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STUDIES OF CONTAMINANT DIFFUSION IN AN AQUITARD AND GROUNDWATER REMEDIATION BY REACTIVE METALS AT DOVER AIR FORCE BASE, DELAWARE

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13. ABSTRACT (Maximum 200 words)

This project focused on analysis of in-situ concentrations of chlorinated hydrocarbons in an aquitard underlying the site of a prior field-scale investigation of pump-and-treat remediation in sheet-pile "test cells" at Dover AFB, DE. Another aspect was the conduct of exploratory long-term column investigations of zero-valent metal barrier technologies, as applied to contaminated groundwater taken from the aquifer surrounding the cells.

During the post-pumping period, unique conditions of zero flow were maintained within the sheet-pile enclosures. Extensive soil coring was conducted at times corresponding to roughly seven and sixteen months after the termination of the prior project. New modeling approaches were developed both to (1) apply concentration profile information toward more accurate estimation of plume history (inverse modeling for forensic interpretation); and (2) obtain predictions of the post-pumping contaminant movement (multi-layer diffusion modeling). Results were used to (1) test the assumption that diffusion alone affected contaminant fate, and (2) conduct additional forensic interpretations and field-scale simulations.

The column investigations provided long-term verification of halogenated alkene removal under essentially *in situ* groundwater conditions, including continuous removal of cis-1,2-dichloroethene. Results also confirmed that dichloromethane is not removed and showed apparent breakthrough of two other chemicals, tentatively identified as dichloroethanes.

14. SUBJECT TERMS
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PREFACE

The report describes (1) field, laboratory, and computer modeling investigations related to the analysis of *in situ* concentrations of DNAPL-derived contaminants (chlorinated hydrocarbons) in an aquitard underlying the site of a prior field-scale investigation of pump-and-treat remediation in sheet-pile "test cells" at Dover AFB, DE; and (2) the results of an exploratory long-term column-scale investigation of reactive metal barrier technologies, as applied to the removal of chlorinated solvents from site groundwater. Primary objectives of the aquitard characterization work were to further our understanding of diffusion in these zones and to develop improved simulation approaches for using soil core information in interpretive and predictive modeling. The separate column-scale activities took advantage of existing facilities at the site to further our knowledge regarding the long-term efficiency of zero-valent iron and other reactive metal materials that can be used in semi-passive *in situ* remediation systems to control contaminant migration in groundwater.

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EXECUTIVE SUMMARY

This project followed a prior field-scale investigation of pump-and-treat remediation at Dover AFB, DE, in which sheet-pile test cells were used to isolate two adjacent segments (3.7 m x 9.9 m x 15.9 m deep) of an unconfined aquifer underlain by a comparatively impermeable aquitard. These two cells had been previously installed at the location of a long-extant groundwater plume containing chlorinated solvents and their degradation by-products (PCE, TCE, TCA, *cis*-1,2-DCE, vinyl chloride) as well as aromatic organic contaminants (benzene, xylene, naphthalene, 2-methyl-naphthalene). The more permeable regions of the aquifer with the cells had been flushed with clean groundwater through pump-and-treat operations over the course of the prior research, and soil cores were collected both before and after pumping. Data from these prior efforts presented a clear picture of diffusion-controlled aquitard contamination, in which persisting sorbed chemicals in the aquitard were found to provide a long-term source of contaminant to the more easily flushed aquifer. Rates of contaminant release from the aquitard were found to depend strongly on the spatial variability in the initial contaminant distribution as well as on the spatial variability of the aquitard sorption properties.

In the project reported here, we furthered our analysis of the prior coring results by experimentally investigating the concentration development in the aquitard following the pump-and-treat remediation and by developing better models of interpretation and simulation. During the eighteen months following pumping cessation, contaminants in the aquitard continued to diffuse both downward, deeper into the aquitard, and upward, into the previously well-flushed conductive zone The well-controlled and understood concentration history in this overlying porous medium allowed us to verify our computer modeling approach and to make better forensic and predictive interpretations of our coring results. Overall, the results confirm that diffusion and sorption are the major processes affecting contaminant fate in this aquitard, and that low concentrations of DNAPL contaminant can be expected to diffuse out of this zone for many decades to come. The modeling approaches developed in this project will be applicable at virtually any contaminated location, and the phenomena studied are likely to be important for any remediation effort, irrespective of the technology utilized.

The second aspect of the project, involving column-scale investigations of reactive metal barrier materials, has shown that effective long-term removal of chlorinated ethenes can be achieved, while also confirming that these systems may have little effect on certain chlorinated alkane contaminants. In general, the results have shown that expectations from prior laboratory work apply under the conditions of longer-term operation, with the *in situ* groundwater from the Dover site, and at low feed-water velocities perhaps typical of field-scale operations. Overall, the reactive iron materials studied in this project performed in reasonable agreement with laboratory and field studies conducted by others. After passage of over 150 pore volumes of groundwater through the columns (over a period of 400 days), the first 25% of the reactive metal medium was visibly impacted by precipitation products. However, both columns tested continued to remove all chlorinated alkenes to below detection limits throughout the project period.

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Section I. INTRODUCTION

Contamination of soil and groundwater with industrial solvents is a major problem for the Air Force, and one of the most intractable of all DOD cleanup challenges. Common solvents such as perchloroethylene (PCE) and trichloroethylene (TCE) have been used for decades to clean weapon systems. When accidentally spilled on the ground, these liquids filter through the earth under the influence of gravity. Denser than water, when released in sufficient mass they may continue to trickle even below the water table until they either play out (i.e., dissipate as a series of suspended residuals and/or fully dissolve into the surrounding groundwater) or encounter a soil layer that they cannot penetrate, forming a pool. Because solubility with water is low and dissolution rates are slow, full dissolution into the groundwater is expected to require years, decades, or longer. Once below the water table, the chemical pools or residuals are nearly impossible to locate or remove, yet they provide a chronic source of contamination to the groundwater that passes by the source zone. Collectively, these solvents and other similar materials are known as dense, nonaqueous-phase liquids, or DNAPLs. It has been estimated that nearly one third of Air Force contaminated sites have a DNAPL component.

When DNAPL source zones persist in the subsurface, the associated chemicals will slowly dissolve in groundwater and thus be transported downgradient. Groundwater plumes of these DNAPL contaminants can ultimately occupy extremely large volumes of the saturated zone, wherein, through processes of surface adsorption and phase partitioning, they also contaminate a large mass of the geologic media. Given sufficient time, the dissolved chemicals will also diffuse into regions that are not accessible to advective groundwater flow, such as particle-scale meso- and micro-pores, as well as regions that are relatively impermeable compared to the rest of the geologic medium, such as the interparticle pore spaces of clay or silt zones. In this manner, the relatively impermeable regions (including lenses within the aquifer as well as aquitards that bound it) can become significantly contaminated over time and in a manner that cannot be quickly remediated by most currently available means. Once the concentrations in "mobile" water decrease, slow diffusion of contaminants back from these "immobile" regions may represent long-term sources of contamination and a continuing concern with respect to health and environmental risk. In this way, in addition to the DNAPL itself, the contaminated "immobile" zones

throughout the plume are important aspects of the long-term problem.

For the reasons noted above, current remediation efforts in subsurface environments typically suffer from inaccurate estimates of the mass of contaminant present, a poor understanding of when (or whether) clean-up has been achieved, and an inability to predict how the subsurface contamination will respond, over the long term, to applied treatments. The achievable removal efficiencies are often unclear and there is growing recognition that complete subsurface cleanup may commonly be impossible at any price. Within this context, there is a recognized and critical need to develop a better understanding of the long-term subsurface behavior of the halogenated organic chemicals that comprise DNAPL contamination and to develop alternative engineered controls that can minimize the impacts of their slow long-term release from source regions and immobile zones.

The research reported in this report relates to both of the above-stated concerns (better understanding of long-term contaminant fate and improved methods of engineered control) in the context of the large-volume downgradient dissolved and sorbed plume. This work follows and supplements a 3-year field investigation at Dover AFB (Mackay et al., 1997) in the following two disparate but highly relevant areas of research:

1. subsurface coring to investigate changes in contaminant concentrations in aquitards over time, including the modeling of this concentration profile development, both for forensic interpretation and for evaluation of implications to remediation design; and

2. column-scale investigations of zero-valent metal "barrier" technologies, which represent some of the more promising approaches of controlling the groundwater migration of contaminants emanating from long-term sources.

Both aspects of the work were able to take good advantage of existing facilities at the site, established during the prior project. More specifically, the soil coring work was able to benefit substantially from both the previously measured results of long-extant aquitard contamination and from our unique ability to maintain zero-flow groundwater conditions in the aquifer at this site. The column-scale investigations benefited from the available shelter, pre-installed groundwater wells (tapping the pre-existing contaminant plume external to the test cells), and on-site sampling, water treatment, and analytical equipment (Mackay et al., 1997).

This report describes each of the above two major thrusts in roughly similar detail; however, we emphasize that the vast majority of project resources and effort were focused toward the first issue (aquitard modeling and profiling), and that the column effort was conducted primarily as an exploratory effort. The aquitard coring work has been more extensively described through related peer-reviewed publications, as referenced herein. We anticipate future publications in both areas of endeavor.

A. OBJECTIVES

The broad objectives of this research effort were (a) to carefully evaluate the issue of aquitard contamination and associated aquifer concentration "rebound" within two isolated and pre-treated aquifer test-cells at Dover AFB, DE; and (b) to conduct some exploratory long-term pilot (column-scale) investigations of passive barrier remediation technologies that use zero-valent metals for the chemical transformation of halogenated organic contaminants in groundwater. More specific tasks in each of these areas are described below.

1. Evaluation of Contaminant Concentration Development in a Groundwater Aquitard and its Effect on a Nearby Aquifer

The principal focus of this effort was the continued evaluation of contaminant concentrations within the aquitard and adjacent aquifer region, using additional soil core samples taken from each of two field-scale "test cells" created and studied over the course of the prior project (Mackay et al., 1997). These two cells have been designated as the "continuously pumped cell" or CPC (last evaluated in April, 1996) and the "pulsed pumped cell" or PPC (last evaluated in May/June 1996). Toward this end, additional coring exercises were undertaken on two separate occasions, separated by at least 6-months from prior coring events. The contaminant concentration evaluation included extraction of core from the subsurface, sub-sampling of subsurface material from an array of closely spaced vertical locations within each core segment, and laboratory analysis of both PCE and TCE concentrations as a function of depth. An important aspect of the effort was the continued development and application of appropriate mathematical models for the interpretation of results. The latter was undertaken to provide due consideration of and comparison with similarly obtained "contaminant profiles" from the time frames immediately prior

to and after the "flushing" of pollutants from the aquifer over the course of the prior project (Mackay et al., 1997). In this context, the mathematical modeling is used not only to verify the nature of the diffusion process, but also to apply results to field-scale interpretations. The latter include both "forensic" interpretations (to better understand the plume history at the site) and "predictive" simulations (to better understand the potential effects of future remediation efforts).

Prior to and following the above coring analyses, the on-site analytical system was used to determine "rebound" concentrations of pollutants in the aquifer porewater, using selected monitoring points of the previously established multilevel piezometers (Mackay et al., 1997).

2. Long-term Column Investigations of Chlorinated Solvent Removal By Zero-valent Metals under Field Conditions

The objective of this research was to evaluate the long-term performance of two reactive metal materials in treating contaminated groundwater at Dover AFB, DE. In particular, a goal was to determine if long term exposure to site water and/or contaminants can have important impacts on treatment efficiency or metal reactivity.

B. BACKGROUND

The Air Force Research Laboratory, Airbase and Environmental Technology Division, (formerly Armstrong Laboratory, Environics Directorate) previously sponsored a three year research effort at Dover AFB, DE. The goals were (1) to carefully isolate two nearly identical portions of a naturally occurring aquifer contaminated with DNAPL constituents; (2) to completely characterize the soil matrices and contamination profiles within the two aquifer cells; and (3) to study the relative effectiveness of conventional pump-and-treat systems in one cell versus a pulsed pumping regime with conventional treatment in the other cell (Mackay et al., 1997). The results effectively demonstrated that reduced rates of pumping (as achieved through pulsed pumping) could offer substantial cost savings relative to more conventional treatment schemes in that similar levels of clean-up could be obtained while lowering the on-going operating costs.

Relevant details of the project site and of the prior project results are presented in subsequent chapters, as appropriate. Most central to the currently reported effort was the prior coring of

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aquitard samples and the analysis of these for halogenated contaminants. These results provided important new insights regarding the role of impermeable zones in affecting the cost and efficacy of long-term remediation efforts (Ball et al., 1997a; Ball et al., 1997b; Liu and Ball, 1998). In particular, aquitard contamination at the Dover site was shown to represent a long-term source of contamination "rebound" in the overlying aquifer, once pump-and-treat remediation was terminated. However, the time frame of the previous project (and of the "pump-off" periods in particular) was not sufficiently long to provide a complete understanding of the aquitard effects.

Because of the long-term chemical recalcitrance of DNAPL contaminants and their slow rates of continuing release to groundwater (resulting from both slow DNAPL dissolution and mass transfer effects of the type described above), there has been an increased interest in evaluating the efficacy of *in situ* "passive" and "semi-passive" remediation technologies, including several related studies and on-going field demonstration projects at DOD sites, including Dover AFB. Where existing conditions permit, the most "passive" alternative is "monitored natural attenuation" which relies on natural processes, most notably intrinsic biological degradation, to destroy contaminant mass and limit plume migration. A number of "semi-passive" approaches have also been developed for conditions dictating a need for engineered intervention; these so-called "barrier" technologies include continuous permeable barriers, "funnel-and-gate" systems, and discontinuous permeable barriers (e.g., arrays of unpumped wells or boreholes backfilled with permeable media). These technologies rely upon the flow of contaminated groundwater through zones within which engineered systems induce or support the chemical transformations of contaminants to more benign products. The goal of these systems is to stop or limit the migration of toxic contaminants beyond the engineered system. Currently, reactive iron materials are by far the most commonly promoted reactant for use in such semi-passive barrier technologies.

The physical facilities that remained at the Dover site from our prior project (available shelter, groundwater wells, water pumping and treatment systems, and previously leased analytical facilities) allowed extremely cost-effective long-term testing of two reactive metal "barrier" technologies. These tests were conducted within small columns fed essentially continuously with contaminated groundwater drawn from the aquifer underlying the Dover AFB site. Such an approach ensured that the reactive media experienced geochemical conditions that were very similar to those *in situ*.

The current project was thus undertaken in order to make additional advances toward the specific objectives outlined above, while taking best advantage of the previously developed facilities, methods, and understanding. No known Air Force agency/command or other agency had the necessary in-house capability or the specific knowledge of the soil stratigraphy and subsurface characteristics at this particular, well-characterized site to efficiently perform the tasks needed to meet these objectives within the required time frame. Thus a subcontract was established under the U.S. Army Research Office Scientific Services Program. In fact, the effort described in this report was only economically feasible by taking advantage of the three years of characterization and research effort applied to each of the sheet pile containment cells at the site, and the three years of research effort already expended there. The physical value of the existing containment cells (material and installation) is estimated at roughly $250,000 (including well instrumentation) and the combined worth of the existing facility and prior characterization effort is valued at well over $700,000.

C. PROJECT APPROACH

1. Overview and Context

The project was initiated by collaboration between Johns Hopkins University and the University of Waterloo to maintain existing analytical and process equipment at the site and to plan coring and sampling "events", during which the additional aquitard and multilevel sampling could be conducted. This group then worked with staff at Dover AFB, DE (hereafter referred to as DAFB) and the local Groundwater Remediation Field Laboratory (hereafter referred to as GRFL) to help schedule events and maintain the site. Analytical equipment previously set up in a commercial trailer at the site (Mackay et al., 1997) was provided at no cost for project use by the University of Waterloo. Rental of the commercial trailer was maintained during the current project for the housing of the analytical equipment, field sampling supplies, and pilot-column equipment. Pilot columns and pumping equipment installed for exploratory purposes in summer 1997 (under funding by the University of Waterloo) were maintained for the full duration of the current project, such that data from this project could be combined with those from the initial exploratory operation.

The previous development and history of this site is as described in detail elsewhere (Mackay et al., 1997). Briefly, site preparation (occurring in September of 1994) included the installation of side-by-side sheet piling boxes, driven from surface through the aquifer into the underlying aquitard. In the period between October 18 and October 27, 1994), each box (or "test cell") was instrumented with various types of wells, and soil core were taken at many of the locations of subsequent well installation. A similar coring exercise was conducted at the termination of the prior project – i.e., following the project's "pump-and-treat" operation, which involved "flushing" of the aquifer region of each cell by means of groundwater extraction, treatment, and reinjection (Mackay et al., 1997). It is important to note that the pump-and-treat operation did not commence until October 1, 1995, with groundwater in the cells remaining stagnant (and not subjected to engineered treatment) between the initial coring event and the beginning of pumping. The multilevel sampling of groundwater before and after this stagnation period indicated no obvious major changes in the concentrations of the major halogenated analytes. (We note, however, that the earlier sampling was not sufficiently detailed to observe spatial variations or more subtle changes of concentration – i.e., those well-under an order-of magnitude.) Termination of pump-and-treat in the continuously pumped cell (CPC) was on March 5, 1996, and final sample coring occurred between March 5 and March 8, 1996. Termination of pump-and-treat in the pulse-pumped cell (PPC) was on June 5, 1996, and final sample coring occurred between June 5 and June 8, 1996. Details of the pumping operation are as described elsewhere (Mackay et al., 1997).

Overviews of the approach in each major project area are provided below, as related to the two major tasks outlined under Objectives. For further details regarding approach and methodology in these two areas (in-situ concentration development and column-scale study), readers are referred to their individual discussions in Sections II and III, respectively.

2. *Evaluation of Contaminant Concentration Development in a Groundwater Aquitard and its Effect on a Nearby Aquifer*

This aspect of the work was approached by proceeding simultaneously with the acquisition of new field-scale data and the development and application of novel mathematical models for data interpretation. Overviews of the approach taken in each area are given below, and the effort is

further described in Section II.

a) Field Coring and Subsample Analysis

In the period January 20 to January 28, 1997, we conducted additional aquitard coring (with PCE and TCE analysis in closely spaced subsamples) at each of six plan locations (3 in each test cell). These results provide contamination profiles at a time corresponding to roughly 10 months since the termination of groundwater pump-and-treat (and prior coring) in the CPC and to roughly 7.5 months since the termination of groundwater pump-and-treat (and prior coring) in the PPC.

In the period September 28 and 29, 1997, we conducted additional aquitard coring (with PCE and TCE analysis in closely spaced subsamples) at each of two plan locations in the PPC test cell. These results provide contamination profiles at a time corresponding to roughly 15.5 months since the termination of groundwater pump-and-treat (and prior coring) in the PPC.

b) Modeling Evaluation of Subsurface Coring Results

In order to better understand and interpret the observed contamination profiles, we have continued to develop and apply novel mathematical approaches for incorporating our understanding of the chemistry and physics of aquitard sorption and diffusion. Our specific approach and associated developments in this area of work are somewhat complex and are more fully described in Section II.B.3.

3. *Long-term Column Investigations of the Treatment of Chlorinated Solvents By Reactive Metals under Field conditions*

In late July 1996, three experimental pilot columns were set up at the site. One contained Ottawa sand (control column), the second contained granular iron (Masterbuilder iron, Gillham et al., 1997), and the third contained Masterbuilder granular iron that had been "enhanced" by addition of a plated nickel coating (Gillham et al., 1997). Both reactive iron materials were provided by EnviroMetals Technologies (ETI), Inc., Guelph, Ontario. To ensure that the reactive metals were exposed to groundwater as representative as possible of that *in situ*, the groundwater was pumped directly to the column influent port from the contaminant plume by means of a pump

whose intake line terminated roughly 45 feet beneath the surface and at the location of a highly contaminated stratum. A key aspect of the project was the long-term operation of the columns, in order to elucidate any temporal variations in column behavior over an extended period of exposure to the contaminated groundwater. The columns were operated essentially continuously for over 400 days, corresponding to roughly 170 pore volumes for the iron column and 150 pore volumes for the enhanced iron column. Influent and effluent samples were analyzed by onsite, using the previously established automated analytical system (Mackay et al., 1997). The resulting data were used to estimate maximum values for the apparent half-lives of those contaminants for which treatment was noted. These results were compared to prior results from other field- or laboratory-based studies of the reactive metals. The column effort is described further in Section III.

Section II. CONTAMINANT CONCENTRATION DEVELOPMENT IN A GROUNDWATER AQUITARD AND ITS EFFECT ON AQUIFER REMEDIATION

A. BACKGROUND -- PRIOR WORK

In a 1994-1996 field-scale test at Dover AFB, DE (Mackay et al., 1997), the more permeable regions of two 3.7-meter by 9.9-meter by 15.9-meter deep test cells were flushed with multiple pore volumes of clean groundwater, either continuously (in the continuously pumped cell, CPC) or intermittently (in the pulse-pumped cell, PPC). As part of this prior effort, measurements of PCE and TCE concentrations were made on subsurface core samples from each of the cells, prior to and following the "pump-and-treat" operation. Total concentrations (sorbed plus aqueous) of PCE and TCE were determined throughout the permeable region of the aquifer and to depths of up to 1.8 meters down into a less permeable underlying aquitard. The results from these two coring periods are discussed separately below.

1. Coring Results from October 1994

The methods and analytical results from the soil coring effort prior to the initial of pump-and-treat within the test cells are presented in full detail elsewhere (Ball et al., 1997b; Mackay et al., 1997). Most of these initial results were based on composite samples (typically comprising four equally spaced subsamples), as was necessary in order to reduce the number of individual analyses to be conducted while still allowing us to provide good volumetric coverage for characterizing total contaminant mass in each test cell, which was a primary goal of the prior work (Mackay, et al., 1997). Of special interest, however, were the results obtained for a single core from which an especially high density of individual (non-composite) aquitard samples were taken. For this core, individual analyses were conducted on subsamples taken at 2.5-cm to 5-cm intervals over the entire 3 meters represented by the bottom 2 core segments, of which roughly 1.2 meters was in the aquitard. This core is identified as PPC-11, the location of which is shown in **Figure 1**.

Modeling analyses begun during our previous project showed that the results from this core could be readily explained in terms of a simple diffusion model and the measured variation in

PPC
CPC

○PPC11 ○CPC11

●PPC12 ●CPC12
▲PPC16 ▲CPC16
○PPC9 ○PPC7 ○CPC9 ○CPC7
▲PPC19 ▲CPC13
▲PPC20
●PPC13

○PPC5 ○CPC5
▲PPC17 ▲CPC17
●PPC14 ●CPC14

○PPC3 ○PPC1 ○CPC3 ○CPC1

●PPC15 ●CPC15
▲PPC18 ▲CPC18
○PPC10 ○CPC10

9.9 m

—1.5m—

—3.7m—
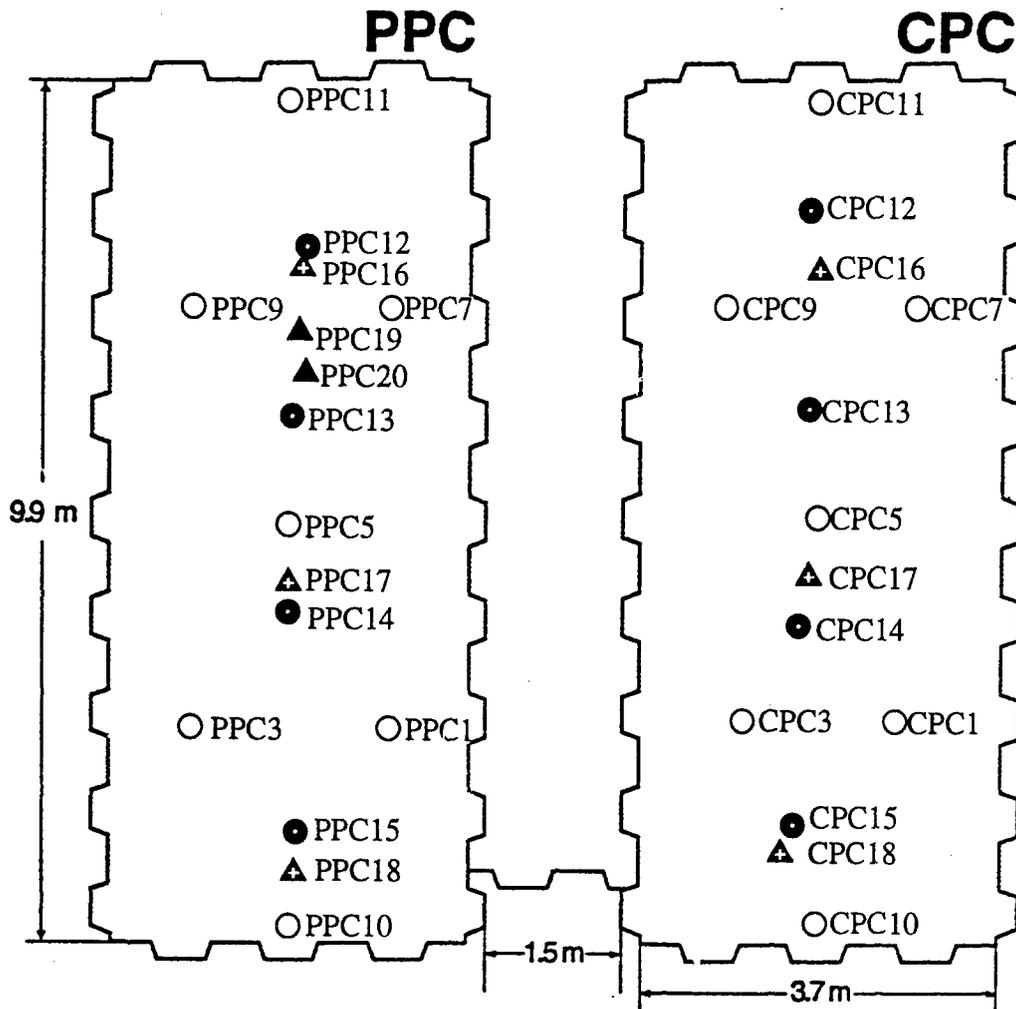
○	Pre-pumping* (10/18/1994-10/27/1994)
●	At pumping termination**
▲	237-244 days after PPC pumping termination** (1/28/1997-2/4/1997)
▲	480 days after pumping termination** (9/28/1997)

  * Pumping initiated on 10/1/1995 in both cells
** Pumping terminated on 3/5/1996 in CPC cell and on 6/5/1996 in PPC cell

Figure 1.   Location of Core Collection

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sorption properties among the different geologic layers sampled (Ball et al., 1997a). Within any one of these geologic layers, the data showed approximately smooth concentration gradients that we took to be indicative of both (1) good analytical precision and (2) reasonably uniform sorption and transport properties within the individual layers. Total contaminant concentrations showed sharp increases at the interfaces between the various formations, consistent with an independent assessment of the sorption properties of the three materials, and the overall profiles were shown to be well modeled by an assumed mechanism of diffusion through laminate slabs. Using a somewhat crude assumption that the concentration history within the groundwater plume at the site could be described in terms of one or two "step" changes, the aquitard profiles were subjected to a "forensic" modeling interpretation in order to make inferences regarding the nature of the concentration history at the aquitard's upper boundary (i.e., within the overlying aquifer). The results suggested that PCE contamination in the overlying groundwater had arrived between 10 and 15 years prior to the core sampling, with increased concentrations possibly occurring within the year immediately prior. Modeling of TCE data suggested that this plume also arrived at the site within the last 10 to 15 years, but that overlying concentrations had declined in the three years immediately prior to the core sampling. These forensic interpretations were found to be consistent with the observed plume locations at the time of our coring, as estimated from an independently conducted delineation of the regional PCE and TCE groundwater plumes at DAFB (Ellis et al., 1996).

We also showed how the field results could be used in conjunction with analytical modeling to estimate a hypothetical diffusive flux out of the aquitard during an idealized aquifer remediation (Ball et al., 1997a; Liu and Ball, 1998). Contaminant removal was shown to be particularly slow from the more strongly sorbing deeper aquitard layer (dark gray silt loam, or DGSL). Also, some initially slower fractional removal rates for TCE reflected the deeper initial location of most TCE mass. For both contaminants, removal rates were found to decrease quite dramatically over time owing to continued diffusion down into the aquitard and slow removal rates from the DGSL layer.

Perhaps the most important conclusion to be drawn from the prior work was with regard to the general applicability of the methods used. In particular, this case study amply demonstrated the potential value of aquitard sampling for site characterization. Aside from providing important

information about contamination in the impermeable zone, the careful analysis, characterization, and interpretation of a single field core can be used to provide valuable insight into the history of the overlying groundwater contamination. Key to the proper analysis are (1) good accuracy and precision of the experimental data; (2) careful characterization of the impermeable porous media (including the identification of potentially sharp property changes across geologic strata); and (3) accurate modeling of the relevant fate and transport properties. Remaining uncertainty of the modeling interpretations was associated primarily with our concerns about whether unrecognized heterogeneity of the porous medium might be affecting the results, and our inability to absolutely rule out the possibility of vertical advection of groundwater or chemical transformation of analytes. In these regards, it was clear that we could learn a great deal about the utility of this approach and the validity of our prior efforts by conducting additional coring and modeling at this site. In addition to providing more information about aquitard heterogeneity, future coring samples would have the additional advantage of having been under well-understood boundary conditions in their most recent history (i.e., after installation of the sheet-piling walls that isolated the area from the surrounding contaminant plume).

2. *Coring Results from March and June, 1995*

Also as part of our prior work (Mackay et al., 1997), subsurface coring and associated VOC analysis was conducted on four cores in each cell. These cores were designated as CPC-12 through 15, which were taken and sampled between March 5 and March 7, 1997, after termination of CPC pumping, and PPC 12 through 15, which were taken and sampled between June 5 and June 7, 1997, after the last pumping period in the PPC. Locations of these cores are also shown in **Figure 1**.

For the final coring, individual closely spaced sampling was conducted, in recognition of the importance of this high level of resolution toward diffusion-based interpretation of the data. In order to meet the somewhat separate objective of obtaining total mass estimates within the test cells, these cores were spaced evenly over the length of each test cell (**Figure 1**) and their results used to make total estimates of remaining concentrations in each test cell (Mackay et al., 1997).

The postpumping core results (presented and discussed in Mackay et al., 1997) clearly illustrated that the pump-and-treat operation (in either continuous or pulsed mode) had very

effectively removed contaminants from the more permeable aquifer sands, but that concentrations remained near their prepumping levels within deeper aquitard regions.

3. Motivation for Follow-up Study

Unfortunately, the time and budgetary constraints of the prior project were such that a full mathematical (diffusion-based) interpretation of the coring results could not be conducted. Moreover, the results gave clear indications that the uppermost regions of the aquitard had begun to feel the influence of the low concentration "boundary condition" that had been created by the pumping of clean water through the permeable strata in contact with the aquitard. In this context, it was quite apparent that a longer-term investigation of contaminant rebound could provide a better verification of the proposed mechanism of diffusion, and that this site was uniquely appropriate for such a study because of the excellent control of groundwater flow afforded by the sheet-piling test cells. More specifically, the sealed sheet-piling walls and low permeability aquitard could be presumed to provide a totally stagnant flow condition in the absence of water injection or withdrawal from the cells (**Figure 1**). This unique opportunity formed the basis for proposing and conducting a follow-up study of the continuing contaminant diffusion within the aquitard and deeper aquifer strata.

B. OBJECTIVES

The overall goal of the aquitard coring and modeling was to better evaluate, model, and understand the issue of aquitard contamination and associated aquifer concentration "rebound" within two isolated and pretreated aquifer test-cells at Dover AFB, DE. Both new field data and further model development and application were sought in order to verify the nature of the diffusion process and to better understand our ability to apply results to field-scale interpretations. The latter include both "forensic" interpretations (to better understand the plume history at the site) and "predictive" simulations (to better understand the potential effects of future remediation efforts). More specific objectives of the research were as follows:

1. Continue to develop and apply appropriate mathematical models for the interpretation of the coring results obtained in the prior project. Such continued model development was focused toward two objectives:

a) fundamental research into appropriate solutions of the "inverse" problem associated with estimating plume histories from concentration profiles in aquitards; and

b) refining our estimate of the aquifer concentration history at the DAFB site, as needed for the better approximation of "initial" (June, 1995) conditions applicable to the cores taken at later dates (item 2 below).

2. Acquire new results of aquitard and aquifer concentrations at time periods sufficiently long after the cessation of pump-and-treat to observe contamination "rebound" in the aquifer and continued movement of chemicals in the aquitard. These cores serve to

    a) demonstrate the nature of the effect that a contaminated aquitard can have on the adjacent aquifer; and

    b) provide important new field data with which to test our modeling assumptions.

3. Develop and apply the necessary modeling approaches for predicting contaminant movement under stagnant conditions (for comparison with the field data from the second objective). In particular, we needed to develop a multilayer diffusion model that could incorporate our previous understanding of aquitard diffusion and initial conditions with a condition of chemical diffusion up into the deeper region of a now stagnant aquifer.

Although not a specific objective of the current project, our ultimate intention has been (and is) to apply the results from this project toward better simulation and design of alternative monitoring approaches and clean-up strategies.

C. EXPERIMENTAL APPROACH

1. Field Coring and Subsample Analysis

In the period January 20 to January 28, 1997, we conducted aquitard coring, with PCE and TCE analysis for closely spaced subsamples, at each of six plan locations (3 in each test cell). These cores have been designated as CPC- (or PPC-) 16, 17, and 18, and were taken at the locations indicated in **Figure 1**. The results provide contamination profiles at a time corresponding to roughly 10 months since the termination of groundwater pump-and-treat (and prior coring) in the CPC and to roughly 7.5 months since the termination of groundwater pump-

and-treat (and prior coring) in the PPC.

On September 28 and 29, 1997, we conducted additional aquitard coring (with PCE and TCE analysis in closely spaced subsamples) at each of two plan locations in the PPC test cell. These cores have been designated as PPC-19 and PPC-20, and were taken at the locations indicated in **Figure 1**. The results provide contamination profiles at a time corresponding to roughly 15.5 months since the termination of groundwater pump-and-treat (and prior coring) in the PPC, or roughly double the time since the January cores.

2. *Aqueous Sampling of Multilevel Piezometers*

For aqueous sampling, we took advantage of the multilevel piezometers previously installed at the site (Mackay et al., 1997). These piezometers were constructed of 1/8-inch stainless steel tubing. Eight piezometers existed at each of 18 plan locations, bundled to a single 1.3 cm (1/2 inch) PVC stalk and with each piezometer extending to a different sampling depth. Readers are referred to Table 1 of the prior project report (Mackay et al., 1997) for details. These piezometer bundles were originally installed within the same external steel casing from within which prior aluminum core tubes had been taken (Mackay et al., 1997; Starr and Ingleton, 1992). Once the casing was fully extracted, aquifer material below the water table collapsed back into the open hole against the piezometer bundle, firmly holding it in place. The plan locations of these multilevel piezometers have been shown in our prior report (Mackay et al., 1997) and elsewhere (see Figure 1 of Ball et al., 1997b). There are a total of 18 multilevel piezometers, including 10 locations at which October 1994 cores were also taken. These ten locations are PPC-1, -3, -5, -7, and -9 and CPC-1, -3, -5, -7, and -9; see **Figure 1**.

In the period January 23 to January 31 1997, we conducted aqueous sampling and analysis for VOC concentrations from the two deep-most points of all 18 multilevel piezometer locations. The January 1997 sampling of these piezometers was conducted in the days immediately *after* the taking of January 1997 core from the same test cell. We deliberately did not conduct *any* aqueous sampling in the period between the prior coring (March or June, 1995) and the taking of the January 1997 cores in order to avoid any possibility that the withdrawal of groundwater might affect contaminant distributions in subsequently taken cores.

In January 1997, we also measured pH and dissolved oxygen at all depths in six different plan locations (CPC-2, CPC-5, CPC-8, PPC-2, PPC-5, and PPC-8). The objective of this effort was to confirm that aerobic conditions still existed in the groundwater, as created during the prior flushing project. Such conditions should tend to inhibit reductive transformations of the chlorinated species, simplifying our modeling of the transport processes. We have been encouraged in this regard by the very good mass balances achieved in our prior work (Mackay et al., 1997).

In the period between July 16 and August 14, 1997, and prior to the coring of September, 1997, we conducted additional multilevel piezometer sampling at four locations. In particular, we took a series of samples over the course of this four-week time interval at the two deep-most sampling depths at each of two plan locations. The two plan locations are referred to as CPC-2 and PPC-2, and are located between CPC-1 and CPC-3 and between PPC-1 and PPC-3, respectively (**Figure 1**). The intent of these samples was to provide a brief history of continuing contaminant "rebound" in the deeper region of the aquifer, but at a location sufficiently far removed from subsequently planned cores (PPC-19 and PPC-20, **Figure 1**) as to avoid the possibility of disturbing the *in situ* contaminant concentrations at the coring locations.

3. *Modeling Evaluation of Subsurface Coring Results*

In order to better understand and interpret the observed contamination profiles, we have continued to develop and apply novel mathematical approaches for incorporating our understanding of the chemistry and physics of aquitard sorption and diffusion.

a) A preliminary interpretation of the "initial" (i.e. prepumping) contamination profiles at the site, as measured in November of 1994. More specifically, we completed the analysis and publication of our preliminary "forensic" interpretations of these results in terms of some inferred plume histories (Ball et al., 1997a), by invoking an assumption of step changes of concentration in the overlying aquifer and employing our previously developed analytical solution (Liu and Ball, 1998).

b) Development of an improved method of forensic interpretation, in which boundary concentrations are allowed to be smooth functions of arbitrary form (Liu and Ball, 1998b).

c) Reevaluation of the inferred boundary concentrations (developed under task 1 above), using newly developed methods (Liu and Ball, 1998) and incorporating both the "initial" (November, 1994) and "final" (May/June, 1995) coring results. In addition to providing an improved estimate of the overlying plume history (needed for task "d" below), this exercise allows us to further verify our process understanding by (a) confirming that the inferred boundary conditions during "postpumping" agreed qualitatively with our expectations, and (b) allowing a direct comparison of the similarities and differences in the individual forensic interpretations from these two sets of cores.

d) A final confirmation of our understanding in this system by comparing model predictions with our most recently obtained sets of coring results (January 1997 and September 1997). For these locations, we have had to infer the concentration profiles which existed in June, 1995 (i.e. at the termination of pumping) by applying our estimated history of boundary conditions (from task "c" above) to the specific physical/chemical situation at these core locations, as independently determined from the core logs and sampled core materials. For this purpose, a new modeling approach was needed that allowed the modeling of more than two layers following an arbitrary (user specified) initial condition. The analytical solution for this model was also developed under this project and has been separately published (Liu et al., 1998). An overall schematic of the approach (taken from Liu and Ball, 1997) is provided in **Figure 2**.

D. MATERIALS AND METHODS

1. Field Coring and Subsample Analysis

The core sampling and subsampling techniques applied at the DAFB site have been described elsewhere (Ball et al., 1997b). Briefly, 1.5-meter segments of aquitard cores were brought to the surface in 5.1-cm internal diameter aluminum core tubes (Starr and Ingleton, 1992), core segments were longitudinally split in the field, and subsamples of the water-saturated core material were obtained in the field by means of 8 mm ID stainless-steel coring devices. All subsamples were field-preserved in methanol for subsequent analysis of *in situ* concentrations of TCE and PCE, using a hot (70°C) methanol extraction technique. This method facilitates diffusion of the contaminants from intraparticle regions of the solid phase, and has been recognized to

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┌─────────────────────────────────────────────────────────────┐
│ f(t) = concentration history at upper boundary (in aquifer)  │
└─────────────────────────────────────────────────────────────┘
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┌──────────────────────┐   ┌──────────────────────┐   ┌──────────────────────┐
│ Observed profile for │   │ f(t) used to estimate│   │ Predicted profiles   │
│ **PPC-13** at time = T2; │ │ profile for **PPC-16, -19** │ → │ for **PPC-16, -19** │
│ used to infer f(t) * │   │ at time = T2 *   │   │ at time = T3, T4 ** │
└──────────────────────┘   └──────────────────────┘   └──────────────────────┘

Notes:
* Liu and Ball, 1998a (analytical solution for step function)
  Ball et al., 1997 (application of step function to data)
  Liu and Ball, 1998b (inverse method for arbitrary function; application to data)
** Liu et al., 1998 (analytical solution for multi-layer advection-dispersion
  Liu and Ball, 1998b (application of multi-layer solution to data)

Figure 2. Schematic Diagram of Modeling Approach

provide much better recovery of tightly bound organic contaminants than simple purge-and-trap or other commonly applied methods (Ball et al., 1997b; Huang and Pignatello, 1990). Minimum quantification limits for the method have been estimated at approximately 1 μg/kg for PCE and 2 μg/kg for TCE, assuming a 5-gram subsample (Ball et al., 1997b).

As a final caveat relative to the VOC analysis technique, we note that the extraction efficiencies from the aquitard material have been estimated to be 83% and 91% for single-step extraction of PCE and TCE, relative to multiple extraction results with selected field samples (Ball et al., 1997b). These results, together with some separate spiked extraction studies, suggest that the reported aquitard data may reflect a negative bias. Although this bias should have little effect on *relative* concentrations within the aquitard, it will affect comparisons at the aquitard/aquifer interface, since estimated extraction efficiencies in the *aquifer* approached 100%

for the first extraction (Ball et al., 1997b). For the purposes of the modeling efforts described subsequently in this paper, we will use the single extraction results as representative estimates of relative concentrations in the aquitard. Extraction efficiencies are taken into account only when comparing the apparent aqueous concentrations at the aquifer/aquitard interface (Ball et al., 1997a).

2. Aqueous Sampling of Multilevel Piezometers

Aqueous samples from the January 1997 and late summer 1997 multilevel sampling efforts were taken using a similar method as in our prior project (Mackay et al., 1997). Briefly, groundwater was drawn to the surface from each multilevel monitoring point individually by means of a peristaltic pump, with sample collected in a flow-through vial located between the piezometer and sampling pump. More specifically, groundwater from the stainless steel multilevel sampling tubes was made to pass through headspace-free 40-ml EPA glass vials by means of custom-fabricated two-port stainless steel caps with 1/8 inch stainless-steel inflow and outflow lines and viton o-ring seals. Only a short length of viton tubing was used to connect the multilevel sampling line and the flow-through VOC sampling vial, such that groundwater had very little exposure to organic polymeric materials prior to passing through the glass vial. After at least three vial volumes of groundwater were flushed through the system, the sampling caps were removed and the vials were sealed (headspace-free) with Teflon-lined septa and screw caps.

In the multilevel sampling for VOC concentrations, a total of 106 aqueous samples were taken from 45 piezometer sampling points, comprising the 2 deepest sampling levels at each of 20 plan locations, and an additional shallower depth at 5 locations. The plan locations included all 9 ML-nest locations in each cell as well as 2 depths at the ML-1 location outside of the cells. These external sampling piezometers were sampled in order to provide high concentration samples for comparative analysis in our laboratories here at JHU. 65 of these samples were analyzed in the field within one week of collection, including at least one sample from each piezometer as well as selected duplicate samples. 35 of the aqueous samples were duplicates, stored under refrigeration for 3 to 4 weeks on site and then subsequently analyzed to check for losses during storage (estimated at roughly 20%). These duplicate samples are not subsequently reported.

The samples were analyzed on-site, using the Automated Sampling and Analytical Platform (ASAP System, A+RT, Millpitas, CA). This system was operated in an identical manner as in the previous project (Mackay et al., 1997) and as briefly described in Chapter 3.

The primary means of quality control for the field analytical system was the routine analysis of standards, referred to as calibration control check (or CCC) samples. One important note is that although we had difficulties with maintaining quality control on chromatographic response factors over some of the project period (as described in Chapter 3), we were careful to bracket all sample results during the January 1997 analytical period with freshly prepared calibration standards and to use appropriate averaged response factors for all quantification. Our level of accuracy and precision for these results is thus believed to be generally better than for the August multilevel sampling period, or for most of the column results as described in Chapter 3. In general, we estimate the accuracy and precision of analytical results for the January multilevel samples to be on the order of 10% to 15%, based on quality control standards analyzed during this period (standard deviation of replicate analyses).

On February 2, 1997, dissolved oxygen (DO) and pH were measured in aqueous samples from 6 wells (PPC-8, PPC-5, PPC-2, CPC-8, CPC-5, and CPC-2 in continuous-pumping cell) to check for any major changes of these parameters in the aquifer groundwater during the postpumping period. Sampling for pH and DO was conducted using peristaltic pumps to pull groundwater from the piezometer points, with in-line measurements of both pH and oxygen using microprobes (Microelectrodes, Inc., Bedford, NH, Models 8-705 and 8-730) for pH and DO. Further details of the method are provided elsewhere (Mackay et al., 1997).

3. Modeling Evaluation of Subsurface Coring Results

A generic analytical solution to a two-layer diffusion problem was developed based on the characteristics of the DAFB two-layer aquitard (Liu and Ball, 1998). In the modeled problem, a layer of finite thickness is assumed to lie directly below the aquifer and a second layer of different transport properties and an assumed infinite thickness (representing the DGSL) is assumed to lie below this. These layers were modeled in order to simulate the two aquitard layers previously identified at Dover AFB, and previously identified as an orange silty clay layer (OSCL) and an underlying dark gray silt loam (DGSL). Although the assumption of infinite thickness for the

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DGSL does not represent the actual situation, this assumption can be justified because contaminants in the aquitard are not expected to penetrate the second layer within the time frame of the model application (for example, 1000 years) owing to the slowness of the diffusion process and the high sorption capacity of the layer. The developed analytical solution is generic in the sense that the boundary concentration and initial concentration for this two layer system could be arbitrary functions, and thus applicable to any two layer diffusion system.

For the evaluation of the specific subsurface coring results in the DAFB aquitard, the analytical solution was useful in evaluating two kinds of problems. The first of these was the estimation of the boundary concentration changes at the interface between the aquifer and aquitard, assuming the contaminant release history in the field site to be represented by a step function (Ball et al., 1997a; Liu and Ball, 1998). The second application of this diffusion model was to evaluate the potential remediation risks of cleaning up the contaminated aquifer due to slow mass diffusion from the underlying aquitard under an assumed boundary concentration during remediation (Ball et al., 1997).

To relieve the constraint that the aquifer boundary concentration must follow a step function, we investigated a more sophisticated method, of inverse modeling for estimating the boundary concentration at the aquifer/aquitard interface. This method is hereafter referred to as the "regularized least square method" and will be more fully described in an upcoming publication (Liu and Ball, 1998). In this method, the boundary concentration to be estimated is assumed to be any arbitrary smooth function. This function can then be estimated by minimizing an objective function consisting of a term of squared errors between the calculated and observed data, multiplied by a regularization term. The introduction of a regularization term in the objective function serves to reduce oscillation and impose smoothness on the solution. Such a smooth function is perhaps more appropriate for the DAFB situation than our previously assumed step changes in concentration, since advection and dispersion processes will tend to smooth out concentration changes in the contaminant plume. By applying this solution to the observed profiles in both the October 1994, and June 1996 coring results, we are able to obtain a revised estimate of the concentration history at the site up to the June 1996 time.

Once the overlying groundwater history has been estimated, this boundary concentration can

be used (together with the aquitard layer thickness information of **Table 1** to infer the contamination distributions that existed at the termination of pumping (e.g. June 1996 for the PPC) at the locations of subsequent coring at the site (e.g., at locations PPC-16 through PPC-20, **Figure 1**). Finally, we can predict the concentration profiles that we would expect to develop in both the aquitard and aquifer under the stagnant hydraulic conditions that existed between the termination of pumping and the time of actual sampling. For this purpose, we have developed an analytical solution for contaminant diffusion in multilayer porous media (Liu et al., 1998). Comparison of such predictions with the measured data (e.g. in PPC 16 through PPC-20) can allow us to verify our assumptions regarding the diffusive mass transfer process in the aquitard, thus validating our other model applications and conclusions. The overall logic of this approach is as previously illustrated in **Figure 2**.

E. RESULTS

1. Field Coring and Subsample Analysis

a) Coring Results from January 1997

Sampling results from the coring conducted between January 20 and January 28, 1997, are presented for PCE and TCE in **Figure 3** and **Figure 4**, respectively. In these figures, the January results are shown adjacent to our previous results from spring of 1996. As evident from the figure, the general trends of the January 1997 results are similar to those observed at the end of the pumping project (March and June, 1996). More specifically, concentrations of both TCE and PCE are severely reduced near the aquifer/aquitard interface, reflecting the diffusion of material out into the overlying aquitard.

Concentrations down within the aquitard vary significantly from core to core (**Figures 3** and **4**) and depend strongly on the location of an interface between two geologic strata within the aquitard. These strata have been extensively characterized in our prior work (Ball et al., 1997b) and are identified on the basis of color and particle size distribution as an orange silty clay loam (OSCL) and a dark gray silty loam (DGSL). Depth locations of the interface between these materials (and of the interface between the overlying aquifer) have been estimated for all 30 of the cores taken from within the two test cells, as shown in **Table 1**. The upper surfaces of the OSCL

TABLE 1. CORE LOCATIONS WITH DEPTHS TO AQUITARD LAYERS

Core ID	x (m) (East-West) From GS datum*	y (m) (North-South) From GS datum*	Depth to OSCL (m) Local	Depth to OSCL (m) From GS datum*	Depth to DGSL (m) Local	Depth to DGSL (m) From GS datum*
PPC-1	6.45	7.6	14.38	14.44	15.14	15.19
PPC-3	8.55	7.6	14.	13.98	14.79	14.77
PPC-5	7.53	5.15	14.13	14.09	14.96	14.92
PPC-7	6.45	2.55	14.08	14.06	14.72	14.71
PPC-9	8.55	2.55	14.16	14.16	14.88	14.87
PPC-10	7.5	10.	14.1	14.2	14.95	15.05
PPC-11	7.55	0.1	14.	14.13	14.75	14.89
PPC-12	7.35	1.83	14.06	14.06	14.83	14.83
PPC-13	7.5	3.85	13.97	13.97	14.87	14.87
PPC-14	7.53	6.2	14.09	14.1		
PPC-15	7.43	8.85	14.19	14.2		
PPC-16	7.4	2.08	14.12	14.07	14.77	14.72
PPC-17	7.53	5.85	14.2	14.19	15.21	15.2
PPC-18	7.45	9.35	14.39	14.39	15.13	15.13
PPC-19	7.43	2.84	14.05	14.07	14.82	14.84
PPC-20	7.36	3.33	14.	13.99	14.77	14.76
CPC-1	1.05	7.5	14.59	14.59	15.01	15.01
CPC-3	2.7	7.5	14.53	14.54	15.03	15.04
CPC-5	1.9	5.05	14.58	14.64	15.21	15.28
CPC-7	0.85	2.53	14.31	14.41	15.06	15.16
CPC-9	2.9	2.53	14.07	14.45	14.57	14.95
CPC-10	1.9	9.95	14.71	14.88		
CPC-11	1.9	0.1	13.91	14.	14.59	14.67
CPC-12	2.	1.38	14.18	14.16	14.89	14.87
CPC-13	2.	3.75	14.52	14.58	15.16	15.22
CPC-14	2.1	6.35	14.71	14.73	15.17	15.19
CPC-15	2.15	8.75	14.63	14.7	15.2	15.27
CPC-16	1.9	2.1	14.25	14.25	14.8	14.8
CPC-17	2.	5.75	14.67	14.69	15.22	15.24
CPC-18	2.28	9.1	14.7	14.74	15.17	15.2

* GS datum is a point 0.34 meters below a benchmark established at northeast corner of the CPC, on top of the sheet piling wall.
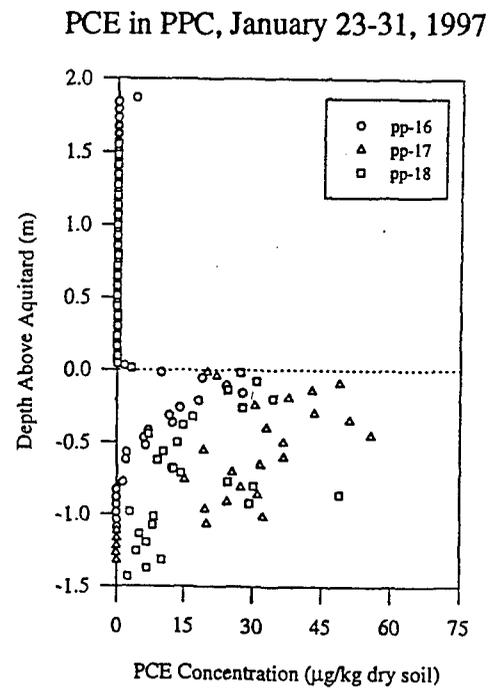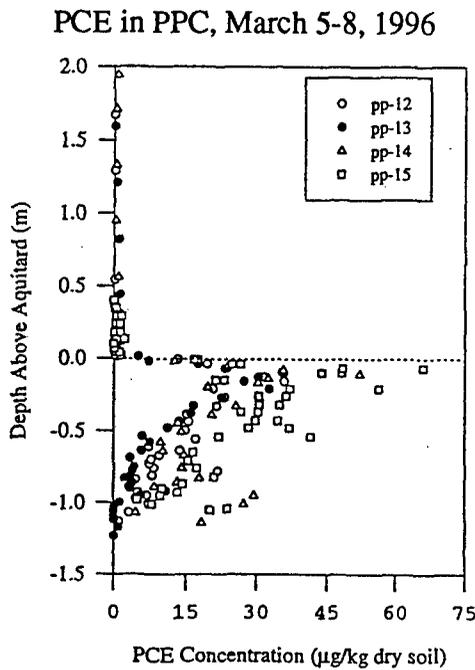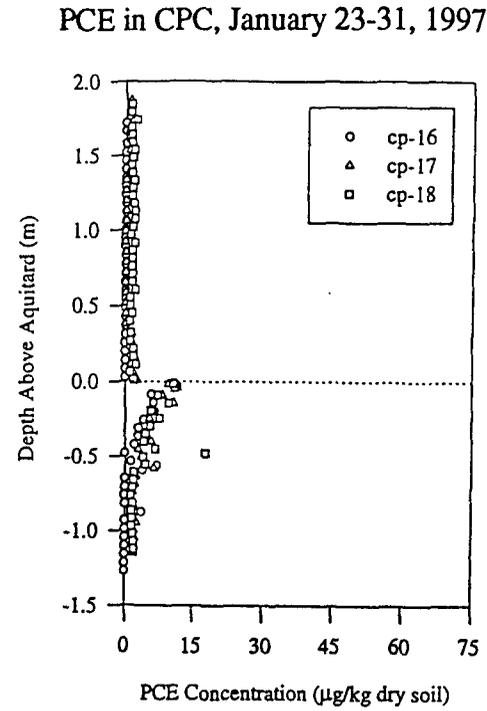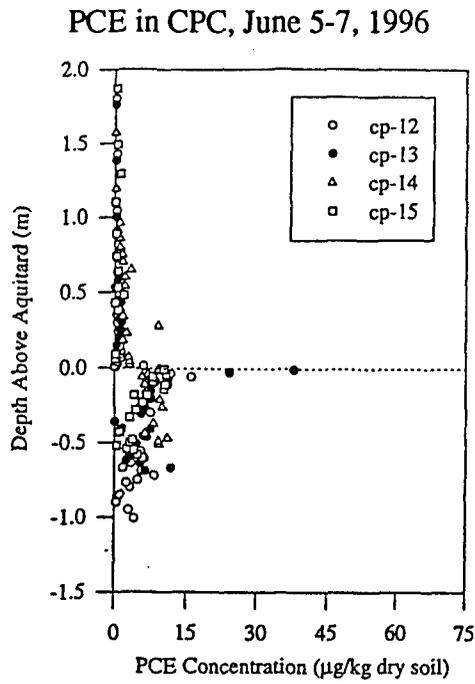
**Figure 3.** Core Sampling Results for PCE in Spring, 1996, and January, 1997.

TCE in CPC, June 5-7, 1996
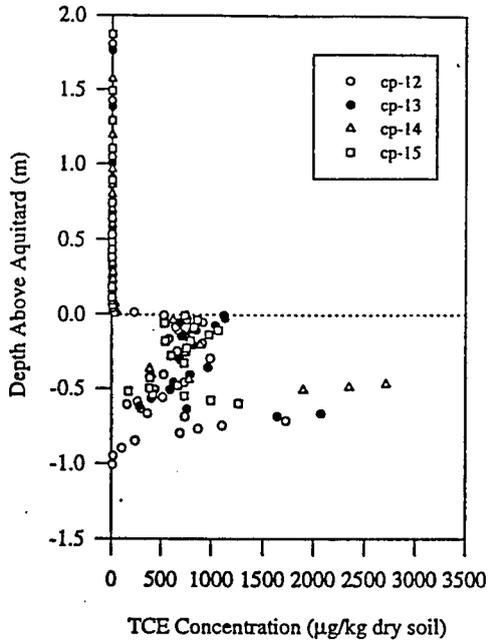
TCE in CPC, January 23-31, 1997
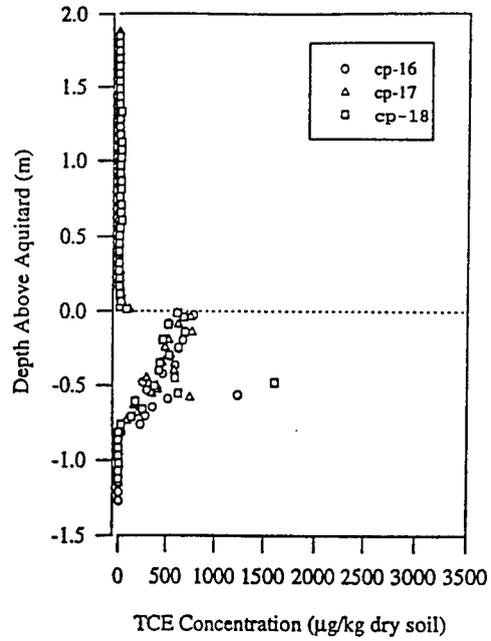
TCE in PPC, March 5-8, 1996
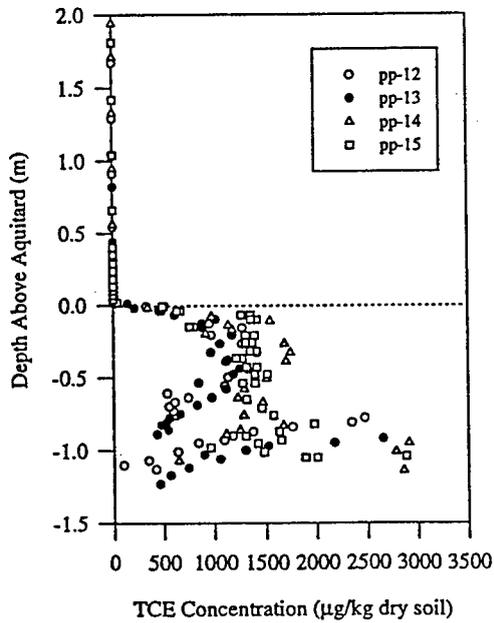
TCE in PPC, January 23-31, 1997
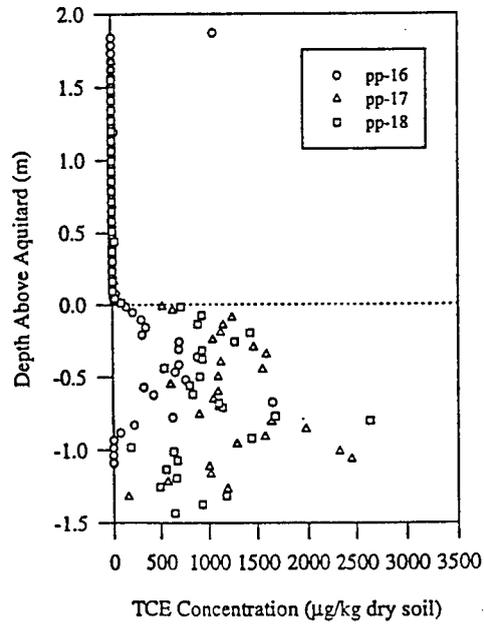
Figure 4. Core Sampling Results for TCE in Spring, 1996, and January 1997.

and DGSL layers within the two test cells have been estimated using automated contouring procedures (SURFER, Golden Software, Golden, CO) and are as shown in **Figure 5**.

A closer inspection of the coring results for PCE is provided in **Figure 6** for the three cores of the CPC and in **Figure 7** for the three cores of the PPC. Coring results for TCE are shown in **Figure 8** for the cores of the CPC and in **Figure 9** for the cores of the PPC. Generally, the results confirm our prior finding of significant changes in *total* concentration at boundaries between different geologic media, but with approximate continuity of aqueous concentration. Overall the data also show continued contaminant diffusion, with lower concentrations near the aquitard surface but deeper penetration of contamination. Unlike the earlier profiles, however, these January profiles also reflect upward diffusion out of the aquitard and into the now stagnant aquifer. At the time of this writing, the modeling of these results is ongoing, following the approach previously shown in **Figure 2**. Preliminary results of the modeling efforts are therefore only briefly described in this report (Section 2.5.3 below). Here we note that the modeling effort also involves a further analysis of the June 1996 and October 1994 coring results, and that the overall continued modeling effort is being funded through a Dupont Educational Aid Grant made available to W. Ball.

b) Coring Results from September, 1997

Sampling results from the PPC coring conducted September 28 and 29, 1997, are presented for PCE and TCE in **Figures 10** and **11**, respectively. As with the January results, these results confirm our prior finding of significant changes in measured *total* concentrations at the boundaries between different geologic media. Also as before, the data reflect continuing contaminant diffusion both upward and downward, except that movement has now occurred over a longer-duration. Although modeling interpretations are ongoing, preliminary results are briefly described in Section II.E.3 subsequently.
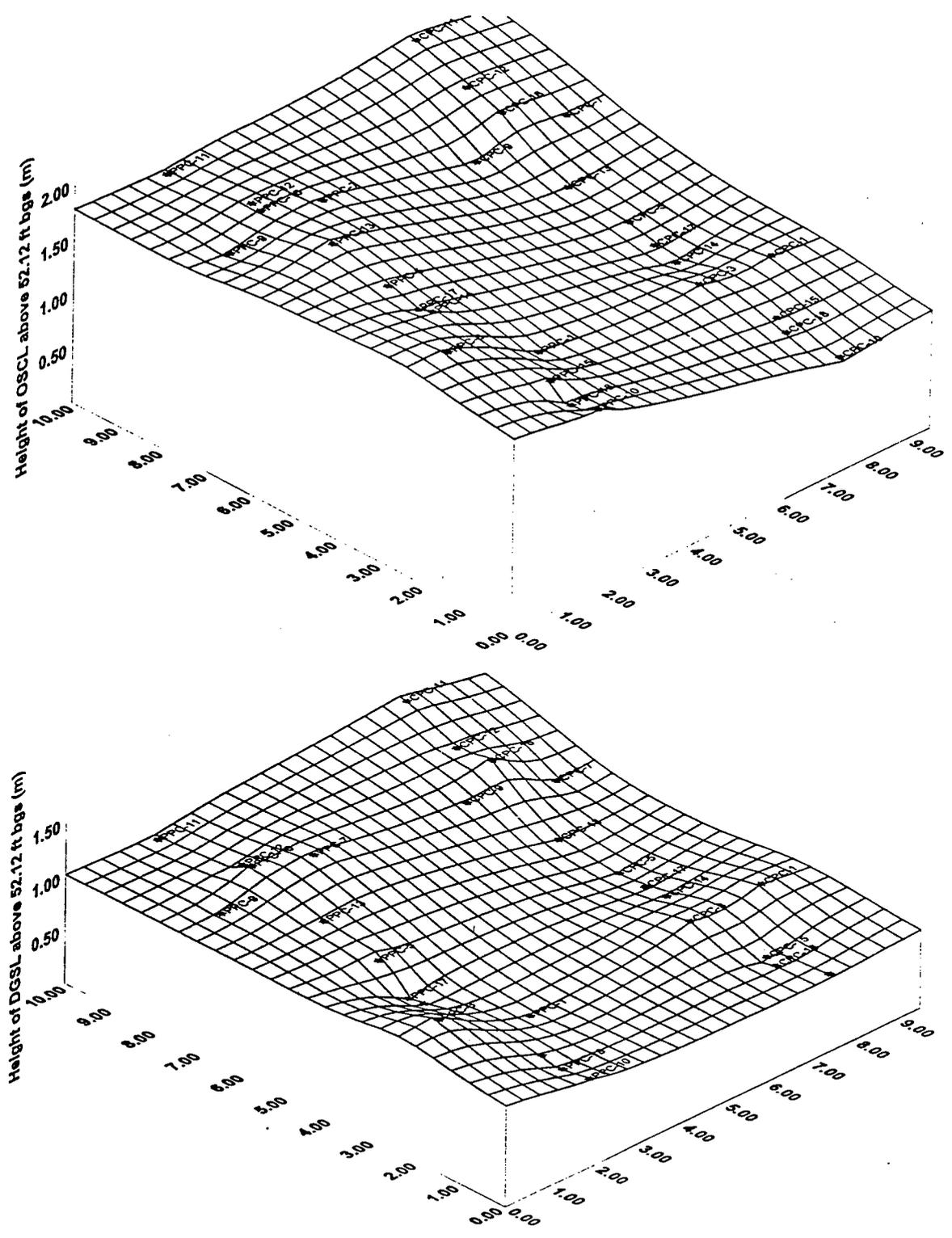
Figure 5. Surface Contour Map of OSCL and DGSL Layers
(Cores at the unmarked locations in the bottom figure did not contain the DGSL interface.)
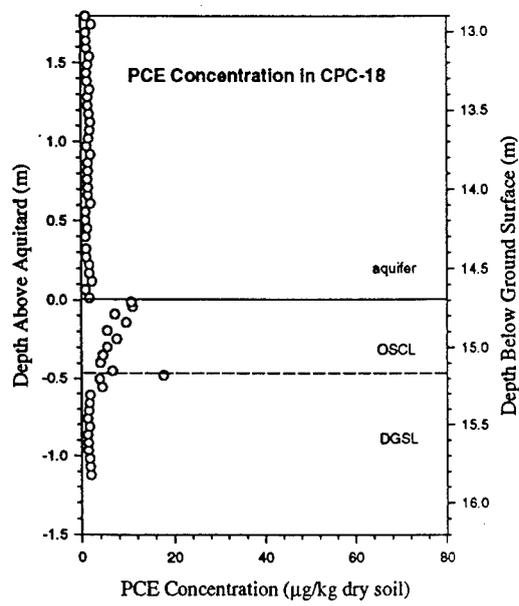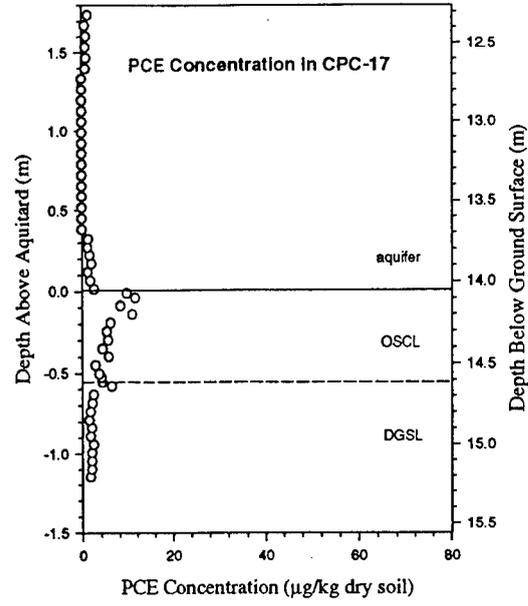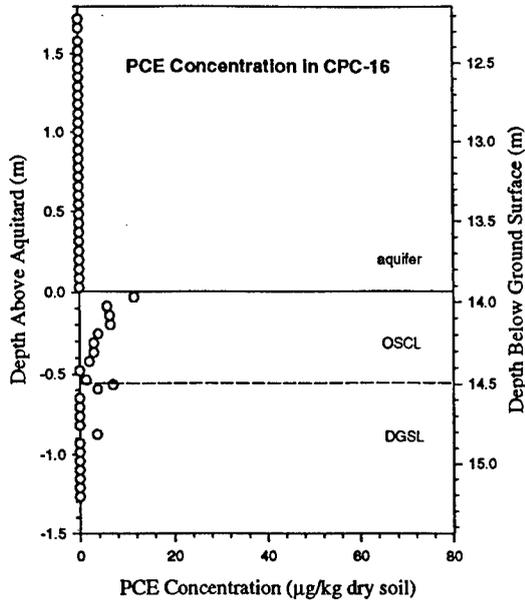
Figure 6. CPC Core Sampling Results for PCE in January, 1997.
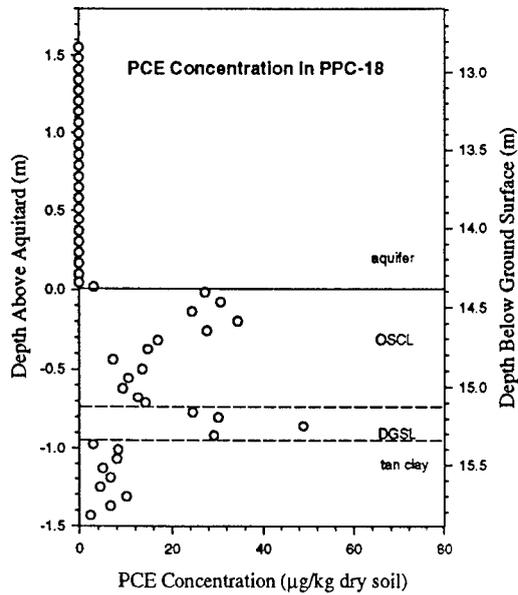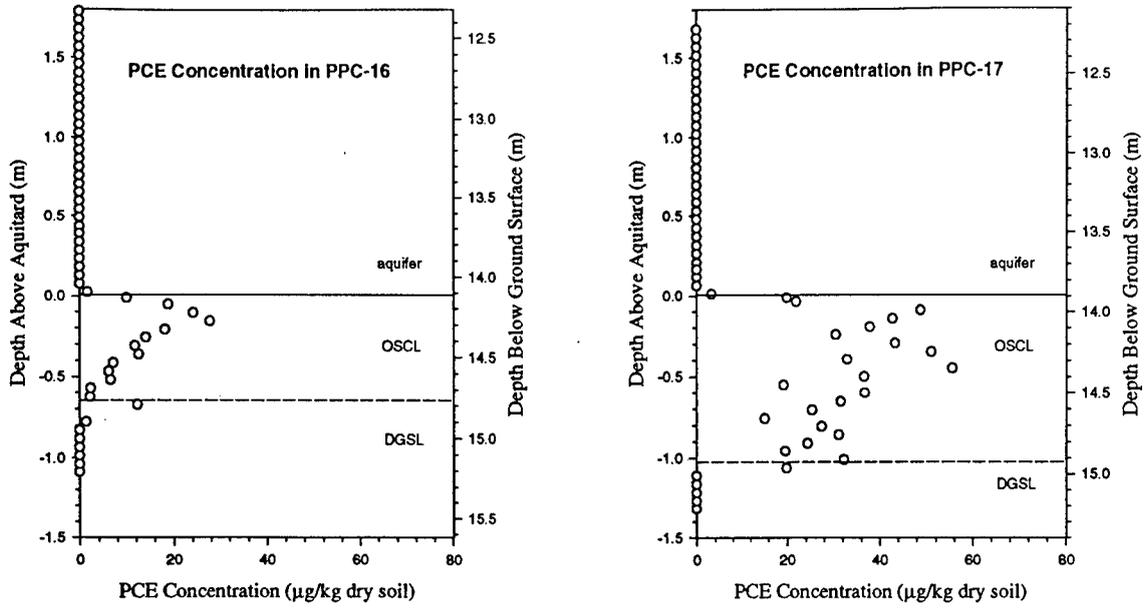
Figure 7. PPC Core Sampling Results for PCE in January 1997.
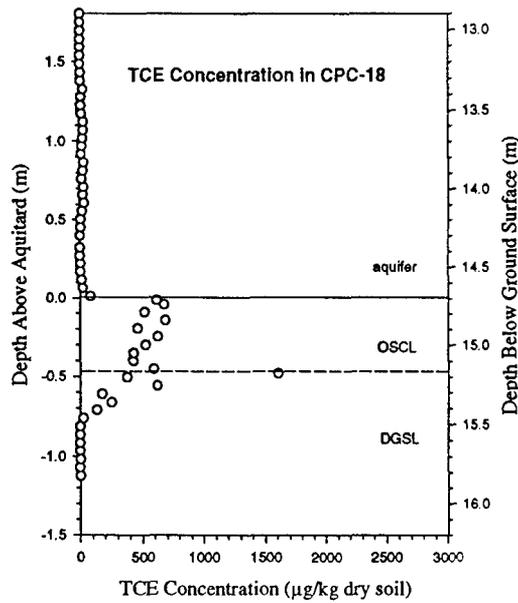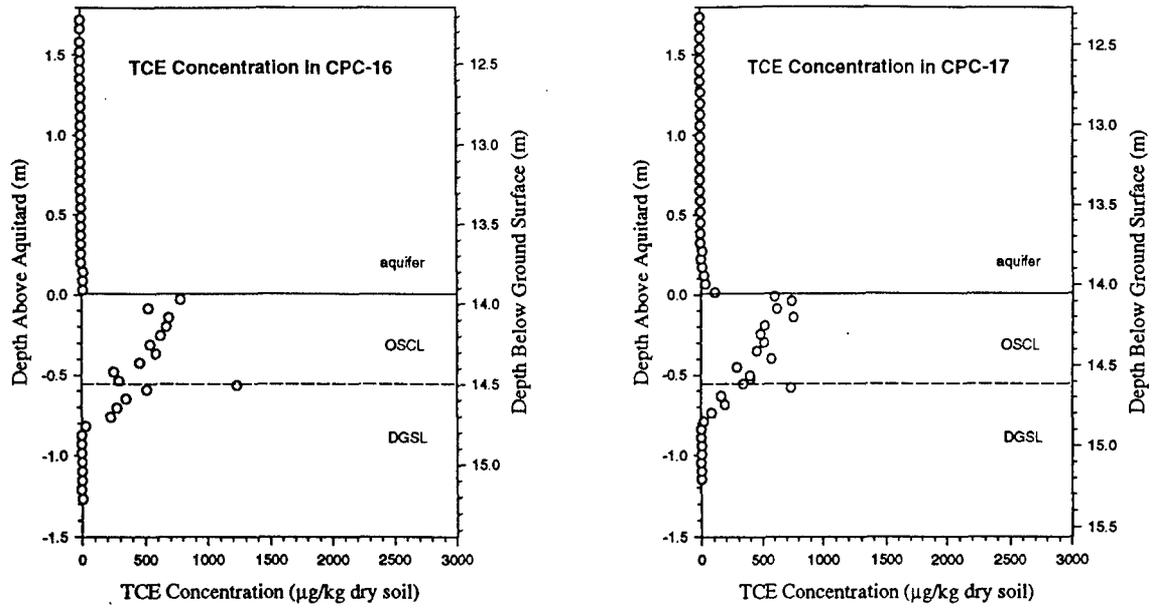
Figure 8. CPC Core Sampling Results for TCE in January 1997.
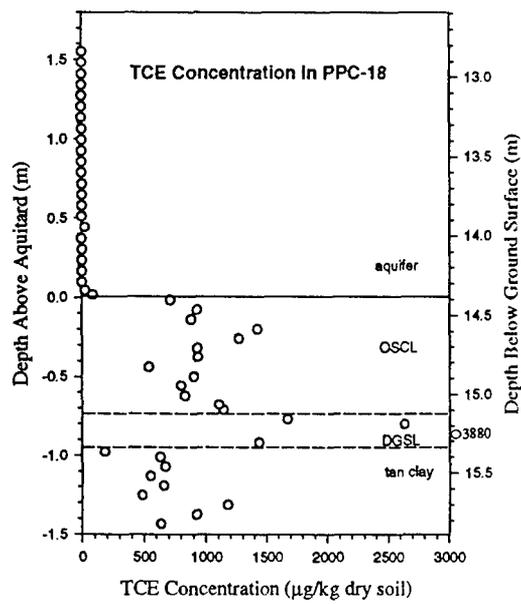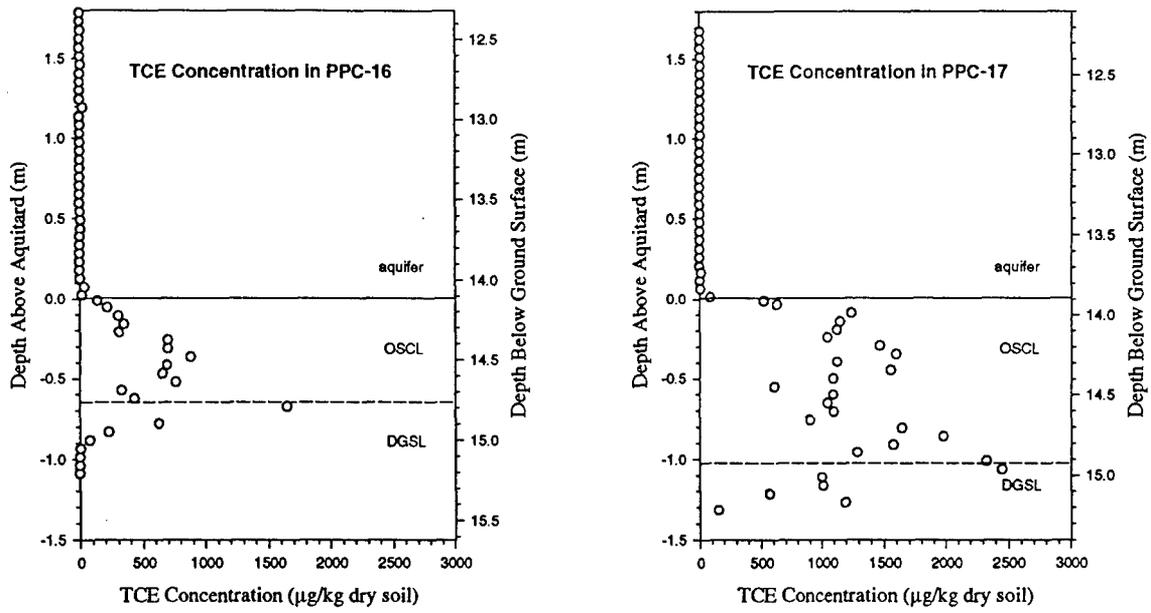
Figure 9. PPC Core Sampling Results for TCE in January 1997.
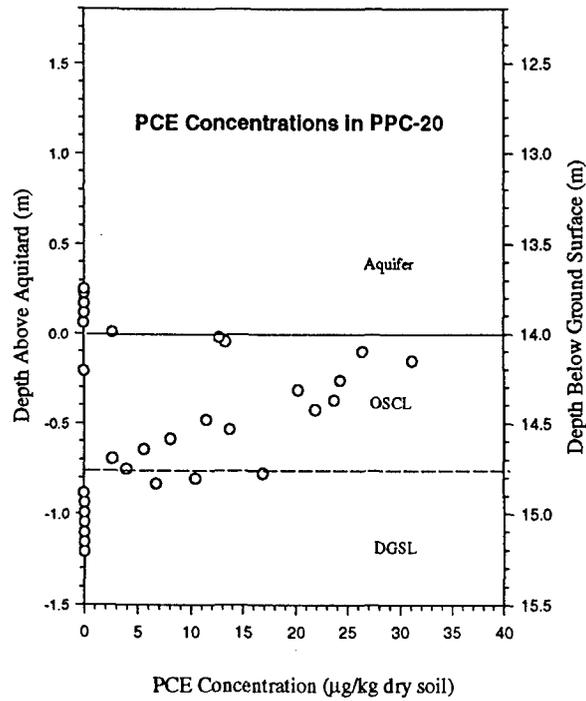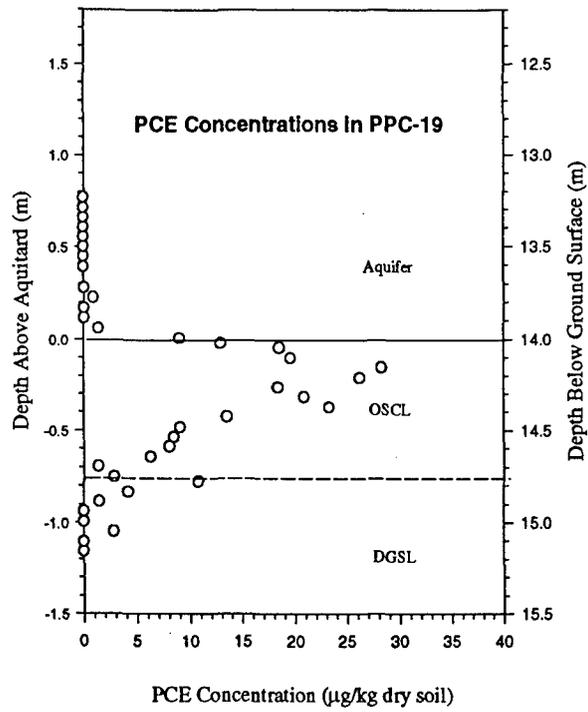
Figure 10. PPC Core Sampling Results for PCE in September 1997
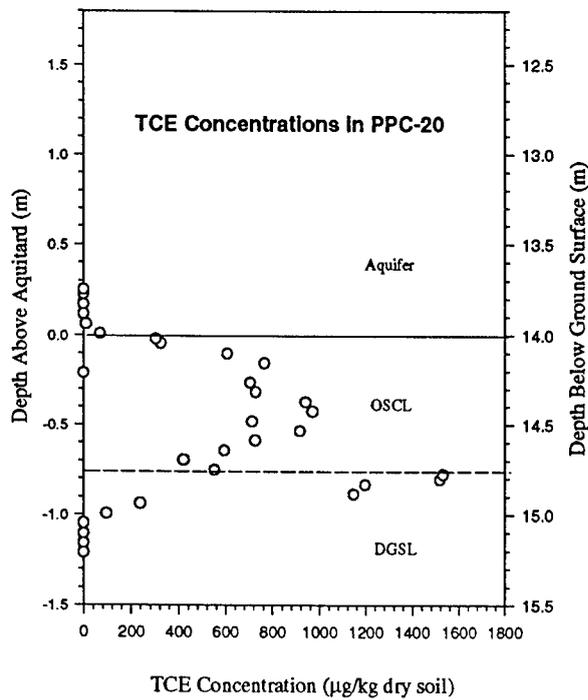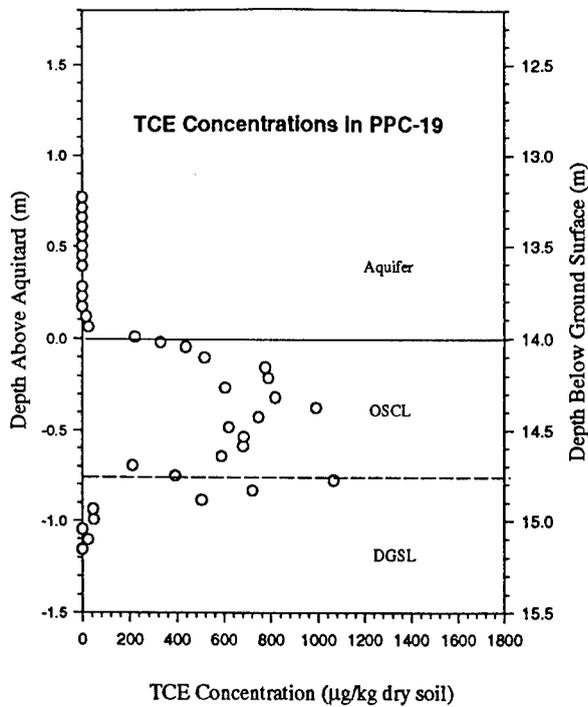
Figure 11. PPC Core Sampling Results for TCE in September 1997

2. *Aqueous Sampling of Multilevel Piezometers*

a) Multilevel sampling results from January 1997

Aqueous "snapshots" of in-cell VOC concentrations were obtained immediately after our January 1997 coring exercise. Sampling and analysis of multilevel piezometers was performed in the field during the period from January 20 to January 30, 1997. Dissolved oxygen (DO) and pH were measured in separate testing on February 2, 1997.

(1) Aqueous Measurements of pH and DO. These results confirm that the site pH remains between 5.5 and 6.5 in the orange sand, with a wider range of pH results (between 4.5 to 7.5) observed in the overlying finer material. DO results showed that dissolved oxygen remains above 3 mg/L throughout most of the aquifer, although some lower values (on the order of 1 mg/L) were found in the deepest sampling points of the CPC. These samples may be at locations very near (or even slightly below) the aquifer/aquitard interface. The DO is likely to reflect some combination of poor flushing during the prior pumping research, diffusion of oxygen from the flushed zones into the aquitard, and remaining chemical reduction capacity in the deeper aquifer sands and aquitard materials. Interestingly, DO in the deepest levels of the sampled PPC wells (PPC-ML-2, PPC-ML-5, and PPC-ML-8) were all above 3 mg/L. These ML points are believed to lie within a higher permeability zone that lies immediately above the aquitard interface in this cell.

(2) Aqueous Concentrations of VOCs. In the January 1997 multilevel sampling for VOC concentrations, a total of 41 piezometer sampling points inside the test cells were sampled, including the 2 deepest sampling levels at each of 18 plan locations, and an additional shallower depth at 5 locations. The January aqueous sampling detected concentrations of PCE; TCE; 1,1,1-TCA; cis-1,2-DCE; m- and p-xylene; and naphthalene, with results as shown in **Figures 12 to 14**. Note that concentrations are shown in terms of "depth above aquitard" and that some of these multilevel locations are believed to lie below the aquitard surface -- i.e., within a cored "hole" down into the aquitard. The points nonetheless draw water, because it is believed that the "hole" down into the aquifer was backfilled by slumping sand from above when the steel drive casing was removed from around the multilevel sampling tube nest, at the time of well-installation. This
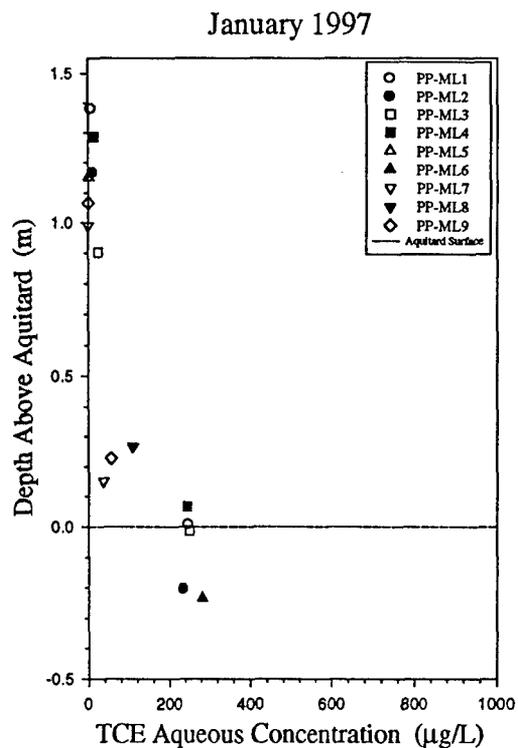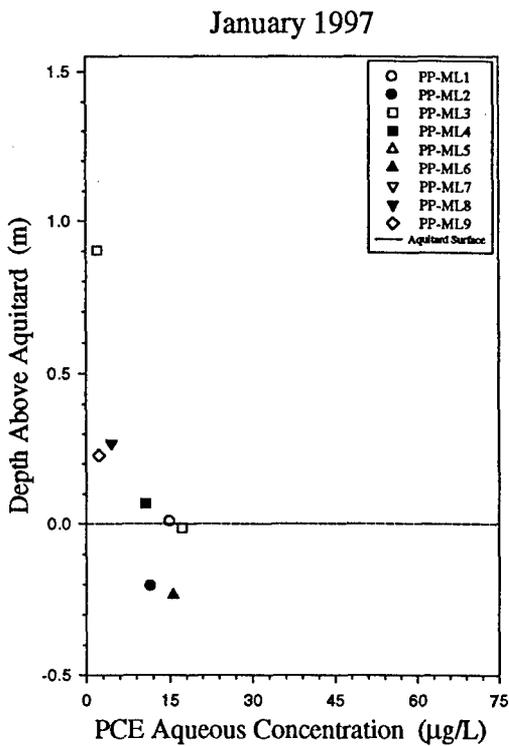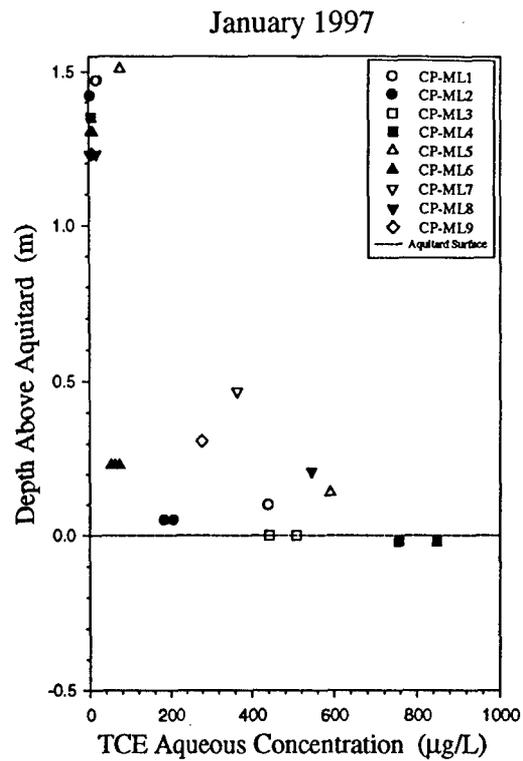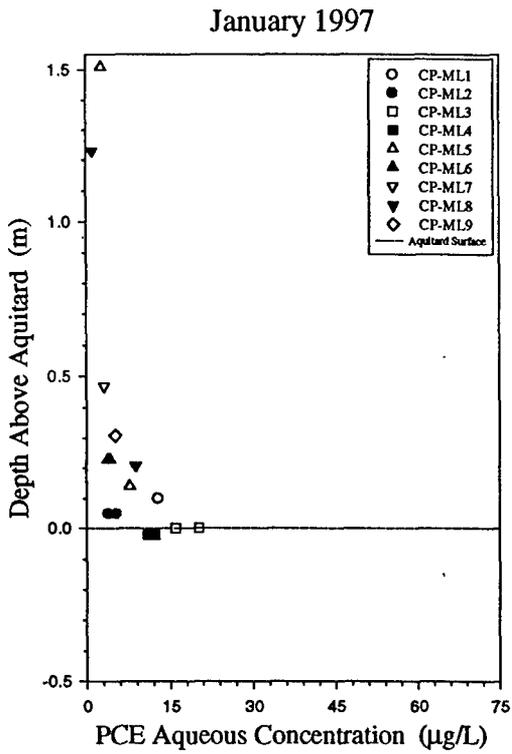
Figure 12. Multilevel Sampling Results for PCE and TCE on January 23-31, 1997

January 1997

January 1997

January 1997
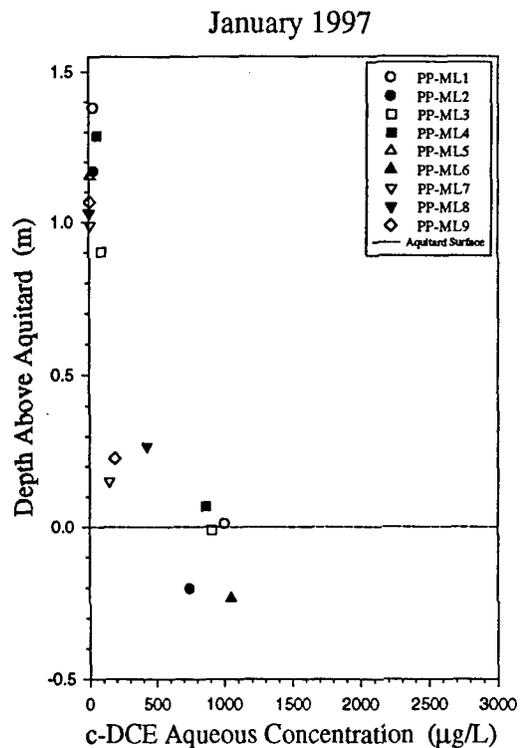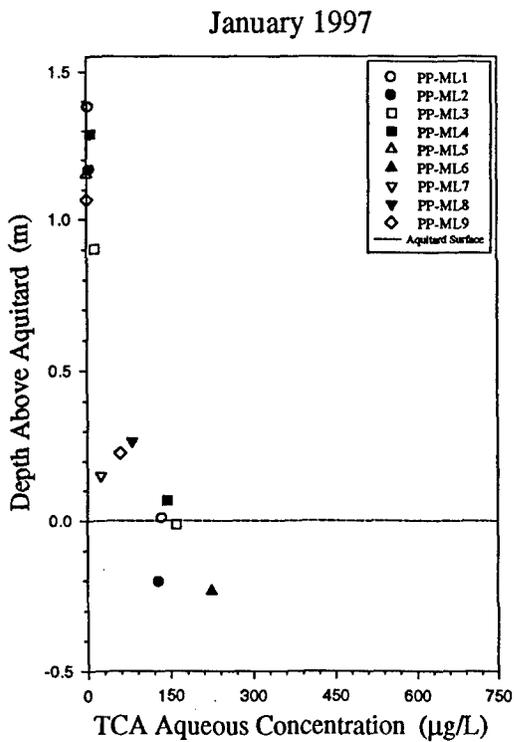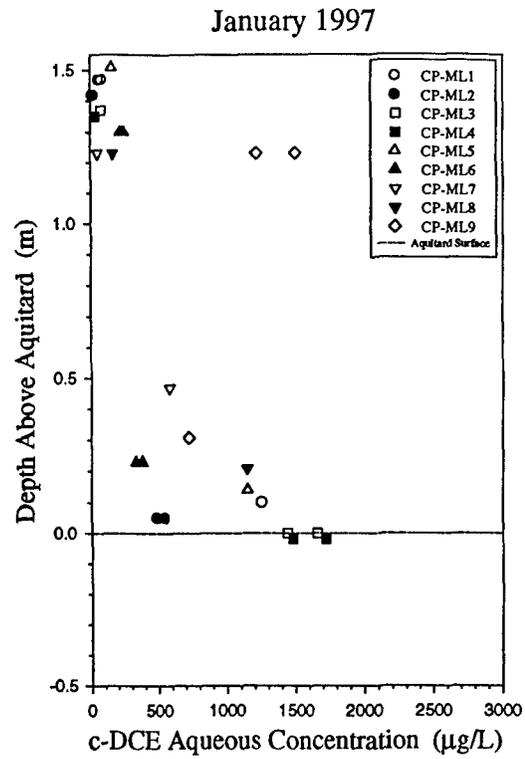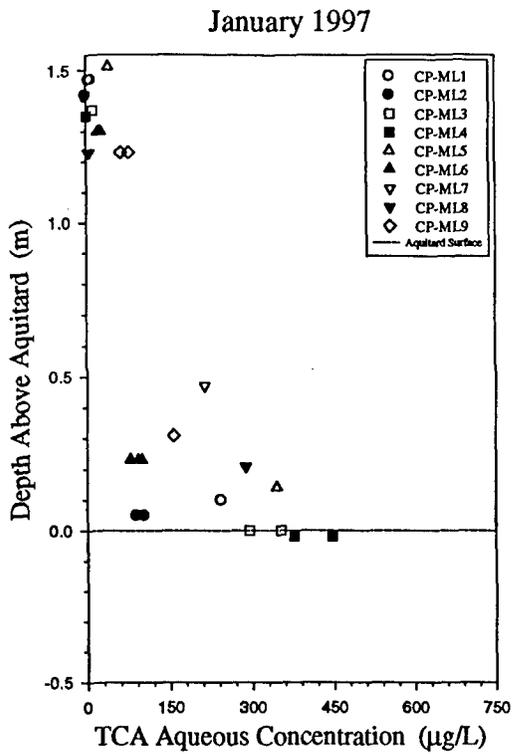
January 1997

Figure 13. Multilevel Sampling Results for 1,1,1-TCA and cis-1,2-DCE on January 23-31, 1997
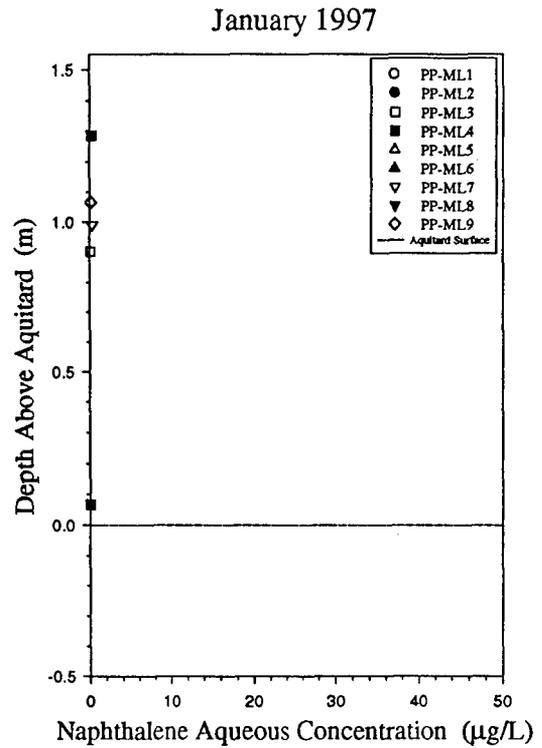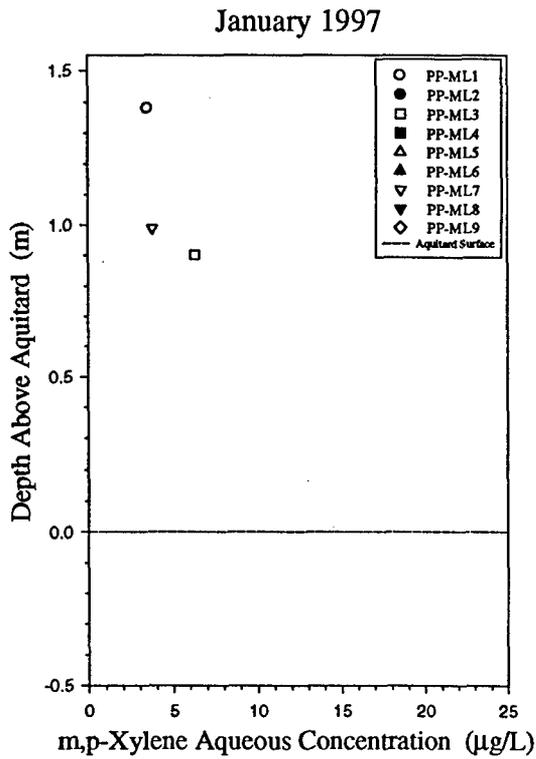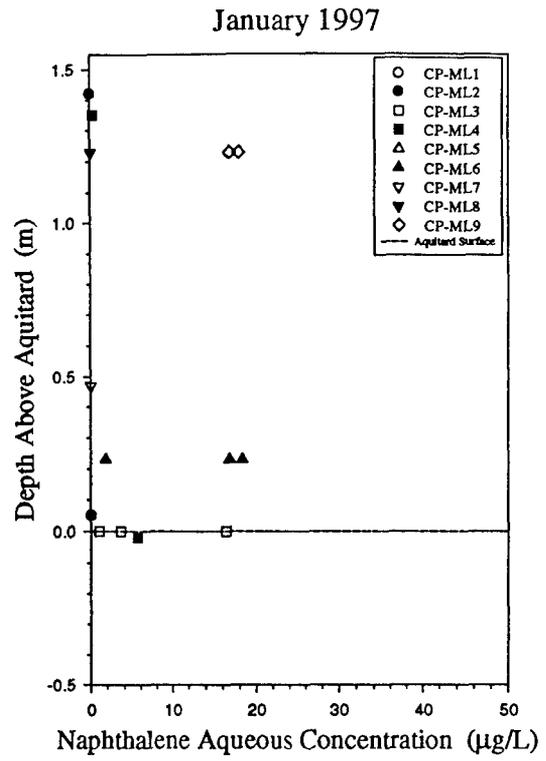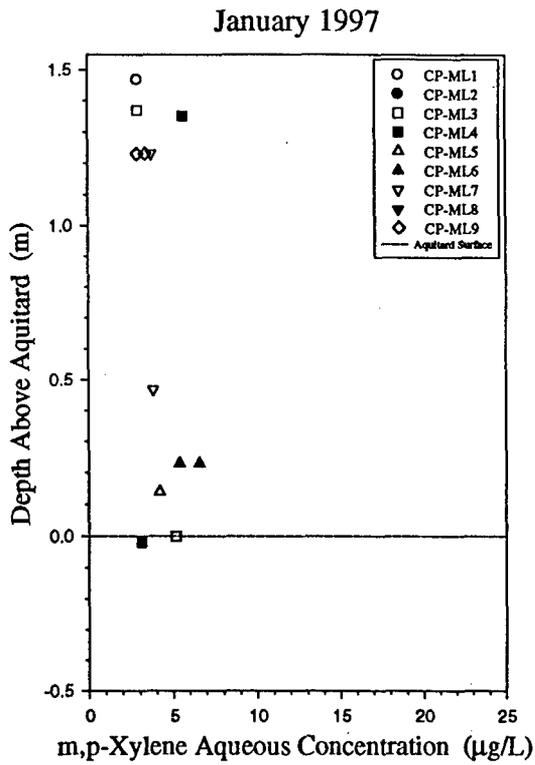
Figure 14. Multilevel Sampling Results for Xylene and Naphthalene on January 23-31, 1997

situation occurred because some of the ML-nests were constructed before core-logs were available. Also, note that the depths for sampling points at CPC/PPC-2, CPC/PPC-4, CPC/PPC-6, and CPC/PPC-8 have had to be estimated, since soil cores were not taken at these points. Such estimation has been based on the interpolation of information from surrounding cores. In addition to the uncertainty of the ML location with respect to the aquitard surface, we also have uncertainty with regard to the nature of the flow paths and sampling volumes surrounding the ML points. Overall, we are concerned that samples of the deeper aqueous concentrations may be more heavily influenced by aquitard (or aquitard-adjacent) pore water than are the core sub-samples from the same nominal depth.

Because of the issues noted in the prior paragraph, we find the ML data far less satisfactory than coring results at indicating rebound concentrations. A particular concern is that the ML samples may not be of high enough resolution or precision to sensitively measure the contaminant rebound process, which can be quite sensitive to the precise spatial location of the sampled water. Nonetheless, some further investigation of the aqueous samples was conducted in July and August of 1997, when we undertook a temporal study of aqueous concentrations at several selected points. These results are described in the following section.

b) Multilevel sampling results from July and August, 1997

Multilevel samples from the period between July 8 and August 19, 1997 were taken at the two deep-most sampling depths at CPC-2 and PPC-2, which are located between CPC-1 and CPC-3 and between PPC-1 and PPC-3, respectively (**Figure 1**). These samples provide a picture of continuing contaminant "rebound" concentrations in the deeper region of the aquifer over this six-week period. Results for the four chlorinated solvents are shown in **Figure 15** for the CPC and in **Figure 16** for the PPC. As evident from these figures, the data show a clear trend of higher concentration at the deeper level. Deeper well concentrations are at roughly similar concentrations as those observed in January 1997 (**Figures 12 and 13**), whereas the shallower well (2-7, at roughly 1.0 to 1.5 meters above the aquitard surface) shows considerably higher concentrations than previously observed. Qualitatively, these results are consistent with expectations based on diffusive "rebound." Steady or even declining concentration at the deepest elevation at later times are consistent with our coring observations and modeling. More
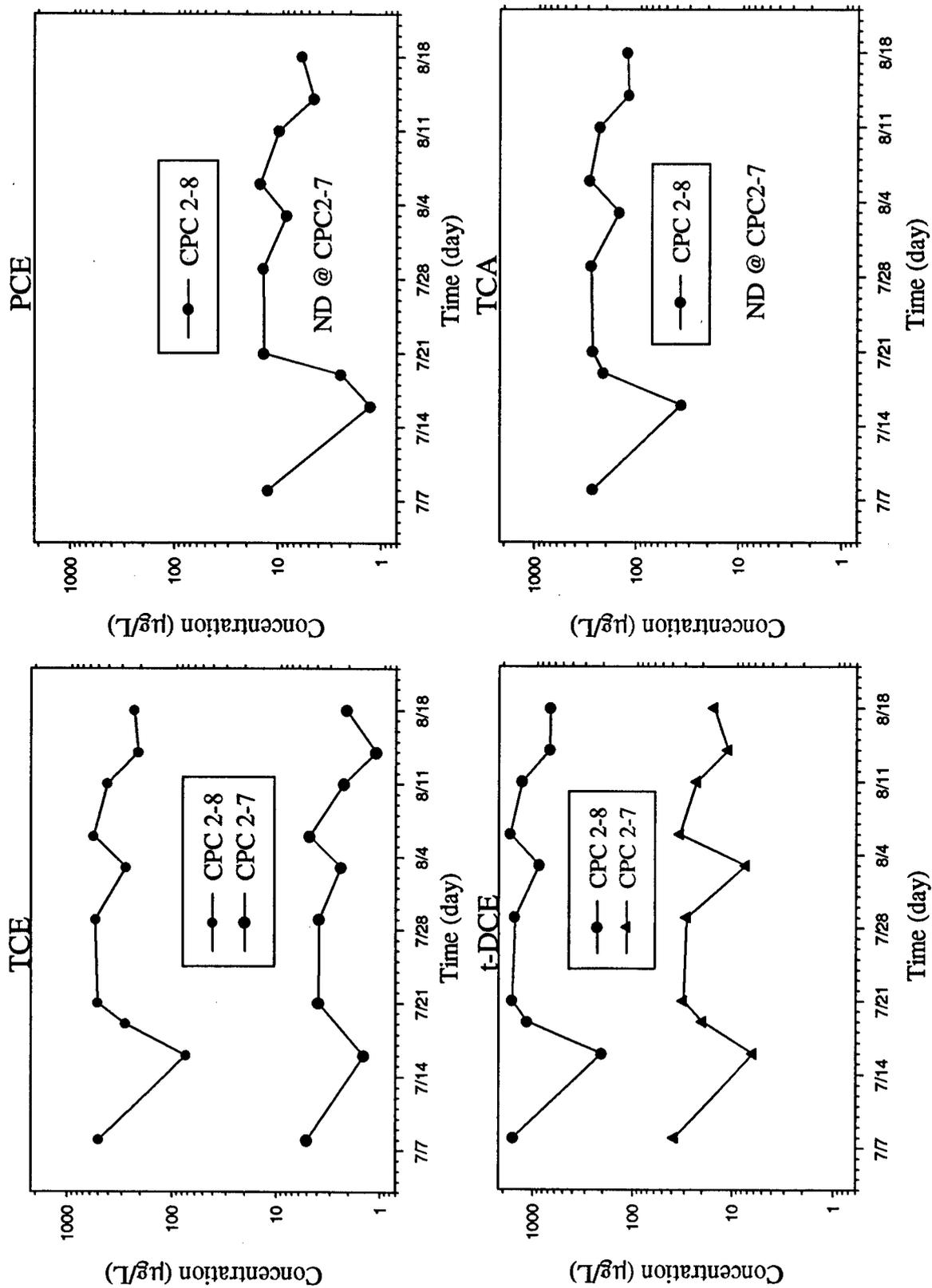
Figure 15. Aqueous Concentrations in Lower Aquifer from CPC-2 Multilevel Piezometers (July to August, 1997)

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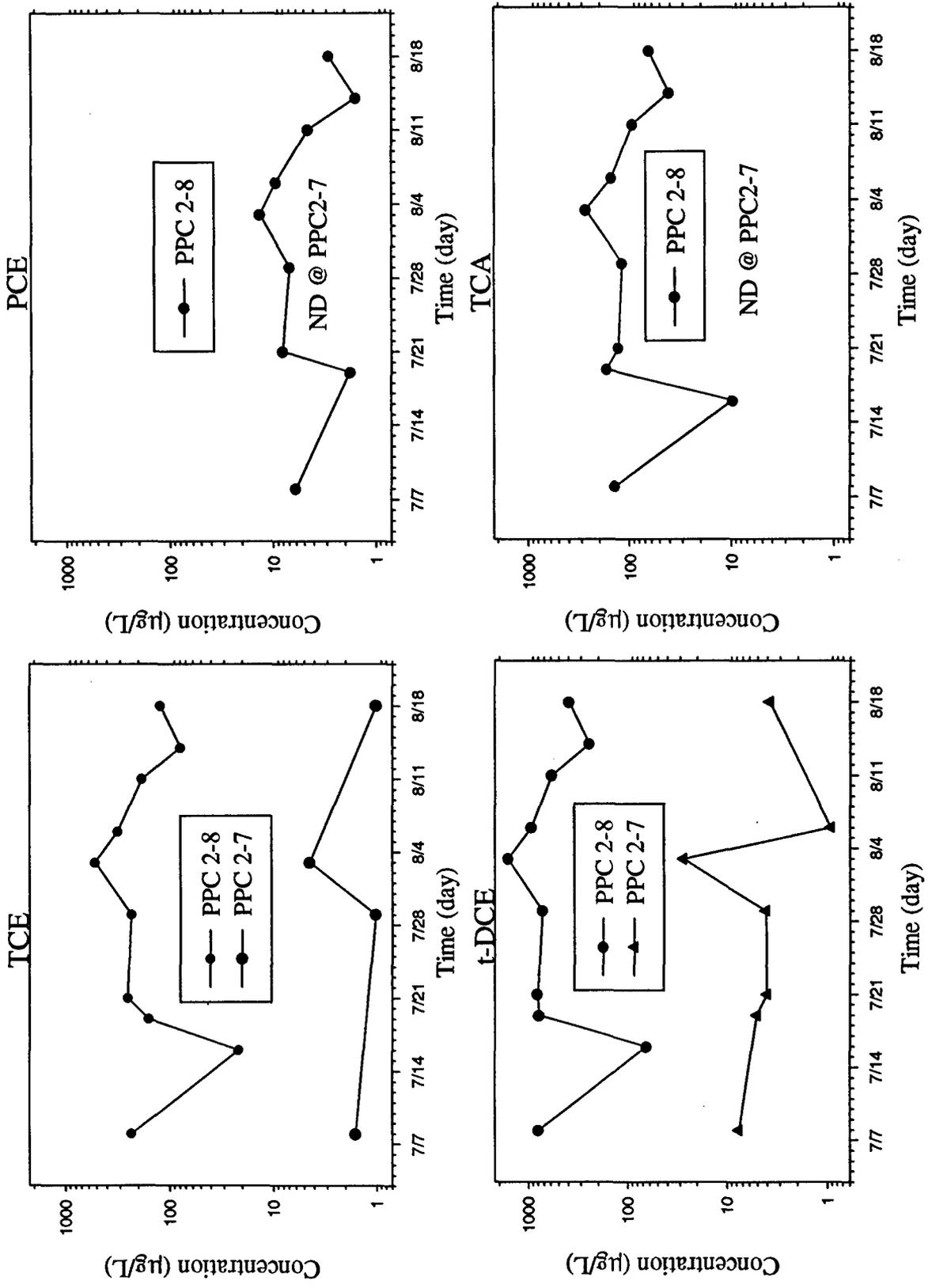
Figure 16. Aqueous Concentrations in Lower Aquifer from PPC-2 Multilevel Piezometers (July to August, 1997)

specifically, the flux from below is expected to eventually decline to a value below the continuing flux to above, once the contaminant concentrations below the aquitard surface have dropped to a sufficiently low level. (These upper aquitard concentrations continuously declined in the period since the overlying groundwater was first flushed.)

The time variability of the aqueous concentration data is believed to be indicative primarily of sampling and analytical variability, and is therefore not particularly revealing of underlying processes. In these regards, we place more emphasis on the soil core results, which are further spaced over time, better resolved with regard to spatial location, and of better analytical precision.

3. Modeling Evaluation of Subsurface Coring Results

a) Inverse modeling of subsurface coring results

As noted under Background, an inverse interpretation of aquitard measurement data at PPC-11 had been previously performed under an assumption of a two-step boundary concentration. A regularized least square method was developed over the course of the current project and applied toward a reinterpretation of the measurement data at PPC-11 (Liu and Ball, 1998). The revised method has also been applied toward interpretation of the June, 1996, results for PPC 13 (obtained immediately after the termination of PPC pumping).

In general, these results confirm our prior findings that that PCE at this site has generally increased with time at the aquifer/aquitard interface, suggesting a PCE plume gradually approaching the site. The PCE plume in the overlying aquifer was estimated to have arrived at the site about 15 years ago. These results have been qualitatively confirmed by independently conducted groundwater sampling efforts at the DAFB site [Dames & Moore, 1994; Ellis, 1996], suggesting that inverse interpretation of observed data may provide useful information regarding the contaminant source history. The results also indicate that for a case with relatively simple boundary concentration history, both inverse methods can catch the general trend of contaminant source history, suggesting that the step method may be the more appropriate approach for the current case, owing to its simplicity. On the other hand, the inverse estimation results for TCE indicate that this chemical has had a comparatively more complicated boundary concentration history in that it increased with time at earlier time, then decreased in concentration until the

sampling time. For this relatively complicated boundary concentration change, the two inverse methods generated significantly different interpretation results. The two step method suggested the TCE plume arrival in the overlying aquifer about 13 years ago, while the more recently applied method (regularized least-square method) suggested that TCE first arrived about 25 years ago. In this case, a TCE plume arrival 25 years ago is perhaps more compatible with independently obtained plume mapping of TCE at the large scale around the site and other available information (Dames & Moore, 1994; Ellis et al., 1996). It may be that the oversimplified two-step assumption is not appropriate for the TCE case, justifying application of a more complex method to solve the inverse problem, such as the regularized least-squares approach.

Our newly conducted study of PPC-13 added to our confidence in the above conclusions. In addition to allowing a second calculation of aquifer concentrations in the period prior to October 1994, the estimated results from PPC-13 allowed us to make additional inferences about the concentration history during the period between the PPC-11 and PPC-13 sampling times, when the test cell was being pumped. PPC-13 was selected for this evaluation because of its physical proximity to PPC-11 (about 4 meters south) which facilitates a more direct comparison with the prior PPC-11 results and also allows us to better assume a similarity of the concentration history in the overlying aquifer. As will be discussed in detail in a forthcoming publication (Liu and Ball, 1998), the comparisons of estimated results between PPC-11 and PPC-13 were favorable regarding the plume arrival time and the inferred concentration history up to October 1994. The concentrations inferred from PPC-13 for the period between October 1994 and June 1996 show an initially constant level, followed by a period of sharply declining concentrations over time, and eventually reaching very low concentrations. These results are in excellent agreement with our expectations, since there was an initially stagnant period in the cell (prior to the initiation of pumping in November, 1995), followed by the period during which the aquifer region of the test cell was subjected to flushing by clean water (between November 1, 1995 and June 5, 1996). All of these results suggest that the inverse interpretation of observed data may provide useful and important information regarding the contaminant release history at the site. However, caution must be exercised in this kind of inverse interpretation. As discussed elsewhere (Liu and Ball, 1998), the inverse interpretation is a highly nonunique problem. For our case, both the step

assumption approach and the regularized least-squares methods were able to produce boundary conditions that were reasonably consistent with the measured data, despite some important differences among the assumed functions. In general, the inverse interpretation of observed data is not only a non-unique problem, but also one that can be significantly biased by either errors in the measured data or in the characterization of the porous media, including an incomplete description of heterogeneity.

b) Diffusion Simulation during the Current Project Period

Our newly derived analytical solution for multilayer diffusion (Liu et al., 1998) was used to simulate the concentration profiles obtained at PPC-16 and PPC-19. These cores were taken at about 238 days and 480 days, respectively, after the termination of PPC pumping. Unlike the inverse applications for PPC-11 and PPC-13 (where only data in the aquitard were used), the diffusion simulations for the cases at PPC-16 and PPC-19 involve a comparison with measured concentrations in both the aquitard and the aquifer, where groundwater has presumably remained stagnant since June of 1996. Therefore, the simulation of diffusion profiles requires an assumption regarding the initial concentration profile in both the aquitard and aquifer. For the purpose of the prediction of concentration profiles for PPC-16 and PPC-19, the choice of "initial" time for the simulations was the June, 1996, sampling time of PPC-13, when pumping was terminated at the end of the clean water flush in the PPC. Thus, an appropriate choice of initial concentration in the aquifer is zero at that time. However, it would be inappropriate to assume that the June, 1996, concentrations within the aquitard at locations PPC-16 and PPC-19 would have been the same as measured at PPC-13, since the thickness of OSCL is different at each location. In this case, we applied our estimated boundary concentration history (inferred plume history) from PPC-11 and PPC-13, to obtain an estimate of the "initial" (June, 1996) concentration profiles at PPC-16 and PPC-19 (Liu and Ball, 1998). With these inferred concentrations as an initial condition, we were then able to apply our multilayer diffusion model (Liu et al., 1998) to predict the concentration profiles that we would expect to exist in PPC-16 and PPC-19 at their respective times of sampling.

The results of these diffusion simulations are shown in **Figure 17** for PPC-16 and **Figure 18** for PPC-19. As shown in these figures, the simulated results for both PCE and TCE compare

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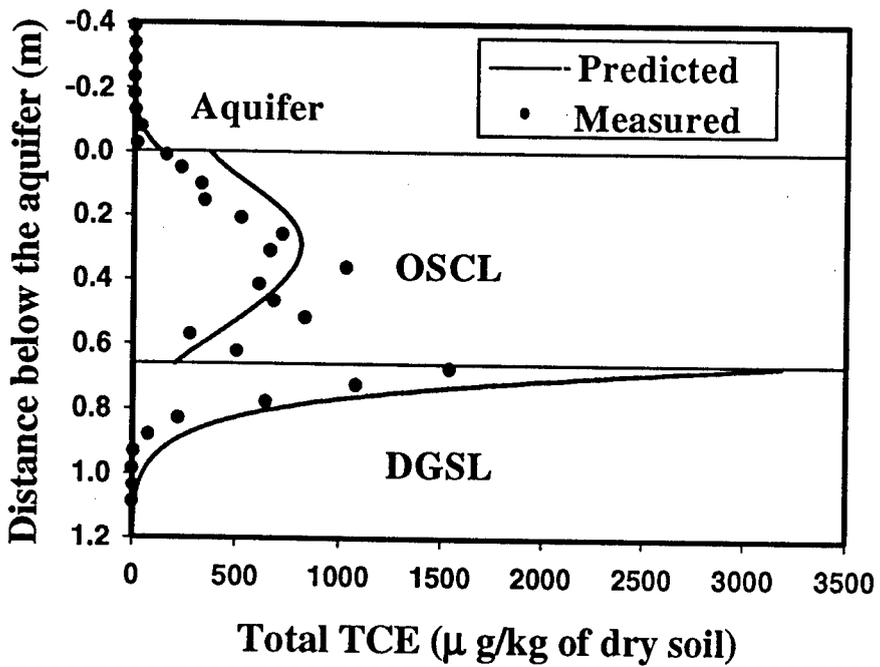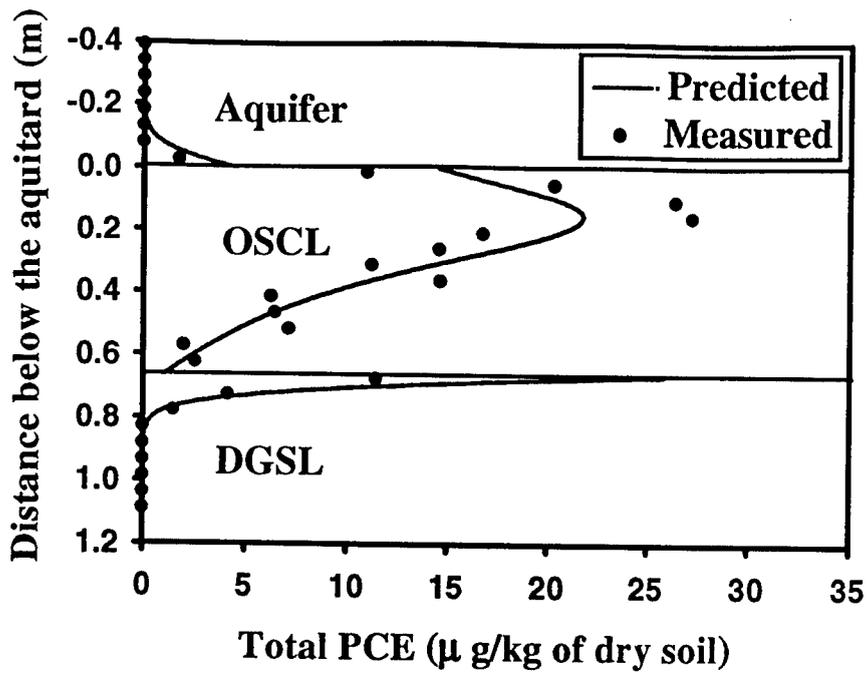
Figure 17. Comparison of Predicted and Observed Concentration Profiles for PCE and TCE in PPC-16
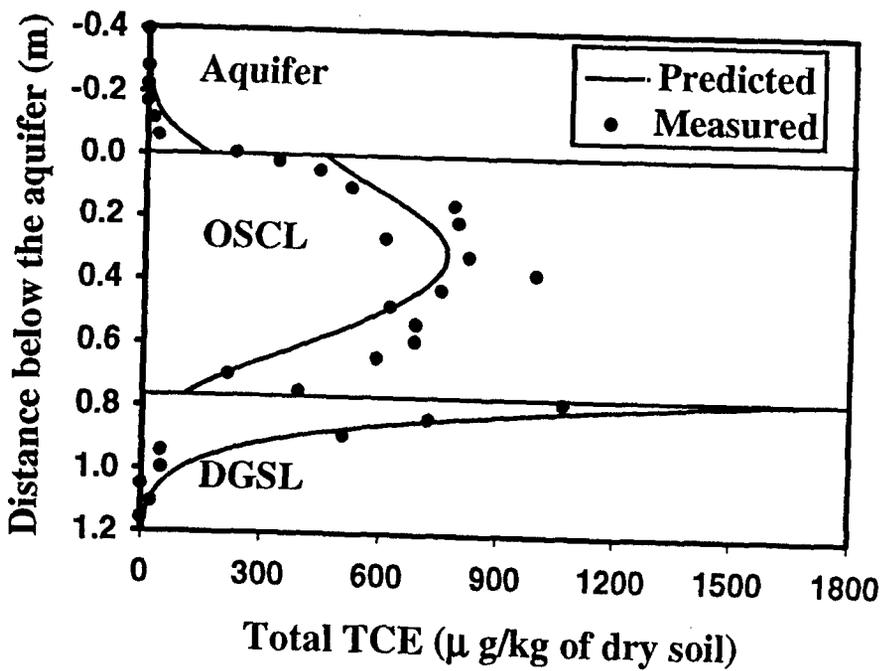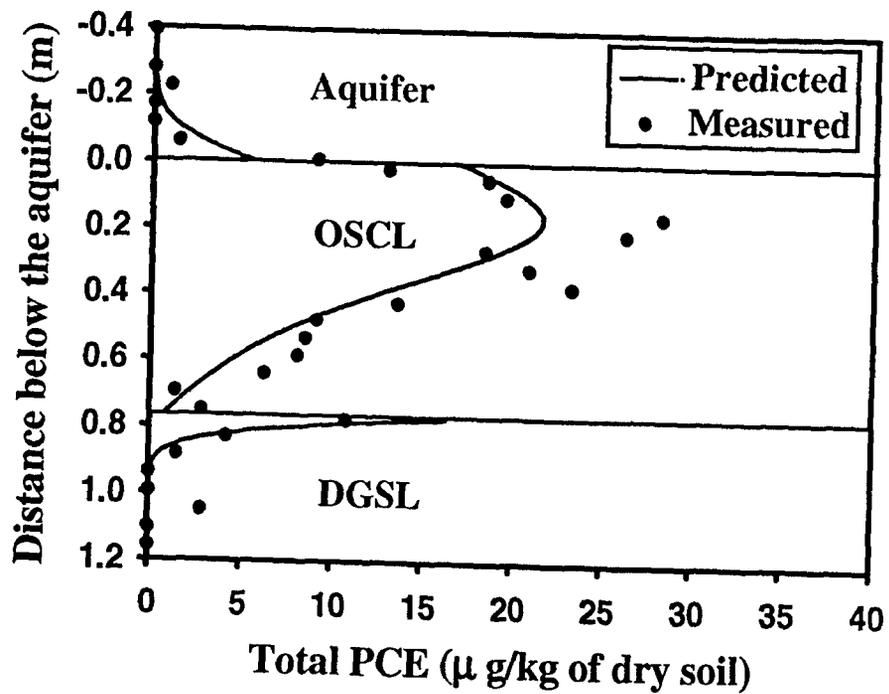
Figure 18. Comparison of Predicted and Observed Concentration Profiles for PCE and TCE in PPC-19

very favorably with measured data, suggesting that our assumed mechanism of retarded diffusion is the principal process controlling contaminant fate in the aquitard. Comparing the assumed "initial" concentration with the simulated concentrations at later time (**Figure 19**) shows how the model simulates PCE and TCE diffusion both back up into the aquifer and downward into the deeper aquitard. The latter process continually lowers contaminant concentrations throughout the aquitard (via spreading and dilution) but will significantly increase the difficulty of ever achieving any "complete" aquitard cleanup (Ball et al., 1997a).

Thus, the data obtained over the course of this project, in combination with the developed analytical models, have allowed us to obtain a better understanding of the fate of contaminants in aquitard regions. With our improved confidence in predictive modeling, we anticipate being able to make better predictive assessments regarding expected system responses to future actions. This should lead to the development of more appropriate methods of contaminant remediation or containment, as well as a better basis for establishing regulatory controls.
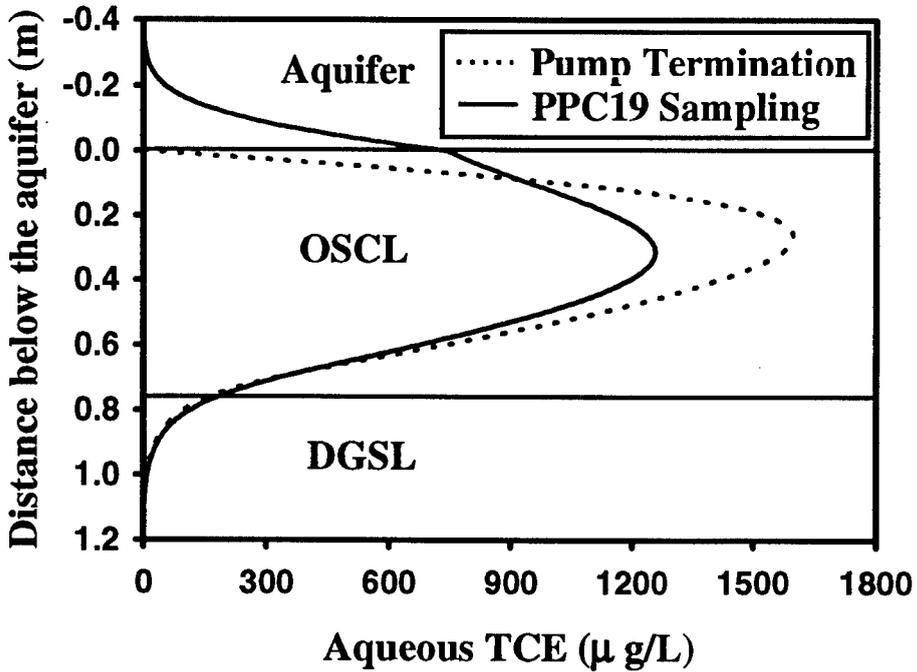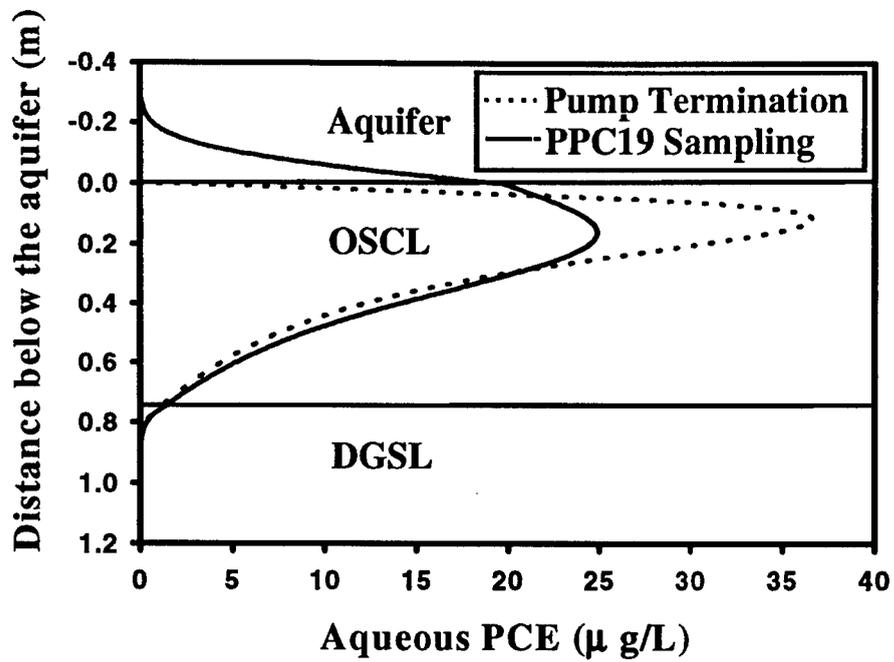
Figure 19. Simulated Contaminant Movement over Time between Pump Termination and Time of Sampling (PPC-19)

Section III. LONG-TERM COLUMN INVESTIGATIONS OF CHLORINATED SOLVENT REMEDIATION BY REACTIVE METALS UNDER FIELD CONDITIONS

A. BACKGROUND

As at many DOD sites, the groundwater under Dover Air Force Base (DAFB) is contaminated with various organic chemicals, including chlorinated solvents that have been used at the base for parts cleaning and other purposes. The contaminants present in groundwater beneath the area under study in this work (near Building 459) include vinyl chloride (VC), 1,1-dichloroethylene (1,1-DCE), dichloromethane (DCM), *trans* 1,2-dichloroethylene (t-DCE), *cis* 1,2-dichloroethylene (c-DCE), 1,1,1-trichloroethane (1,1,1-TCA), trichloroethylene (TCE), and tetrachloroethylene (PCE) as well as aromatic hydrocarbon contaminants such as benzene, xylenes, naphthalene, 2-methylnaphthalene, and other contaminants (e.g. lindane).

Due to widespread dissatisfaction with the effectiveness of pump-and-treat and other pumping-based methods of groundwater remediation, *in situ* passive remediation technologies have recently been investigated by many researchers and put into practice at many sites worldwide. Laboratory-scale experiments with simulated groundwater have shown that all of the previously mentioned chlorinated solvents, with the exception of DCM, are degraded by reactive metals in batch systems (Gillham and O'Hannesin, 1994; Schreier and Reinhard, 1994; Johnson, et al., 1996). The most promising metal being investigated is iron, which is not only inexpensive but relatively safe in applications where treated water may ultimately be delivered to potable water systems. Prior to this project, the vast majority of laboratory and pilot investigations of the effectiveness of reactive metals for treating contaminated groundwater have been conducted using synthetic or contaminant-spiked water and/or have been of a comparatively short duration.

B. OBJECTIVE

The objective of the column-scale investigation was to evaluate the long-term performance of two alternative reactive barrier materials in treating contaminated groundwater at Dover AFB, DE. In particular, a goal was to determine if long-term exposure to site water and/or

contaminants can have important impacts on treatment efficiency or metal reactivity. The two reactive media evaluated were Masterbuilder granular iron (hereafter also referred to as "iron" or Fe), and "enhanced" Masterbuilder iron (Gillham et al., 1997; hereafter also referred to as enhanced iron or Fe/Ni). Through field operation using comparatively long columns (40.6 centimeters) and residence times (on the order of 1 hour), a goal was to evaluate potential field-scale geochemical alteration of the media, recognizing that the effects may vary with both time of exposure and distance along the flowpath through the media. Specific studies of reaction rate (e.g., as might be obtained by evaluating removals after smaller fluid residence times) were beyond the scope of this preliminary study. On the other hand, it was foreseen that the partially "weathered" reactive metal media from these pilot investigations could later serve as an interesting resource for future studies.

C. EXPERIMENTAL APPROACH

In late July, 1996, three columns were set up at the site of the former pulsed-pumping research project (Mackay et al., 1995; Mackay et al., 1997). One contained Ottawa sand (control column), the second contained the Masterbuilder granular iron, and the third contained the "enhanced" Masterbuilder iron (Fe/Ni; Gillham et al., 1997). Both reactive iron materials were provided by EnviroMetals Technologies (ETI), Inc., Guelph, Ontario. To ensure that the reactive metals were exposed to groundwater as representative as possible of that *in situ*, the groundwater was pumped directly to the column influent port from the plume (drawing primarily from the highly contaminated stratum 45 feet beneath the surface). The columns were operated essentially continuously for over 400 days, corresponding to over 150 pore volumes in the Fe/Ni column and over 170 pore volumes in the iron column.

D. MATERIALS AND METHODS

1. Column Construction, Packing and Installation

The custom-fabricated acrylic columns were equipped with stainless steel screens at each end to retain the granular media. Each column had an internal height of 40.6 cm and an internal diameter of 3.18 cm, thus providing an internal volume of approximately 320 cm^3. The three

columns were packed and prepared on-site before initiation of the tests. Prior to packing, a subsample of the material (more than sufficient to fill a column) was placed in a beaker and weighed. During packing, the columns were oriented vertically and filled in lifts of approximately 15 to 30 cm^3 (bulk volume) of packing material (iron, enhanced iron, or sand). Successive lifts were poured into the column from the top, homogenized with the previous lift using a long, tined rod, and then packed down repeatedly with a solid rod that roughly matched the column's internal diameter. This process was repeated until the column was filled. The beaker (with leftover material) was weighed again to allow calculation of the mass of material added. Known internal column volume and solid density of the materials allowed calculation of the pore volume in each column (see **Table 2**). The columns were installed securely in a vertical orientation in a custom-built rack within the trailer on site. Distilled water was pumped through each column at approximately 0.05 ml/min for 3 days to wet the material, and the columns' influents then switched to the supplied groundwater source.

TABLE 2. PHYSICAL AND FLOW CHARACTERISTICS OF THE TEST COLUMNS.

Parameter	Sand Column	Iron Column	Fe/Ni Column
Internal volume, excluding screens (mL)	316.7	316.7	316.7
Pore volume (mL)*	130.2	191.3	206.4
Flow rate (mL/hr)	3.48 ± 0.84	3.42 ± 1.1	3.18 ± 0.96
Residence time (hr)	37.4	55.9	64.9

*Based on particle densities (sand=2.7, iron=7.86, enhanced=7.9 g/cc) and masses (sand=507.3, iron=985.7, enhanced=867 g).

2. *Column Feed and Sampling*

Figure 20 shows a schematic of the column and plumbing setup. Stainless steel (SS) tubing was used as much as possible throughout; PVC fittings and short sections of Tygon tubing were used as necessary. Groundwater was drawn from the well via 1/8" SS tubing (with its open end situated about 45 feet below ground surface) and pumped into a 1-inch O.D. PVC standpipe within the trailer by means of a peristaltic pump (Model 7553-70, Cole-Parmer, Chicago)

operating at a rate of roughly 8 ml/minute. At three adjacent ports along the standpipe, groundwater was drawn off by a multi-channel peristaltic pump (Ismatec Model 7332-00, Cole-Parmer, Chicago) to provide equal influent flow (roughly 3 ml/hr) to each column which resulted in residence times indicated in **Table 2**. The groundwater extraction/supply rate exceeded the total required for column influent at all times. The overflow from the sealed standpipe was discharged to a vessel located outside the trailer, from which it was periodically pumped to a treatment system. An additional larger peristaltic pump was used to continuously pull roughly 200 ml/minute out of the sampling well in order to continually bring in "fresh" contaminated groundwater from the upgradient plume. This water was also pumped to the on-site treatment system.
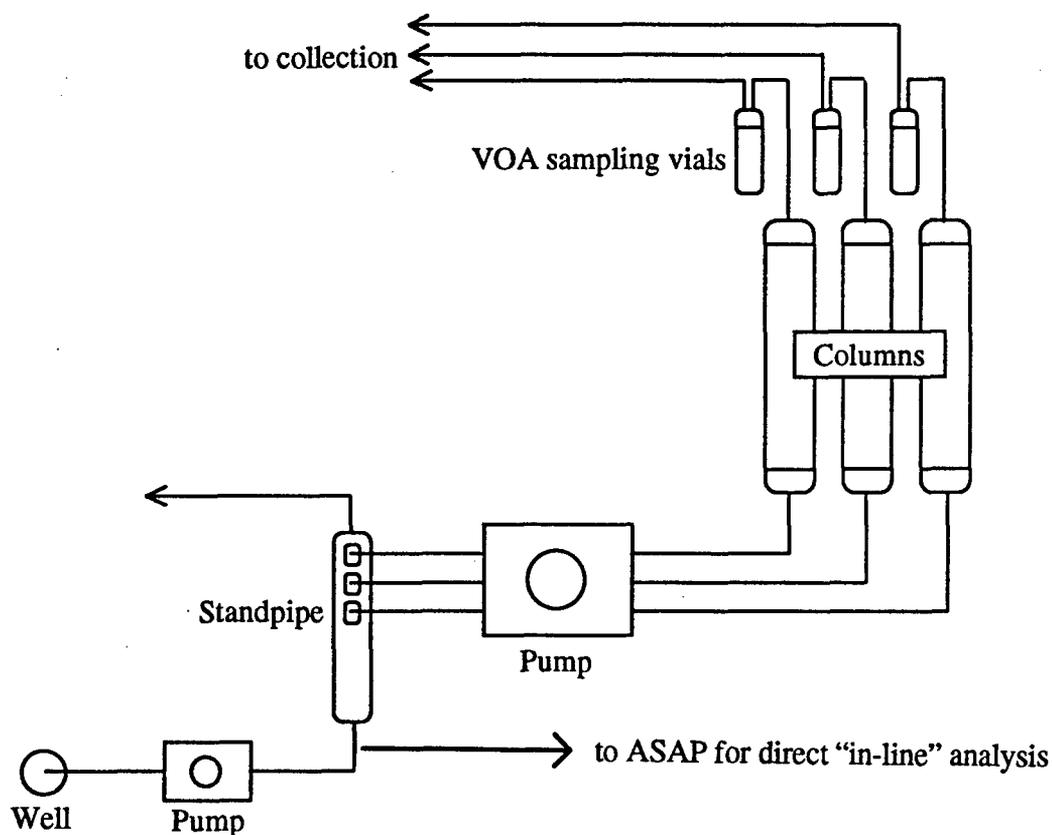
Figure 20. Schematic of Column Setup

Influent samples were drawn periodically by the sampling/analytical system from a port upstream of the column distribution ports. This sampling port was plumbed directly to the sampling/analytical system so that no bottles or manual liquid transfer was required. These are termed "on-line" samples and were analyzed as described in the following section.

Effluent from each of the three columns flowed into 40-mL glass VOA vials through custom-fabricated stainless steel caps with inflow at the bottom of the vial, outflow at the top, and viton o-ring seals. After filling, these vials could thus be maintained headspace-free until the vial volume was removed and subjected to on-site analysis. Bottles were typically flushed by 5 to 7 bottle volumes of effluent water before removal, as achieved by continuous collection over a 2 to 4 day period between samples. Once removed from the effluent line, the vials were quickly capped with Teflon septa and analyzed as rapidly as possible, usually within 24 hours. These samples are termed "off-line" samples. Finally, all effluent from each column was collected and the cumulative volume periodically measured to estimate average flow rates.

3. Analytical Methods

All routine samples ("on-line" influent samples and "off-line" effluent samples) were analyzed by means of the on-site Automated Sampling and Analytical Platform (ASAP System, A+RT, Millpitas, CA). Drawing water either from a dedicated line ("on-line") or a VOA bottle ("off-line"), the ASAP system automatically flushes and fills a stainless steel sample loop (one of various calibrated sizes). Analysis of the water in the loop is also an automated process, involving the countercurrent stripping of the volatile organic chemicals from the aqueous samples into a helium gas phase, followed by trapping onto a Tenax column. Compounds are then desorbed from the trap by heating and then flushed into a gas chromatograph (Hewlett-Packard 5890E) equipped with a J&W Scientific DB-5 column (30 meters × 0.53 millimeters ID × 5 micrometers film thickness), an electrolytic conductivity/photoionization detector tandem (ELCD/PID, O-I Analytical, College Station, TX). Detector response was processed and recorded by a commercial integrator (ChromJet, Thermal Separation Products, San Jose, CA). Calculated concentration data was transmitted to a dedicated PC computer for storage. During proper operation, the detection limits of the analytical system were equal to or less than 0.1 µg/L for the chlorinated compounds examined in this study with the exception of vinyl chloride which was

detectable above 5 μg/L (Mackay et al., 1997).

4. Routine Quality Control and Instrument Calibration

Routine calibration standards were prepared by injecting known volumes of pre-prepared methanol stock solutions into a specially constructed, headspace-free volumetric syringe, which was subsequently analyzed by the ASAP in a manner similar to an off-line sample. These standards provided a response factor (RF) for each component. This RF was used to calculate the aqueous concentration of each component in the column effluent and influent samples.

Quality control check (QCC) samples were prepared each week in an identical manner as calibration standards and were analyzed along with each batch of column influent and effluent samples. When QCC results deviated by more than 10% from expected values and this fact was noted by the field technicians, fresh calibration samples were prepared and response factors for the instrument re-evaluated. Unfortunately, such deviations were not always noted by the field technicians in a timely manner and thus retention times and response factors were only updated by the field technicians when more obvious problems were noted (e.g. chronic mislabeling of peaks). For these reasons, a considerable amount of work was required after the completion of the tests to review the results, estimate appropriate response factors for each period of operation, and correct the analytical results.

5. Additional Sampling.

In the summer of 1997, an additional sampling program was initiated in an attempt to clarify some unexpected results from the two iron-filled columns. In particular, we sought to confirm the identity of a peak that the on-site system was identifying as 1,1,1-TCA. As shown in detail later, there appeared to be breakthrough of the peak identified as 1,1,1 TCA from the enhanced iron column in about 40 days, and from the iron column in about 100 days. Since prior work by others had always indicated efficient treatment of 1,1,1-TCA, we suspected the peak might have been misidentified by the ASAP. Therefore, we collected additional samples of influent and column effluent for independent analysis at laboratories in the Department of Geography and Environmental Engineering at Johns Hopkins University (JHU). This work was conducted in collaboration with Prof. A. Lynn Roberts and a research assistant (Jay Fennelly) at JHU. The

additional samples were collected directly into glass syringes of either 2 mL or 20 mL volume. For sample collection, the outlet of a syringe was connected directly to the column effluent or groundwater influent sampling line and allowed to fill over time. Syringes were capped and stored submerged in distilled water prior to subsequent analysis at JHU. Various analytical techniques were employed to verify the identity of peak which had been assumed to be 1,1,1 TCA. A 1 mL aliquot of sample was equilibrated with 1.6 mL of air in a sealed vial for headspace analysis by GC equipped with flame ionization detector (FID) and a J&W Scientific GS-Q PLOT column (30 meters × 0.53 millimeter ID). Other samples were concentrated by a factor of 10 or 20 by extraction into hexane. These concentrated extracts were analyzed by GC with electron capture detector (GC/ECD) on two different columns: SPB-5 (39 meters × 0.32 millimeters ID × 1.0 micrometer film thickness; Supelco) and HP-624 (30 meter × 0.32 millimeter ID × 1.0 micrometer film thickness; Hewlett-Packard). Some samples were also analyzed at the University of Waterloo, using pentane extraction, a DB-624 column for separation and a flame ionization detector (FID) for sample quantification.

The JHU analyses determined that, under the conditions of the field analyses (i.e., on the SPB-5 or DB-5 columns), two analytes were coeluting at the retention time identified as 1,1,1-TCA, namely 1,1,1-TCA and 1,2-DCA. When separation was achieved through use of the more strongly retentive HP-624 or DB-624 columns, it was determined that a 1,2-DCA peak was present together with the 1,1,1-TCA peak in all influent and effluent samples, albeit at lower peak area and detectable only by FID. Based on a very limited number of samples analyzed by the FID system (collected at one point in time), it appeared that 1,2-DCA may have been present in the summer, 1997, influent water at concentrations that were roughly 1.5 to 2 times higher than those observed for 1,1,1-TCA. However, since this issue was not clarified until rather late in the study, the field chromatography was never conducted in a manner that allowed routine separation. Thus, for the peak in question, we report hereafter the field results calibrated against a 1,1,1-TCA standard, but label them as a combination of 1,1,1-TCA and 1,2-DCA (abbreviated "TCA/1,2-DCA").

E. RESULTS AND DISCUSSION

In general, both columns performed well throughout the experiment. Because the columns were operated in an upflow mode, we had no difficulties of gas accumulation, although some gas formation (presumably H_2) was apparent in the column effluent and in gas bubbles visible along the clear acrylic column walls. A white precipitate was observed in the first 9 to 11 cm of the reactive metal columns, which we attribute to mineral precipitation (most likely siderite or some other form of $FeCO_3$). Our experimental setup did not allow us to test for changes in hydraulic properties of the material or to examine changes in surface properties of the metals; however, at project termination, the columns were sealed and stored in the JHU laboratories (at 4 degrees C in their fully saturated condition) in order to allow potential future study of the columns and media.

Figures 21 through **24** present the concentration histories for all analytes for the influent to all columns, the effluent from the sand column, the effluent from the iron column, and the effluent from the enhanced iron column, respectively. **Table 3** (on page 59) lists the average and standard deviation for the influent and effluent concentrations.

It is clear from **Figure 21 and Table 3** that the measured influent concentrations vary widely among analytes and also widely for a given analyte. It is our opinion that much of the influent variation for a given analyte is due to sampling and analytical problems, to be discussed in more detail later. Despite this variability in influent data, however, visual comparison of **Figures 21 through 24** leads to the major conclusions of this study:

- All analytes appear in the sand column effluent (**Figure 22**), and thus, as expected, there is no major loss of contaminants during transport through the sand.

- All chlorinated ethenes were completely treated by both the iron and the enhanced iron for the entire duration of the study (over 400 days), and thus did not appear in the columns' effluents (**Figures 23 and 24**).

- Certain chlorinated alkanes were not efficiently treated by either the iron or the enhanced iron and thus appeared in the columns' effluents (**Figures 23 and 24**).

Results for the chlorinated alkenes and alkanes are separately discussed in subsections below.
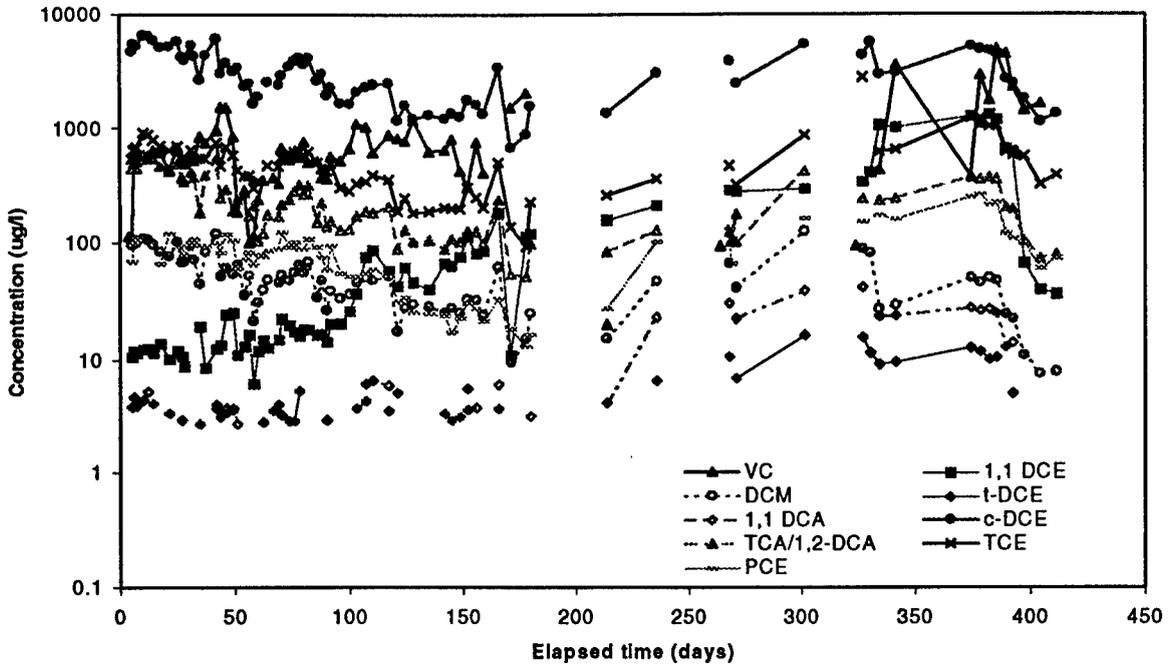
**Figure 21.** Concentration History -- Influent to All Columns
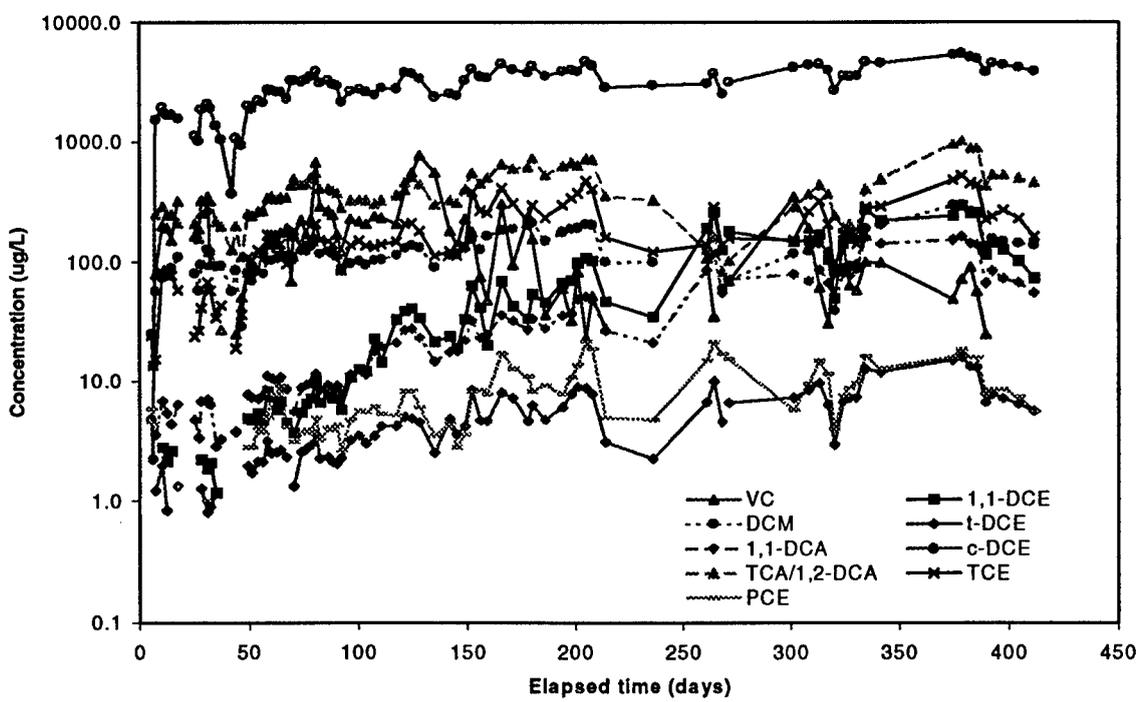
**Figure 22.** Concentration History -- Sand Column Effluent

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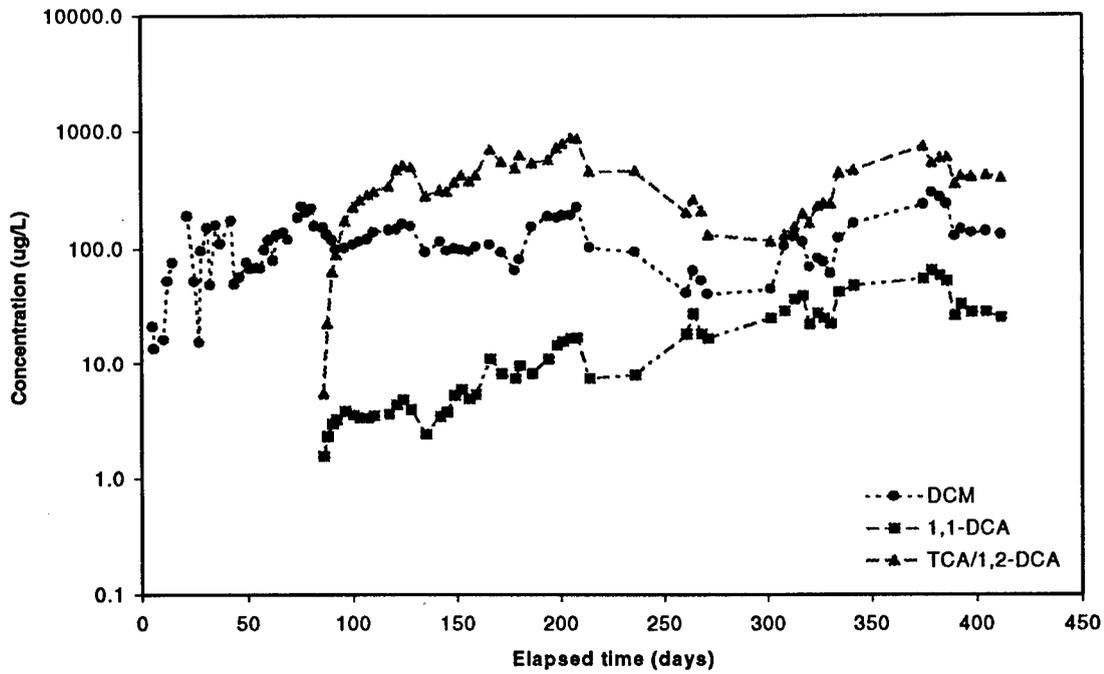
Figure 23. Concentration History -- Iron Column Effluent
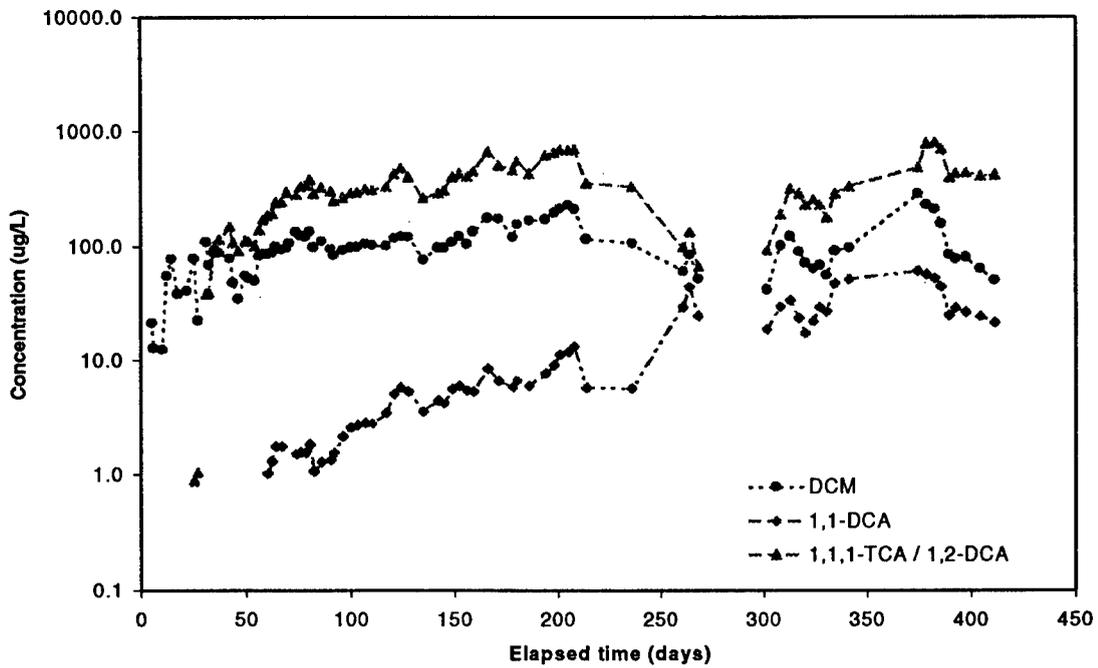

Figure 24. Concentration History -- Fe/Ni Column Effluent

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TABLE 3. AVERAGE AND STANDARD DEVIATION OF CONTAMINANT CONCENTRATIONS IN COLUMN INFLUENT AND EFFLUENTS.

Compound	Influent (µg/L)	Sand Effluent (µg/L)	Iron Effluent (µg/L)	Fe/Ni Effluent (µg/L)	Half life est. from this work (hr)	Half life in literature for 10-15C (hr)
VC	850 ± 921	163 ± 144	ND	ND	≤7-9[1]	4-6
1,1-DCE	169 ± 327	63 ± 79	ND	ND	≤5-6[1]	4-6
DCM	52 ± 29	121 ± 56	115 ± 60	98 ± 54	---[2]	Long[4]
t-DCE	6.0 ± 3.9	4.7 ± 3.6	ND	ND	≤10-11[1]	4-6
1,1-DCA	13 ± 12	35 ± 41	11 ± 15	11 ± 15	≤34-39[3]	24-40
c-DCE	3160 ± 1570	2930 ± 1280	ND	ND	≤4[1]	4-6
TCA/ 1,2-DCA	240 ± 142	375 ± 207	224 ± 247	288 ± 208	---[2]	Mixed[5]
TCE	536 ± 363	196 ± 162	ND	ND	≤4-5[1]	2-3
PCE	86.4 ± 53.2	7.9 ± 5.5	ND	ND	≤6-7[1]	2-3

[1] Assuming a first order reaction throughout the column, the initial concentration is taken as the average influent concentration and the final concentration taken as equal to or less than the detection limit (5 µg/L for VC, 0.1 µg/L for the rest). Half life estimates are rounded to integer values; a range is indicated if the iron and enhanced iron estimates were different when rounded to integer values (if so, the iron estimate is given first).

[2] Half life was not estimated since there was no significant or interpretable difference between the influent and effluent concentrations.

[3] Assuming a first order reaction throughout the column, the initial concentration is taken as the average effluent concentration from the sand column (which is higher than the apparently erroneous "influent" concentration) and the final concentration taken as equal to or less than the detection limit (0.1 µg/L).

[4] DCM is not degraded at a detectable rate by Fe and only very slowly by FeNi.

[5] 1,1,1-TCA is degraded by both Fe and FeNi with a half life of 2-3 days; 1,2-DCA is not degraded at a detectable rate by either Fe or FeNi.

1. Chlorinated alkene treatment

The most important of these findings is that all of the chlorinated ethenes were treated completely by both of the reactive metal columns, within our levels of detection. This agrees with our expectations on the basis of prior studies by others. As shown in **Table 3**, the upper-limit half-lives for the chlorinated ethenes estimated from our work are all above or comparable with

half-lives estimated by Environmental Technologies, Inc. (S. O'Hannesin, ETI, personal communication).

2. *Chlorinated alkane breakthrough*

Figures 25 through 27 present influent and effluent data for all three columns for DCM, 1,1-DCA, and TCA/1,2-DCA, respectively. Inspection of Figure 25 reveals that the estimated influent concentrations of DCM are lower than all of the effluent concentrations for most of the operational period. After considerable thought and examination of the field sampling and analytical equipment, we believe that this result is in large part due to some difficulties in collecting influent water that may cause these results to be unrepresentative of actual concentrations in the influent, and in a manner that may vary with the volatility of the compound being considered. (Our particular concern relates to some potential problems of line and valve clogging that was not diagnosed by our on-site technician for long periods of operation.) Thus, we believe that the estimated influent concentrations may not be useful as a point of comparison in these discussions. It is, however, evident from Figure 25 that the effluent DCM concentrations from all columns are similar throughout much of the operational period, which suggests that DCM is not treated to any significant degree by either of the reactive metals investigated. This finding is consistent with the results of prior laboratory work by others, in which DCM has been shown to persist in the presence of reactive iron materials (see **Table 3**).

In **Figure 26**, the effluent concentrations of 1,1-DCA from both iron columns are lower than the effluent from the sand column. This suggests that there was detectable, but incomplete, treatment of this compound by the reactive metals under the conditions of these tests. We note, however, that 1,1-DCA is a confirmed reaction product from the reaction of 1,1,1-TCA with zero-valent iron (Fennelly and Roberts, 1998), such that the dynamic steady-state concentration for this compound is more complex than one of simple first-order degradation. If we nonetheless apply such simple modeling to estimate reaction rates from our observed influent and effluent concentrations, we estimate that the half life of the reaction is equal to or less than 34 hours in the iron column and 39 hours in the enhanced iron column. These values are roughly consistent with prior experience at ETI (whose personnel estimate half life at 24-40 hours).
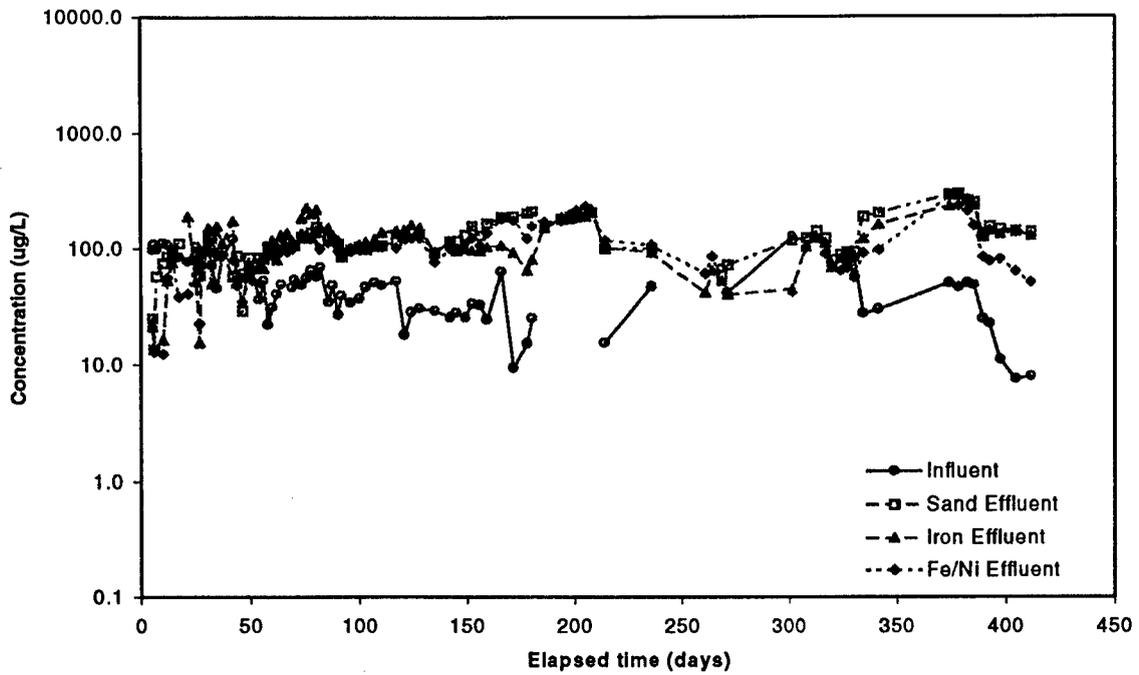
**Figure 25.** DCM Concentration History at Four Locations
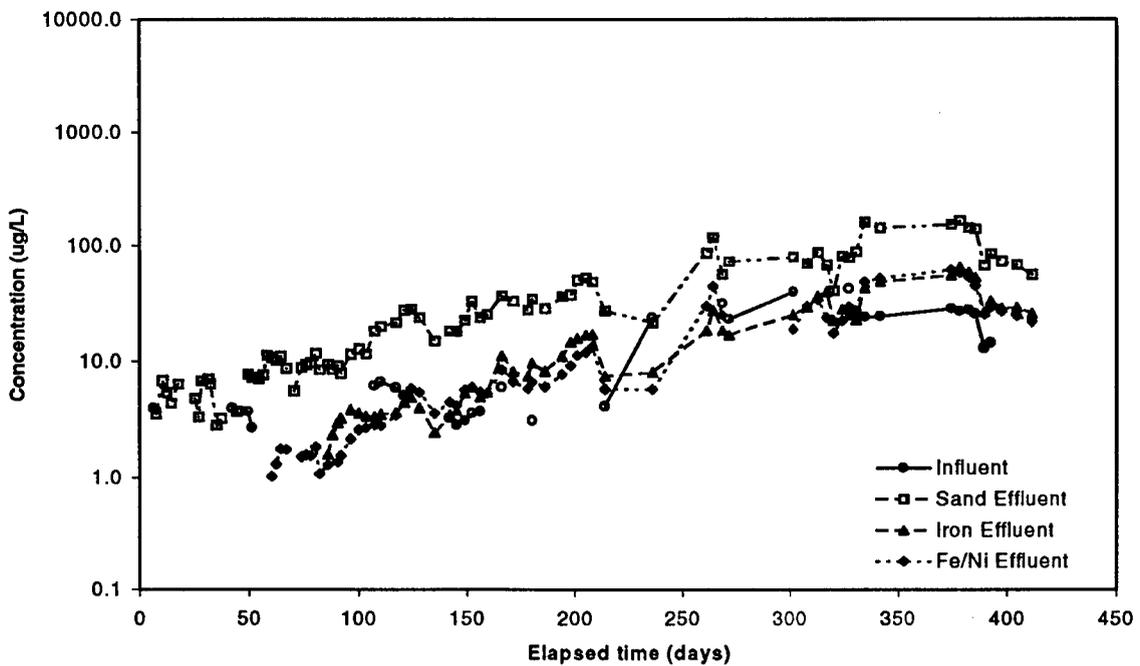
Figure 26. 1,1-DCA Concentration History at Four Locations
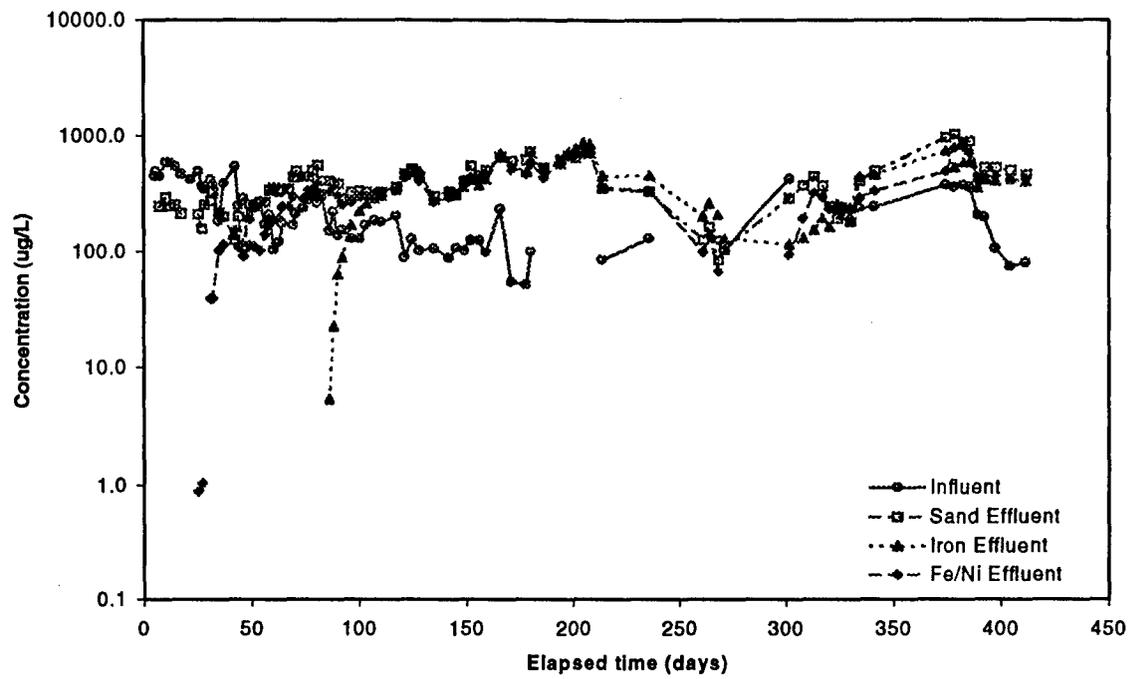
Figure 27. TCA/1,2-DCA Concentration History at Four Locations

With regard to **Figure 27**, we must recall that the data plotted represent two coeluting analytes, 1,1,1-TCA and 1,2-DCA. We know from our independent laboratory results on a few additional samples (see "Additional Sampling" above) that both analytes were present in the influent, at least during the later periods of operation (i.e., summer, 1997). From prior laboratory studies, we also know that 1,1,1-TCA reacts rapidly with zero-valent iron yielding 1,1-DCA as a reaction product (e.g., Roberts and Fennelly, 1998) and that 1,2-DCA reacts slowly, if at all, with zero-valent iron (S. O'Hannesin, ETI, and L. Roberts, JHU, personal communications). Thus, we believe that the chemical detected in the later time effluents of both iron columns is most likely 1,2-DCA, which shows breakthrough in the enhanced iron column at about 30 days and in the iron column at about 80 days. After breakthrough, there appears to be no treatment of the 1,2-DCA by either iron column for the remainder of the tests. This behavior may be indicative of reduced reactivity of the media at later times, possibly owing to the buildup of oxide layers or precipitation products. On the other hand, other possible explanations also exist.

For example, it is possible that the delay in breakthrough of the 1,2-DCA results from sorption of 1,2-DCA to the iron materials, since the sorption of chlorinated organic chemicals to Masterbuilder iron has been shown by Burris et al., 1995. In this regard, however, **Figure 25** indicates that the breakthrough of dichloromethane (DCM) was apparently not subject to major retardation effects. Although DCM is less hydrophobic than 1,2-DCA, some level of DCM retardation should nonetheless be expected if 1,2-DCA breakthrough was delayed by 30 to 80 days. Unfortunately, retardation effects for the other halogenated chemicals could not be evaluated, since they are fully transformed within the column.

A second possible explanation for the apparent 1,1,1-TCA/1,2-DCA breakthrough is that 1,2-DCA concentrations increased in the influent water. Although the combined 1,1,1-TCA/1,2-DCA data in **Figures 21 and 22** do not indicate such a trend, we cannot rule out the possibility of counter-acting temporal variability in the influent concentrations of 1,2-DCA and 1,1,1-TCA. In this regard, **Figure 26** shows that measured influent concentrations of a related compound (1,1-DCA) were in fact observed to rise over the course of our project.

F. CONCLUSIONS

Chlorinated ethenes were treated completely for the total project duration of over 400 days by both iron columns, during which time the Fe/Ni and iron columns were flushed with over 150 and 170 pore volumes of contaminated groundwater from the DAFB field site. The reaction half lives reflected in this work compare well with those from prior work.

For the chlorinated ethanes present in the contaminated groundwater, only 1,1,1-TCA was completely removed during passage through the column. For 1,1-DCA, an apparent partial removal was observed, but calculation of reaction rates were complicated by the fact that this compound is a known reaction product from the simultaneously occurring transformation of 1,1,1-TCA. Ignoring such a production term, the estimated half-life for 1,1-DCA (less than about 40 hours) compares well with estimates from prior work (24-40 hours). Because of analytical difficulties, we could not distinguish between 1,1,1-TCA (which is known to be degraded readily by the reactive iron materials) and 1,2-DCA (which is resistant to degradation). However, we expect that all 1,1,1-TCA was degraded completely during the field test. We therefore attribute the breakthrough results to 1,2-DCA and take this as evidence that this compound was not well-treated by either of the two media. Finally, our results indicate that DCM concentrations were not affected by either reactive metal studied, as expected from prior work.

Overall, the long-term trials of the reactive iron materials at Dover AFB performed in reasonable agreement with laboratory and field studies conducted by others. The results verified that effective removal of chlorinated ethenes can be achieved through reactive metal barriers, while also confirming that these systems may have little effect on certain chlorinated alkane contaminants. The overall removal efficiencies observed were consistent with expectations based on prior laboratory work, and removal of chlorinated alkenes to below detection limits was continuing to be achieved, even after passage of over 150 pore volumes of groundwater through the columns (over a period of 400 days). This effectively complete removal of all chlorinated alkenes was achieved despite the observation that the first 25% of each column was visibly impacted by precipitation products. On the other hand, we could not rule out the possibility that the delayed "breakthrough" of 1,1,1-TCA/1,2-DCA could be indicative of decreasing performance with regard to one or the other of these compounds.

Tests with shorter columns or for longer duration would allow better evaluation as to whether the efficiency of some or all of the iron is compromised by long-term exposure to site groundwater and contaminants. Alternatively, further tests with the previously exposed materials from different locations within the column could also be revealing.

Section IV. SUMMARY AND CONCLUSIONS

A. OVERVIEW

This report describes the results of field and laboratory investigations addressing contaminant fate in the subsurface and associated processes of groundwater remediation and control. The effort included aquitard sampling and modeling as well as pilot- (column-) scale investigations of reactive metal barrier technology.

B. OBJECTIVES

The overall goal of the aquitard coring and modeling was to better evaluate, model, and understand the issue of aquitard contamination and associated aquifer concentration "rebound" within two isolated and pretreated aquifer test-cells at Dover AFB, DE. Both new field data and further model development and application were sought in order to verify the nature of the diffusion process and to better understand our ability to apply results to field-scale interpretations. The latter include both "forensic" interpretations (to better understand the plume history at the site) and "predictive" simulations (to better understand the potential effects of future remediation efforts).

We conducted exploratory pilot (column-scale) investigations of "barrier" treatment technologies. This effort was undertaken to support potential future demonstration projects at this location, and took advantage of existing support structures and analytical facilities. A key aspect of this work was the use of contaminated groundwater pumped directly from the aquifer to the column to ensure conditions as close as possible to those in *situ*. Also important was the long-term operation of the columns, in order to elucidate any temporal variations in column behavior over an extended period of exposure to the contaminated groundwater.

C. RESULTS AND CONCLUSIONS

1. Aquitard Coring and Analysis

Our field coring data present a clear picture of diffusion-controlled aquitard contamination, in

which persisting sorbed chemicals in the aquitard serve as a long-term source of contaminant to the otherwise relatively easily flushed aquifer. Rates of contaminant release from the aquitard are strongly dependent on both the initial contaminant distribution and the properties of the impermeable barrier, and may be largely unaffected by changed conditions in the overlying porous medium.

In addition to providing field evidence regarding rates of aquifer decontamination under pumped conditions, the characterization work and modeling studies conducted in this project have provided new insights into the nature of contaminant transport to and from low-permeability zones. Under some circumstances, contaminant profiles within lower permeability media may be used in a forensic sense to generate insight into the history of contamination in the adjacent higher permeability media. For purposes of predicting rates of contaminant release, good understanding of the initial *in situ* contaminant distribution is critical. Equally important to understand is the nature of the diffusive process that will often control the long term evolution of such contaminant profiles. By better understanding and predicting rates of contaminant release, regulatory actions can be placed in better context relative to their goals, and remediation efforts can be better planned and designed. Several models that are useful toward obtaining such understanding have been developed and tested in this work.

2. Results and Conclusions - Column-Scale Investigations

The column-scale study took advantage of existing facilities at the site to further our knowledge regarding the long-term efficiency of iron and other reactive metal materials that can be used in the creation of subsurface reactive barriers against contaminant migration. The results verified that effective removal of chlorinated ethenes can be achieved through reactive metal barriers, while also confirming that these systems may have little effect on certain chlorinated alkane contaminants. In general, the overall removal efficiencies observed were consistent with expectations based on prior laboratory work, and removal of chlorinated alkenes to below detection limits was continuing to be achieved, even after passage of over 150 pore volumes of groundwater through the columns (over a period of 400 days). Such effectively complete removal of all chlorinated alkenes was maintained despite the observation that the first 25% of each column was visibly impacted by precipitation products. These results demonstrate the

viability of the reactive barrier processes for treatment under the natural geochemical conditions present at Dover AFB, DE, even over relatively long-term operation. However, tests with shorter columns or over greater duration would be required to more quantitatively evaluate whether long-term exposure to site groundwater and contaminants compromises the efficiency of the reactive media (including that at the front end of the column). Alternatively, further tests with the previously exposed materials from the front end of these columns could also be revealing.

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