trichloroethylene (TCE) in the extracted water was initially 40 ppb, consistent with expectations based on the general monitoring of the plume conducted by the Army's consultants over the last several years. The TCE concentrations appear to decrease within the first 100 hours to approximately 30 to 35 ppb, perhaps decreasing further after about 700 hours to approximately 25 to 30 ppb.

The TCE concentrations are drastically reduced after passage of the water through the air stripper, ranging from an initial high of approximately 1.5 ppb to below detection limit. These results imply that the efficiency of the air stripper was 96% or greater over the nearly two months of operation, quite acceptable for a device built in less than a week with parts totalling a few hundred dollars. The total mass of TCE stripped into the atmosphere can be estimated from these data as approximately 120 grams, equivalent to about 86 ml or about 3 liquid ounces of pure TCE. This very small amount is unlikely to have had any detrimental effect on public health; for example, the maximum concentration of TCE in the air discharged from the air stripper would have been 0.1 ppm, well below the applicable standards for occupational exposure. Upon dispersion in the atmosphere, the TCE concentrations from this very small source would have been rapidly decreased.

Figure 16 depicts the concentration of iodide in the water injected into the aquifer over time. Some difficulties were encountered in holding the iodide concentration constant as originally intended, and the concentration rises over the spiking interval of 27.5 hours from 50-60 to 70-90 ppm. It is possible that some of the variability and the high and low extreme data on the plot result from analytical error, and thus the pulse may be adequately described as rising linearly from 55 to 70 ppm. The average injected concentration found from the area under the injection curve and the known injection time was 63.0 ppm. Thereafter, a second, dispersed pulse of iodide with maximum concentration of about 12 ppm is present in the injected water due to the rapid breakthrough and recycling of some of the injected water at the extraction well (Figure 17). This rapid breakthrough of injected, organic-free water may also explain the initial decrease in TCE concentration observed in the extracted ground water (Figures 15 and 17).
Figure 15. Concentration of trichloroethylene in the extracted ground water before and after passage through the air stripper.
Figure 16. Concentration of iodide in the injected water versus time. The pulse from 0 to 27.5 hours resulted from spiking; the dispersed pulse after 27.5 hours was recycled in the extracted water used for injection.
Figure 17. Concentration histories of iodide and trichloroethylene at the extraction well (first 1200 hours of the experiment). Events 1 and 2 were interruptions of injection; see text for discussion.
6.4 MONITORING OF SOLUTE TRANSPORT WITHIN THE AQUIFER

Figures 18 through 22 depict the concentrations of iodide and trichlorethylene measured over the first 800 hours of the field experiment in point A, point B, point C, point D, and monitoring well M, respectively. The raw data are listed in Volume II, Appendix D. Note that both TCE and TCA were present in the aquifer at approximately equal concentrations; only TCE is included in Figures 18 through 22 for clarity since the TCE and TCA behaved very similarly (elution curves difficult to distinguish from one another). On each of the figures the timing of the two interruptions of injection is depicted: event 1 was a brief (few hours) interruption; event 2 was a more prolonged interruption.

Iodide travelled rapidly to point A, arriving approximately ten hours after initiation of injection (Figure 18). The peak of the breakthrough curve occurred at 42 hours. The breakthrough curve can be seen to be composed of dispersed, overlapping responses to the main iodide pulse and the second (recycled) iodide pulse, the latter of which is observable at approximately 70 hours as a shoulder on the right side of the main peak. The TCE and TCA were eluted rapidly from the aquifer. The organic concentrations dropped at the same time as the iodide arrived, suggesting minimal retardation of organic mobility in the stratum sampled by point A.

The organic concentrations reached a minimum concentration of approximately 2-3 ppb at 60-70 hours, after which the concentrations rose slowly through the remainder of the experiment. This concentration rise is counter to expectations based on the assumptions that the injected water travels perfectly horizontally and radially toward the extraction well during the entire duration of the experiment. The likely reason for this rise over time is the departure from these assumptions, possibly because of a significant shift in the direction of the regional ground water flow or more likely due to clogging of the injection well or its gravel pack in the more permeable horizons (where most of the injected water was initially moving). Clogging definitely occurred during the field test: the water level within the injection well rose by 16.5 feet from the start to the finish of the injection. Clogging of the well or gravel pack would lead to a narrowing of the zone flushed by the injected water (compared to the case when stratum was unclogged) and reencroachment of the organic contamination.

The concentration history at drive point B, sampling only 3 feet below drive point A, is significantly different (Figure 19). There is no breakthrough of iodide at significant concentrations during the first 1200 hours of the test. Very low iodide concentrations (maximum 0.3 ppm) were observed over the same period as iodide breakthrough in drive point A, which suggests that sampling of point B created some slight short-circuiting down the drive point casing from the upper, more permeable stratum. No elution of organics was observed in drive point B for 1200 hours, although the background concentration appears to fluctuate somewhat (the spikes are likely to be sampling and/or analytical artifact).
Figure 18. Concentration histories of iodide and trichloroethylene at Drive point A, for the first 800 hours of the field experiment. Events 1 and 2 were interruptions of injection; see text for discussion.
Figure 19. Concentration histories of iodide and trichloroethylene at Drive point B, for the first 800 hours of the field experiment. Events 1 and 2 were interruptions of injection; see text for discussion.
Significant breakthrough of iodide was observed in drive point C (Figure 20) although later than observed at point A. The peak concentration of 5.8 ppm was an order of magnitude lower than the injected iodide concentration. Elution of organics at point C occurred at roughly the same time as the arrival of the iodide; the concentrations dropped relatively rapidly to 3 ppb during the period 120 to 280 hours, but only slowly thereafter. Examination of Figure 20 suggests that retardation of organics was minimal in this stratum.

The behavior of the tracer at point D (Figure 21) was similar to that at point C, except that it arrived a bit sooner and had a slightly higher peak. The organics, on the other hand, were flushed relatively slowly from this horizon; the elution began as the iodide pulse arrived and continued at a less precipitous pace than observed in points A and C. Figure 21 indicates that some retardation of organics occurred during flushing of this stratum.

Figure 22 indicates that iodide breakthrough in the well M (fully penetrating screen) was very similar to that in drive point A (Figure 18). However, close inspection of the two curves indicates that breakthrough at M in fact began slightly before the breakthrough at point A even though the distance from the injection well was greater. This suggests that the bulk of the water sampled by well M was derived from horizons even more permeable than that sampled by point A. Organics elution initially occurred rapidly in well M, but the concentrations decreased to minima of only 4-7 ppb, after which the concentrations rose slowly with time. The behavior of TCE in Figure 22 cannot be described by a single retardation factor, which would require the assumption of a homogeneous aquifer. Instead, it would be expected from Figures 18-21 that the flushing in well M and the shape of the TCE elution curve in Figure 22 would be a flow-weighted sum of the elution behavior in the various strata of the aquifer.
Figure 20. Concentration histories of iodide and trichloroethylene at Drive point C, for the first 800 hours of the field experiment. Events 1 and 2 were interruptions of injection; see text for discussion.
Figure 21. Concentration histories of iodide and trichloroethylene at Drive point D for the first 800 hours of the field experiment. Events 1 and 2 were interruptions of injection; see text for discussion.
Figure 22. Concentration histories of iodide and trichloroethylene at Well M for the first 800 hours of the field experiment. Events 1 and 2 were interruptions of injection; see text for discussion.
7.0 INTERPRETATION OF THE FIELD RESULTS

The monitoring results illustrate graphically that the hydraulic conductivity of the aquifer varies significantly with depth, and that the flushing of the organics may be slower in the lower portion of the aquifer than in other horizons. To evaluate these phenomena more quantitatively, an equivalent arrival time for the breakthrough and elution curves must be obtained. The centers of mass of the breakthrough curves of the iodide pulse are synonymous with the means of the breakthrough curves. The equivalent pulse-means for the organics elution may be calculated from the areas under the elution curves (Levenspiel, 1979); the calculations are presented in Volume II, Appendix E. The arrival times for the centers of mass are listed in Table V. The behavior of the solutes in the various strata may then be compared on the basis of the arrival time of the tabulated centers of mass.

Table V. Arrival times of centers of mass of the iodide and organic solutes at the various points sampled.

<table>
<thead>
<tr>
<th>Point</th>
<th>Arrival Times of Centers of Mass (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Iodide</td>
</tr>
<tr>
<td>I</td>
<td>19.6</td>
</tr>
<tr>
<td>A</td>
<td>46.6</td>
</tr>
<tr>
<td>B</td>
<td>--</td>
</tr>
<tr>
<td>C</td>
<td>199.1</td>
</tr>
<tr>
<td>D</td>
<td>145.6</td>
</tr>
<tr>
<td>M</td>
<td>40.5</td>
</tr>
<tr>
<td>E</td>
<td>68.1</td>
</tr>
</tbody>
</table>

7.1 ESTIMATION OF HYDRAULIC CONDUCTIVITY

Estimation of full-aquifer K from head drawdown/buildup

- Data from extraction well development

Assuming the aquifer is homogeneous and isotropic and the flow regime is steady-state, the full-aquifer hydraulic conductivity can be estimated from drawdown data collected during a pump test by the Thiem equation or the Dupuit-Forchheimer equation (Bear, 1979). The Thiem equation is the governing equation for steady-state well flow in a confined aquifer:

\[ K = \frac{Q \ln(r_1/r_2)}{2\pi B (h_1 - h_2)} \]
where \( Q \) = extraction rate
\( B \) = thickness of aquifer
\( r_1, r_2 \) = radius at head measurement locations 1 and 2, respectively
\( h_1, h_2 \) = head at locations 1 and 2, respectively

For steady-state well flow in an unconfined aquifer, the Dupuit-Forchheimer equation is the appropriate equation:

\[
K = \frac{Q \ln(r_1/r_2)}{\pi (h_1^2 - h_2^2)}
\]

These equations were used to interpret drawdown data collected during development of the extraction well. After 20 minutes of pumping at a rate of approximately 8 gpm, the extraction well head had decreased by 3.1 feet. Drawdowns in the various wells were: 0.03 ft for the fully penetrating monitoring well (M), 0.0 for drive point A, 0.02 to 0.1 ft for drive points B, C, and D, and 0.03 ft for the injection (I) well. These measured drawdowns are so small that we consider them unreliable, probably artifacts of measurement error. Consequently the hydraulic conductivity was calculated with the steady-state well flow equation using the radius of the extraction well and the head measured at the extraction well \( (r_2, h_2) \) and the radius and head at the assumed limit of the cone of depression \( (r_1, h_1) \), where \( h_1 \) is taken as the head before the groundwater extraction began. Preliminary calculations indicated that there was little difference between hydraulic conductivities estimated by the Thiem and Dupuit-Forchheimer equations; thus the Thiem equation was used for the calculations reported here. The full-aquifer hydraulic conductivity was estimated to fall in the range 0.5 to 0.7 ft/hr \( (0.42 \times 10^{-2} \text{ cm/sec to } 0.59 \times 10^{-2} \text{ cm/sec}) \) using the Thiem equation and assuming that \( r_2 \) was on the order of 10 feet to 100 feet. The latter assumption was made since we did not actually know the radius of the limit of the cone of depression; clearly the estimate of hydraulic conductivity is relatively insensitive to variations in \( r_1 \).

- Data from injection-extraction experiment

During the experiment (injection and extraction at equal rates), steady-state conditions would be expected to occur relatively rapidly along a line between the injection and extraction wells. Unsteady-state head changes propagate outward from a well until a source of recharge is found to allow equilibrium conditions to be established (Bear, 1979). Along the line between the two wells in our experiment, the injection well is the source of recharge for the extraction well and the head gradient between these two wells should reach steady-state more rapidly than the heads in other parts of the field site. The appropriate extraction
The drawdown observed in the extraction well was 3.2 feet, constant from less than a minute after injection-extraction began until the end of the experiment; the buildup in the injection well was 3.3 feet initially (rising during the latter part of the experiment because of well clogging). Assuming that steady-state was rapidly established (minutes to a few hours), the above equation can be used to estimate the full aquifer hydraulic conductivity as 0.95 ft/hr (0.80 x 10^{-2} cm/sec).

An alternate approach may be used to interpret the head data during the experiment, treating the aquifer as though it were homogeneous. Under steady-state conditions, the flow field caused by point sources/sinks (wells) in a homogeneous, isotropic aquifer can be described by the velocity potential method (Hoopes and Harleman, 1967a,b; Javandel et al., 1984), given the thickness of the aquifer (B) and the flow rate of the wells (Q). Similarly, the Thiem equation can be used with the principle of superposition to calculate the head distribution under the same conditions (same Q, B and drawdown/buildup at the extraction/injection wells) for an assumed hydraulic conductivity (Bear, 1979). The calculated head distribution and assumed hydraulic conductivity can then be used to calculate the velocity distribution. By comparing the velocity distributions for points between the wells calculated by these two methods, one can find the assumed hydraulic conductivity that leads to a match. The full-aquifer hydraulic conductivity estimated by this matching method is 1.0 ft/hr (0.85 x 10^{-2} cm/sec).

Estimation of relative K in strata from tracer movement

The relative hydraulic conductivities for the strata sampled by the drive points can be estimated from the tracer transport data as the ratio of the average velocity in the fastest stratum to the average velocity of water in the stratum of interest. The average water velocity for flow between the injection well and the sampling point may be defined as the distance of the point from the injection well divided by the time it takes for the center of mass of injected iodide to travel from the injection well to the sampling point. The travel time is equal to the arrival time for the center of mass less the time elapsed as 50% of the iodide mass
was injected (19.6 hr, including consideration of the recycled iodide pulse).

The relative hydraulic conductivities thus estimated for points A, C and D are listed in Table VI. Since no iodide breakthrough was observed at point B, only an upper bound of relative hydraulic conductivity could be estimated (i.e. by assuming that iodide would have broken through eventually if the experiment had been continued past 1300 hours).

Table VI. Calculation of relative hydraulic conductivities.

<table>
<thead>
<tr>
<th>Sampling Device</th>
<th>Arrival of center of mass at point (hr)</th>
<th>Time Elapsed during injection (hr)</th>
<th>Travel time to point (hr)</th>
<th>Distance (f)</th>
<th>Velocity (f/hr)</th>
<th>K/Kmax</th>
</tr>
</thead>
<tbody>
<tr>
<td>Point A</td>
<td>46.6</td>
<td>19.6</td>
<td>27.0</td>
<td>11.75</td>
<td>0.44</td>
<td>1.0</td>
</tr>
<tr>
<td>Point B</td>
<td>&gt;1300</td>
<td>19.6</td>
<td>&gt;1300</td>
<td>9.13</td>
<td>&lt;0.007</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>Point C</td>
<td>199.1</td>
<td>19.6</td>
<td>179.5</td>
<td>9.13</td>
<td>0.081</td>
<td>0.12</td>
</tr>
<tr>
<td>Point D</td>
<td>145.6</td>
<td>19.6</td>
<td>126.0</td>
<td>9.13</td>
<td>0.072</td>
<td>0.16</td>
</tr>
<tr>
<td>Well M</td>
<td>40.5</td>
<td>19.6</td>
<td>20.9</td>
<td>17.09</td>
<td>0.82</td>
<td></td>
</tr>
</tbody>
</table>

The relative hydraulic conductivities of the drive points indicate that the layer sampled by drive point A is much more permeable than those sampled by points C and D, which are in turn more permeable than that sampled by point B. The relative hydraulic conductivities span approximately two orders of magnitude. Note that the high calculated average water velocity for the monitoring well in this study suggests that there are even more permeable strata than that sampled by point A.

A similar variation in hydraulic conductivity (measured in the lab) was found for a sandy aquifer at Borden, Ontario, by Sudicky (1986), although the strata in that aquifer were on the order of one to tens of centimeters thick. In addition, Molz et al. (1986b) simulated tracer behavior in stratified aquifers at the Mobile and Chalk River sites; the relative hydraulic conductivities varied by roughly an order of magnitude in the strata at Mobile (3-6 ft thick) and by somewhat over a factor of 2 at Chalk River (strata on the order of 1 to 6 ft thick). Other studies have found similar variations in hydraulic conductivity with depth in sand and gravel aquifers.

Estimation of absolute K in strata from tracer movement

The absolute hydraulic conductivities in the aquifer strata can be estimated assuming steady-state flow conditions and ideal stratification (i.e., no cross flow between strata). A combination of the velocity potential method and the method of superposition
of the Thiem equation can be used to estimate the absolute hydraulic conductivities. Although the injection/extraction rate into a given layer and its thickness are unknown, they are bounded by the maximum injection/extraction rate (14.0 gpm) and the maximum aquifer thickness (30 ft). The velocity potential model is utilized to calculate the injection/extraction rate per unit thickness \((q/b)\) for the strata \((i = A,B,C,D,M)\) sampled by the monitoring points or well. The appropriate \(q/b\) and the observed head distribution in the wells are input into the equation resulting from the superposition of the Thiem equation; the assumed hydraulic conductivity is varied until the calculated average velocity matches the tracer behavior in that stratum. A more detailed discussion of the method follows.

Using the velocity potential model, the mean velocity (harmonic mean as defined by de Marsily [1986]) between the injection well and a sampling point can be calculated from the velocity distribution for a given \(q/b\). By matching the calculated mean velocity for a \(q/b\) with the observed mean velocity for the tracer (Table VI), the appropriate \(q/b\) is found for the stratum. This method was used to estimate \(q/b\) for the points A,B,C,D and well M. For this exercise, the tracer breakthrough at Well M is assumed to represent primarily strata more permeable than those sampled by the drive points; this appears justified since the observed average tracer velocity at M is considerably higher than observed at the drive points (Table VI). The calculated values of \(q/b\) and assumed layer thicknesses are listed in Table VII. Note that the summation of the layer injection/extraction rates must equal the total injection/extraction rate (14 gpm, or 112.3 ft³/hr). To allow this match, the assumed layer thicknesses were adjusted to the values indicated in the table. Table VII implies that a significant fraction of the aquifer not sampled by the drive points may be composed of highly permeable strata. It appears that there are more high permeability strata than indicated by the examination of the grain size data.

Table VII. Flow per unit thickness estimated by the velocity potential model, assumed strata thicknesses, and estimated flow in the assumed strata.

<table>
<thead>
<tr>
<th>Layer sampled by:</th>
<th>(q/b) (ft²/hr)</th>
<th>(b) (ft)</th>
<th>(q) (ft³/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>8.0</td>
<td>9.0</td>
<td>72.0</td>
</tr>
<tr>
<td>A</td>
<td>3.6</td>
<td>10.0</td>
<td>36.0</td>
</tr>
<tr>
<td>B</td>
<td>&lt;0.05</td>
<td>2.0</td>
<td>0.1</td>
</tr>
<tr>
<td>C</td>
<td>0.35</td>
<td>4.0</td>
<td>1.4</td>
</tr>
<tr>
<td>D</td>
<td>0.50</td>
<td>5.0</td>
<td>2.5</td>
</tr>
</tbody>
</table>

The method of superposition of the Thiem equation utilizes the \(q/b\) calculated above and the observed drawdown/buildup in the
extraction and injection wells. Using this method, the steady-state hydraulic gradient between the injection well and a monitoring well can be calculated for an assumed or known hydraulic conductivity (K). The velocity distribution between the two wells is then calculated by Darcy's Law using the porosity, hydraulic conductivity and its associated hydraulic gradient. The mean velocity between the injection well and the monitoring point can be calculated from this velocity distribution as was done for the velocity potential method. The appropriate absolute K for the layer is found by matching the calculated mean velocity with the observed mean tracer velocity (Table VIII). The estimated hydraulic conductivities (K), listed in Table VIII, range from less than 0.02 ft/hr to 1.95 ft/hr (0.02 x 10^{-2} cm/sec to 1.65 x 10^{-2} cm/sec).

**Table VIII. Calculated mean velocities in and hydraulic conductivities of the strat sampled by the monitoring points.**

<table>
<thead>
<tr>
<th>Layer</th>
<th>Calculated mean velocity (ft/hr)</th>
<th>Hydraulic conductivity (K) (ft/hr) (10^{-2} cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>0.82</td>
<td>1.95 1.65</td>
</tr>
<tr>
<td>A</td>
<td>0.45</td>
<td>1.00 0.85</td>
</tr>
<tr>
<td>B</td>
<td>&lt;0.007</td>
<td>&lt;0.02 &lt;0.02</td>
</tr>
<tr>
<td>C</td>
<td>0.051</td>
<td>0.10 0.08</td>
</tr>
<tr>
<td>D</td>
<td>0.074</td>
<td>0.25 0.21</td>
</tr>
</tbody>
</table>

An equivalent full-aquifer hydraulic conductivity ($K_{equiv}$) can be estimated from the values determined for the strata by:

$$K_{equiv} = \frac{K_M b_M + K_A b_A + K_B b_B + K_C b_C + K_D b_D}{b_M + b_A + b_B + b_C + b_D}$$

where $K_i$ and $b_i$ are the estimated hydraulic conductivities and assumed thicknesses of the strata which the tracer breakthrough at the various wells are presumed to represent. As before, the fully penetrating well M is assumed, for this exercise, to represent primarily strata even more permeable than that sampled by drive point A (since the average tracer velocity is higher).

Using the values in Tables VII and VIII, the full-aquifer hydraulic conductivity is found to be 0.97 ft/hr (0.82 x 10^{-2} cm/sec). Whether fortuitous or not, this value agrees very well with full-aquifer hydraulic conductivity estimates based on drawdown observed during the development of the extraction well (0.5-0.7 f/hr) and the buildup/drawdown observed during the injection/extraction experiment (approx. 1.0 f/hr). All of these estimates of full-aquifer hydraulic conductivity are considerably lower than estimates derived from the previous pump tests cited by Ebasco (1989a), i.e. approximately 16.1 f/hr (386 f/day).
7.2 ESTIMATION OF RETARDATION OF ORGANIC CONTAMINANTS

The retardation factor for migration of the organic contaminants in a uniform porous medium is defined, when sorption is linear and at equilibrium, as the ratio of the average velocity of the water to the average velocity of the organics. Sorption of TCE and TCA at the low concentrations encountered in the Western Tier aquifer is quite likely to be linear (Karickhoff, 1984). Whether equilibrium is attained during the experimental work is discussed briefly later. If we assume that the strata sampled by the drive points are relatively uniform horizontally, the retardation factor for each stratum is equal to the ratio of the arrival time for the center of mass of the organics to the travel time of the center of mass of the iodide (Table V). The retardation factors thus estimated are listed in Table IX.

**Table IX. Estimated retardation factors for TCE and TCA, based on center of mass arrival times.**

<table>
<thead>
<tr>
<th>Sampling Device</th>
<th>Retardation factor for TCE</th>
<th>Retardation factor for TCA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Point A</td>
<td>1.1</td>
<td>1.0</td>
</tr>
<tr>
<td>Point B</td>
<td>unknown</td>
<td>unknown</td>
</tr>
<tr>
<td>Point C</td>
<td>1.2</td>
<td>1.1</td>
</tr>
<tr>
<td>Point D</td>
<td>2.0</td>
<td>1.9</td>
</tr>
<tr>
<td>Well M</td>
<td>2.1</td>
<td>2.2</td>
</tr>
</tbody>
</table>

These results confirm expectations based on visual examination of Figures 18-21: there is insignificant retardation of the organics due to interactions with the sands in the stratum sampled by point A, very slight retardation in the stratum sampled by point C, and retardation by about a factor of two in the stratum sampled by point D. These retardation estimates are compared to those based on laboratory analyses of core samples in Section 8.

Although the overall retardation that would be estimated by this crude technique for the fully screened monitoring well (Well M) is appreciable (-2), this estimate has little meaning and is of no predictive use since the aquifer is not uniform, i.e. hydraulic conductivity and contaminant retardation vary significantly in the vertical direction. Thus the elution curve is very asymmetric (Figure 22).
8.0 COMPARISON OF LABORATORY AND FIELD ESTIMATES

In this section, we compare laboratory and field estimates of hydraulic conductivity and TCE retardation, the derivations of which were discussed in detail in the previous sections.

8.1 COMPARISON OF LAB AND FIELD HYDRAULIC CONDUCTIVITY ESTIMATES

Table X lists the hydraulic conductivity estimates based on field tracer data at drive points A, B, C and D along with the hydraulic conductivity estimates derived by laboratory analysis of core intervals which overlap or are adjacent to those sampled by the drive points.

**Table X. Hydraulic Conductivity Estimates ($10^{-2}$ cm/sec)**

<table>
<thead>
<tr>
<th>Point, sampling interval (ft)</th>
<th>Core no., depth interval (ft)</th>
<th>Laboratory Estimates of K Hazen* M&amp;D* S&amp;W* Perm**</th>
<th>Field Estimates of K from Darcy's law***</th>
</tr>
</thead>
<tbody>
<tr>
<td>A, 65.5-66.0</td>
<td>2, 65.0-66.0</td>
<td>25.0 0.8 10.6 ---</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td>3, 65.8-66.8</td>
<td>24.0 1.2 10.6 ---</td>
<td></td>
</tr>
<tr>
<td>B, 69.0-69.5</td>
<td>1, 69.3-70.3</td>
<td>7.3 0.8 5.3 3.8 &lt;0.02</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3, 68.5-69.5</td>
<td>9.0 2.6 2.8 ---</td>
<td></td>
</tr>
<tr>
<td>C, 78.0-78.5</td>
<td>1, 78.0-79.0</td>
<td>6.8 3.5 0.7 2.6 0.08</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3, 77.8-78.8</td>
<td>3.6 3.3 0.9 ---</td>
<td></td>
</tr>
<tr>
<td>D, 84.0-84.5</td>
<td>1, 84.0-85.3</td>
<td>3.6 2.3 1.4 2.2 0.21</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3, 83.0-84.0</td>
<td>7.3 1.2 2.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3, 86.1-86.3</td>
<td>2.1 1.0 1.8</td>
<td></td>
</tr>
</tbody>
</table>

* Estimates of hydraulic conductivity derived from correlations to parameters from grain size distributions; correlations used were those of Hazen (1893), Masch and Denny (1966), and Summers and Weber (1984).

** Estimates of hydraulic conductivity derived from falling head permeametry conducted at the University of Waterloo (cf. Sudicky, 1986).

*** Estimates of hydraulic conductivity derived from the field results (Section 7).

Assuming that the hydraulic conductivities (K) estimated from the field data are accurate, i.e. reasonably close to the true values, Table X indicates that all of the lab-based methods yield high estimates of hydraulic conductivity. In most cases the hydraulic conductivities estimated from the grain size distributions of core samples are one to two orders of magnitude higher than the field estimates.

However, some insight is gained by comparing relative hydraulic conductivities in the strata estimated by the various methods. Both the method of Hazen (1893) and the method of Summers & Weber (1984) identify the A stratum as the most permeable; the
method of Summers & Weber also distinguishes that the D stratum is slightly more permeable than the C stratum. None of the methods predicts that the hydraulic conductivity in the B stratum would be so much less than in the other strata. Therefore, with respect to identifying the location of apparently important strata, the Summers & Weber (1984) technique appears best for the 3 more permeable strata, while none of the methods identified the lowest permeability stratum.

8.2 COMPARISON OF LAB AND FIELD RETARDATION FACTORS

Table XI lists the retardation factors derived from field tracer and organics data at drive points A, C and D along with the retardation estimates derived by laboratory analysis of core intervals which overlap or are adjacent to those sampled by the drive points.

<table>
<thead>
<tr>
<th>Point, sampling interval (ft)</th>
<th>Laboratory results</th>
<th>Field results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Core no., depth interval (ft)</td>
<td>R</td>
</tr>
<tr>
<td>A, 65.5-66.0</td>
<td>2, 65.0-66.0</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>2, 66.0-67.0</td>
<td>1.0</td>
</tr>
<tr>
<td>C, 78.0-78.5</td>
<td>1, 77.0-78.0</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>1, 78.0-79.0</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>1, 79.0-80.0</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>3, 77.8-78.8</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>3, 79.8-80.9</td>
<td>1.3</td>
</tr>
<tr>
<td>D, 84.0-84.5</td>
<td>1, 84.0-85.3</td>
<td>2.1</td>
</tr>
<tr>
<td></td>
<td>1, 85.3-86.3</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>3, 84.8-86.1</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>3, 86.3-87.4</td>
<td>2.1</td>
</tr>
</tbody>
</table>

It is evident in Table XI that the laboratory estimates of retardation may at times vary sharply from one depth interval to the next. Thus the laboratory analyses of two core samples straddling the depth interval sampled by point A yield retardation estimates of 1.7 and 1.0, whereas the field data suggest a retardation factor of approximately 1.1. It is possible that the true depths of the core intervals and/or the screened section of the drive points may be slightly different from those listed in the table, due to error in initial measurement, slippage of materials inside the cores, etc.

In general, however, the retardation observed in the strata is reasonably consistent with the predictions based on analyses of core samples taken from within the strata. This suggests that
characterization of the features of such aquifers may require many analyses of subsections of continuous cores. It is clear that sorption coefficients determined from only one analysis of one short core sample (typically 6-12") would not necessarily be useful for predicting the removal of the organic contaminants from the aquifer as a whole. This is a simple consequence of the fact that the aquifer is not spatially uniform. This study indicates that for reliable prediction of the concentration decrease in fully penetrating monitoring or extraction wells it would be necessary to have detailed information on the spatial variability of both hydraulic conductivity and contaminant retardation (assuming the distribution of contaminants was well understood).
9.0 CONCLUSIONS

As detailed in previous sections of this report, the answers to the questions posed earlier are as follows:

1) Can a forced-gradient test yield reliable estimates of hydraulic conductivity and contaminant retardation in the Western Tier aquifer?

Yes. Useful estimates of both were generated in this work. The estimates of hydraulic conductivity appear reasonable for the sandy aquifer media, but are considerably lower than previously assumed. The retardation factors for the contaminants are in the range observed at other sites for similar geologic media; no reliable estimates of contaminant retardation were previously available for this site.

It should be emphasized, however, that the vertical variability of the aquifer is such that estimates of hydraulic conductivity and retardation made for the aquifer as a whole (i.e. treated as uniform) are relatively useless in describing the behavior of water and contaminants within the test zone. This may also be true for the more important problem of describing the water and contaminant behavior in the plume as a whole.

2) How important is stratification within the aquifer in controlling contaminant removal rate and therefore cleanup time?

Very important. Variable hydraulic conductivity and contaminant retardation lead to very inefficient flushing. During 1300 hours of injection and extraction, involving over 1,000,000 gallons of water, the contaminant concentrations only ten feet from the injection well in one stratum were not decreased, while in others the contaminants were rapidly removed. Concentrations measured in the fully penetrating well did not fall below usual cleanup criteria (5-10 ppb for TCE) during the period of the test.

3) Can new coring techniques be successfully applied to collect undisturbed samples of the unconsolidated sands for visual inspection and laboratory analysis?

Yes. Very good recovery (90% or greater) was obtained with the wireline piston core barrel sampling device. Techniques applied to date have very low recovery as a rule in such media, leaving the structure of such aquifers relatively unknown and making laboratory studies of such aquifer nearly impossible.
4) How well do laboratory analyses of core samples estimate the hydraulic conductivity of the aquifer, i.e. how do the laboratory estimates compare to the field observations?

Estimates do not compare well on an absolute basis; the field estimates are likely to be the most reliable. Furthermore, there are substantial variations among laboratory estimates from the reviewed methods, and the relative hydraulic conductivities in the various strata examined are not well estimated by any of the methods.

5) How well do laboratory analyses of core samples estimate the contaminant retardation during groundwater transport through the aquifer, i.e. how do the laboratory estimates compare to the field observations?

The retardation estimates based on lab studies of core samples from specific strata compare quite well with the field observations in those strata. This may result in part from the fact that the monitoring was conducted in narrow strata which were relatively uniform in composition, and the core analyses were conducted in enough detail to define the characteristics of the narrow strata. The concentration decrease observed in the fully penetrating monitoring well cannot be modeled by assuming a single retardation factor applies to the aquifer as a whole. These findings suggest that analyses of a few core samples from such aquifers may not yield retardation estimates of much practical value.

6) Can the contaminant retardation be accurately predicted from measurements of the solid organic carbon content of the aquifer media?

No. Considerable error is likely to result. In addition, the measurement of the organic carbon content is not easy, and frequently incorrectly done, leading to additional error and possibly very misleading results. In this work, UCLA analyses of organic carbon content led to underestimation of retardation in the stratum in which retardation was observed in the field experiment, whereas commercial lab analyses of organic carbon content led to significant overestimation of retardation in the same stratum.

In summary, the results of this work suggest that a carefully controlled field test can yield direct observations of cleanup rates and estimates of flow and contaminant transport parameters which are almost certain to be much more accurate and useful than estimates generally available from published correlations or typical laboratory analyses. A forced-gradient field test, involving the injection of contaminant-free water into a plume to flush out (elute) the contaminants, will yield information and insight which is likely to be very useful in the design of plume remediation.
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School of Public Health, M.S. program:
Martin Bloes, Kathryn Becker, Alice Kwan

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2) Prof. Mike Stenstrom on design of air stripping device

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1) Prof. Vijay Dhir on hydraulic and transport modeling concepts

School of Public Health:
1) Prof. William Glaze on analytical methods for field samples

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11.0 REFERENCES


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