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13. ABSTRACT *(Maximum 200 words)*

Experiments were performed to determine the desorption kinetics, diffusion, and advection of two common subsurface VOC contaminants: trichloroethylene (TCE), and chloroform (CF) both individually and as a gas mixtures.

Effective diffusion coefficients of TCE were determined in the absence and presence of CF. At high relative pressure the "effective" distribution coefficient for these vapors decreased and consequently their diffusive transport was enhanced. This result is attributed to the presence of non-linear sorption isotherms for the vapors. Advective transport of TCE and CF also displayed mild gas concentration effects suggesting that the accurate prediction of vapor transport may require consideration of reactions at the gas water interface including vapor condensation and competition.

The breakthrough and subsequent desorptive release of TCE vapor from a column of aquifer sand was well predicted by a transport model that employed a Gamma distribution of mass transfer rate constants. Comparisons of experimental data and model predictions have been successfully made at two different gas flow velocities for sand exposed to low ($P/P_O = 10\%$) and high ($P/P_O = 90\%$) relative pressure of TCE.

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SCHOOL OF CIVIL AND ENVIRONMENTAL ENGINEERING
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F49620-94-1-0157

June 30, 1997

Capt. Michael Chipley
Air Force Office Of Scientific Research
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Dear Mike:

Enclosed please find the final report for our AFOSR-sponsored research project entitled "Vapor Transport in Unsaturated Soil" (project no: F49620-94-1-0157). As we discussed in a recent exchange of e-mail messages, several aspects of the work on this project are ongoing under the auspices of our augmentation grant "Augmentation for Basic Research on Vapor Transport in Soil" (project no: F49620-94-1-0316). As a result, we have not completed the full analysis of our data and its implications. The aspects of this research that have been wrapped up are fully described in the Cornell University M.S. thesis of Mr. Sean Lorden, and representative portions of that material have been extracted for this report. A publication based on Sean's research is currently in preparation. Three additional graduate students are currently involved in the research. Two, Mr. Jason Gilbert and Mr. Brent Alspach are expected to complete their M.S. thesis this summer, and publications based on their work are anticipated to be forthcoming. Preliminary results from their research is summarized in this report. The third student, Mr. Kevin Saunders, will be continuing his research through till the end of the augmentation award (6/30/98).

By the end of the augmentation award, the AFOSR-funded research will have supported the training of four M.S.-level environmental engineers whose future careers will contribute to the solution of this nations environmental problems. In addition to the M.S. thesis of each student, my expectation in that much of this work will be suitable for publication in peer reviewed journals.

I take this opportunity to thank you and the Air Force Office of Scientific Research for your support of these investigations. Basic research of the type done here serves as the foundation for technology, such as that used for remediation of contaminated soils, but also for future applications that we can not yet anticipate. The Air Force's vision in supporting activities of this type is to be commended.

If any additional information is needed regarding our research, or any alterations are needed to this report, please contact me by phone (607-255-7571), fax (607-255-9004), or e-mail (LWL3@cornell.edu).

Sincerely,

Len

Leonard W. Lion
Professor

enclosure

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FINAL REPORT

Project Title: Vapor Transport in Unsaturated Soil

Principal Investigator:
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Project No.: F49620-94-1-0157

Date Submitted: 6/30/97

VAPOR TRANSPORT IN UNSATURATED SOIL

Abstract

The transport of volatile organic compounds (VOCs) is influenced by the form in which VOCs exist and the physical/chemical properties of the porous medium. VOC transport mechanisms in the unsaturated zone include diffusion and advection in the gas phase. VOC advection requires mass transfer of sorbed VOCs to the mobile gas phase, and given the multiple processes that control VOC sorption, transfer rates may be best described using probability distributions. When analyzing the retarded transport of VOCs, it is also important to consider that isotherms for the sorption of gases are typically non linear at high relative pressures, and that VOCs commonly occur at waste sites as mixtures that can display competitive sorption effects. In order to address these issues, experiments have been performed to determine the desorption kinetics, diffusion, and advection of two common subsurface VOC contaminants: trichloroethylene (TCE), and chloroform (CF) both individually and as gas mixtures.

Effective diffusion coefficients of TCE have been determined in the absence and presence of CF. At high relative pressure the "effective" distribution coefficient for these vapors decreased and consequently their diffusive transport was enhanced. This result is attributed to the presence of non-linear sorption isotherms for the vapors. Advective transport of TCE and CF also displayed mild gas concentration effects suggesting that the accurate prediction of vapor transport may require consideration of reactions at the gas water interface including vapor condensation and competition.

The breakthrough and subsequent desorptive release of TCE vapor from a column of aquifer sand was well predicted by a transport model that employed a Gamma distribution of mass transfer rate constants. Comparisons of experimental data and model predictions have been successfully made at two different gas flow velocities for sand exposed to low ($P/P_o = 10\%$) and high ($P/P_o = 90\%$) relative pressures of TCE.

VAPOR TRANSPORT IN UNSATURATED SOIL

Objective:

The main objective of this research was to investigate the parameters that govern advective and diffusive transport of volatile organic compounds (VOCs) in unsaturated porous media, with special attention to vapor condensation, interaction of vapor mixtures, and mass transfer kinetics.

Background/Introduction:

As VOCs travel through a soil, they can be bound by a variety of mechanisms. For example, it is widely known that nonionic hydrophobic compounds such as VOCs can partition from the aqueous phase into soil organic matter. In the unsaturated zone, water exists as a film coating mineral surfaces as well as bulk water condensed in cracks, fissures and pores, and VOC uptake can occur as gaseous VOCs dissolve into this stationary aqueous phase. Additional mechanisms of VOC sorption include condensation in pore space not occupied by water and adsorption at the gas-water interface. The various VOC uptake processes are illustrated in Figure 1.

Unlike partitioning into soil organic matter and dissolution into pore water, the adsorption and condensation reactions of VOCs at the gas water interface are not necessarily governed by a linear isotherm. The adsorption of individual vapors at the gas water interface is also expected to be dependent on the composition of the gas phase as different VOCs may display differing affinities for the surface. Consequently, the magnitude of the sorptive retardation of VOCs is anticipated to depend on the concentration and composition of the vapor phase. Any variability in vapor retardation will, in turn, be manifested in the transient advective and diffusive transport of VOCs.

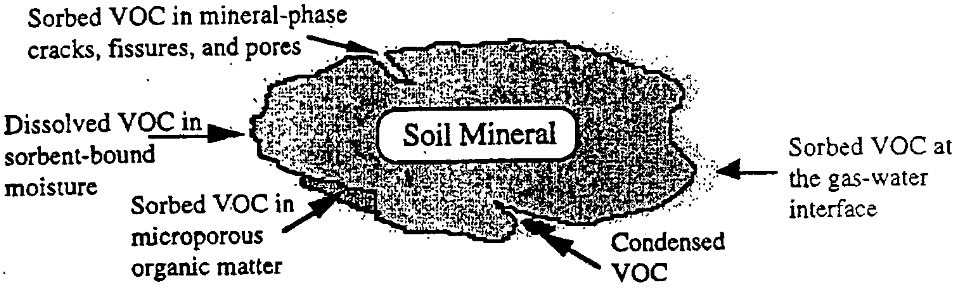


Figure 1. Mechanisms of VOC Uptake on Unsaturated Porous Media.

Any mechanistically based mathematical description of VOC transport in the vadose zone must incorporate mass transfer of VOCs from the porous matrix into the mobile gas phase. Each of the VOC uptake mechanisms indicated in Figure 1 will be governed by different dynamic controls. The distribution of pore sizes and geometries in any given porous medium will result in a variety of diffusional paths and diffusive release rates for VOCs. Also, many different types of organic matter with different VOC sorption affinities and rates are present in soils. Furthermore, some types of VOC uptake (such as condensation and adsorption at the gas-water interface) are not linear partitioning processes, leading to the expectation that there will be nonlinear isotherms and dynamic competition between VOCs. As a result of these complexities, an array of VOC release rates is expected, and the mechanistic processes controlling sorption/desorption kinetics may change over time. This type of problem lends itself to treatment with statistical distributions. A Gamma density function has been employed to describe variable release rates of sorbed hydrophobic organic contaminants from saturated soil systems (Connaughton *et al.*, 1994; Chen, 1994; Chen *et al.*, 1997; Culver et al, 1997) and, given its prior success, this model warrants evaluation for its suitability in the modeling of VOC transport.

Materials/Methods

A fine-grained aquifer sand obtained from a quarry in Newfield, NY was used as the sorbent in this investigation. This sand has previously been characterized with respect to specific surface area (3.3 m^2/g by B.E.T. analysis with N_2), organic carbon content (0.91%), and particle size distribution (93.7% sand, 6.3% silt) (Chen *et al.*, 1995). Three VOCs were chosen for use: trichloroethylene (TCE), chloroform (CF) and perchloroethylene (PCE). These VOCs are common components of solvents and degreasers, and are suspect carcinogens. TCE is one of the most frequently detected subsurface contaminants at hazardous waste sites in this country. Also, results from preliminary sorption studies conducted by Thoms and Lion (1992) showed competitive sorptive interactions between CF, TCE and PCE. The content of this report is principally confined to the experiments performed with TCE and CF.

In support of the VOC transport experiments sorption of trichloroethylene (TCE) was characterized over the full range of relative pressures onto the aquifer sand sorbent at 90% relative humidity. Non-linear adsorption isotherms were developed for water and TCE using the gravimetric apparatus described by Ong and Lion (1991). VOC sorption isotherms were obtained at low relative pressure under water-saturated and unsaturated conditions using the method of Garbarini and Lion (1985) as modified by Peterson *et al.* (1988).

Diffusion Experiments

A number of different column configurations are commonly used in diffusion research, relying on different modes of contaminant introduction and concentration monitoring (Batterman *et al.*, 1996; Hutter *et al.*, 1992; McCarthy and Johnson, 1995; Petersen *et al.*, 1994; Voudrias and Li, 1993). In this research, a modified reservoir-type system was used. The diffusion column setup was modeled after a system successfully implemented in previous work at Cornell (Peterson et al, 1988). Typically, in prior research reservoir setups have relied on vapor source concentrations that correspond to the saturation vapor pressure (P_{sat}) of an individual compound. The apparatus used in this study, however, allowed for variable VOC vapor concentrations and for mixtures of VOCs.

As shown in Figure 2, the diffusion assembly consisted of three distinct sections: the influent chamber, the soil column, and the effluent chamber. All components of the apparatus were constructed from aluminum or stainless steel to minimize any interactions with VOC vapors. The length of the soil column was variable, ranging from approximately 0.5 to 24 inches (1.25 to 61 cm). In the diffusion experiments, the moisture content of the aquifer sand was typically 2.15 to 2.6 percent (dry mass), and the column was packed to achieve total porosities ranging from 0.481 to 0.513.

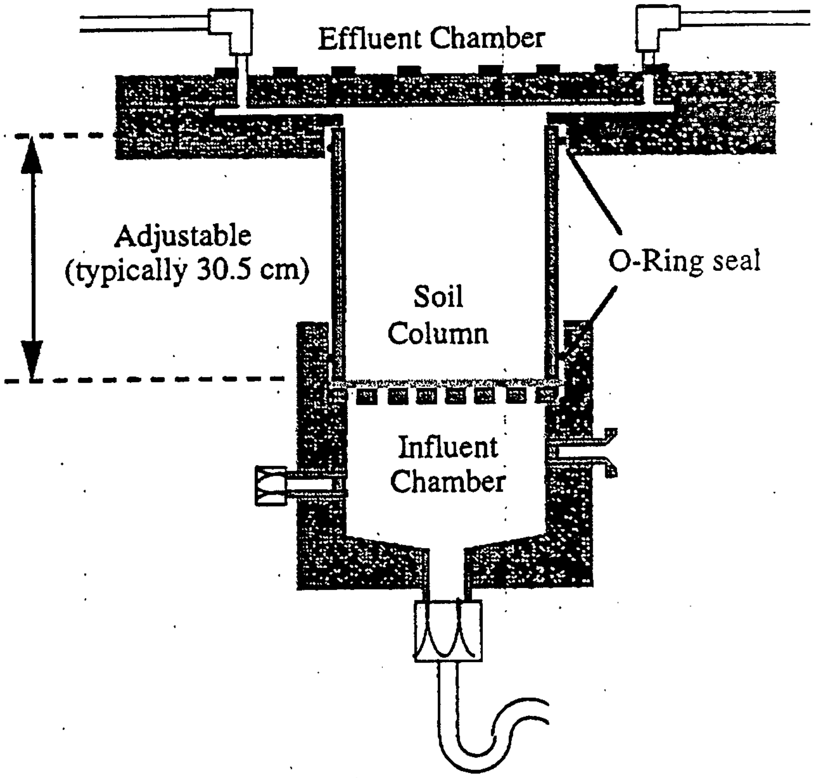


Figure 2. Diffusion Column Assembly: Elevation View.

A cross section of the diffusion apparatus influent chamber is detailed in Figure 3. VOCs in aqueous solution were pumped at a steady rate into the chamber at point B. The drain assembly (H) provided both a steady liquid level within the cell and a "gas seal" preventing any outflow of vapor. In the gas headspace within the chamber, contaminant vapors accumulated as mass transfer of VOCs from dissolved phase to gas phase occurred. The VOC vapor concentrations attained below the aluminum and steel soil support screens (E and F) provided the driving force for molecular diffusion through the soil. The magnitudes of the driving concentrations, or C_0, were manipulated by altering either the aqueous solution concentration or by changing the liquid input flow rate. Influent vapor concentrations were measured during experiments by extracting 0.5 to 1.0 mL gas samples at the sampling port (C), which was sealed with a Teflon backed silicon septum and aluminum crimp cap. The samples were taken using Pressure-Lok™ syringes from Precision Sampling Corporation. Samples were analyzed with a Hewlett-Packard 5890 Series II gas chromatograph that was equipped with a stainless steel column (10 ft. x 1/8") packed with 20% SP-2100™ and 0.1% Carbowax-1500 on 100/200 mesh Supelcoport™ (Supelco, INC.; Bellafonte, PA), a flame ionization detector (FID) and connected to a Hewlett-Packard 3396 Series II integrator. Influent vapor concentrations ranged from approximately 1.5 to 20 percent of P_{sat}.

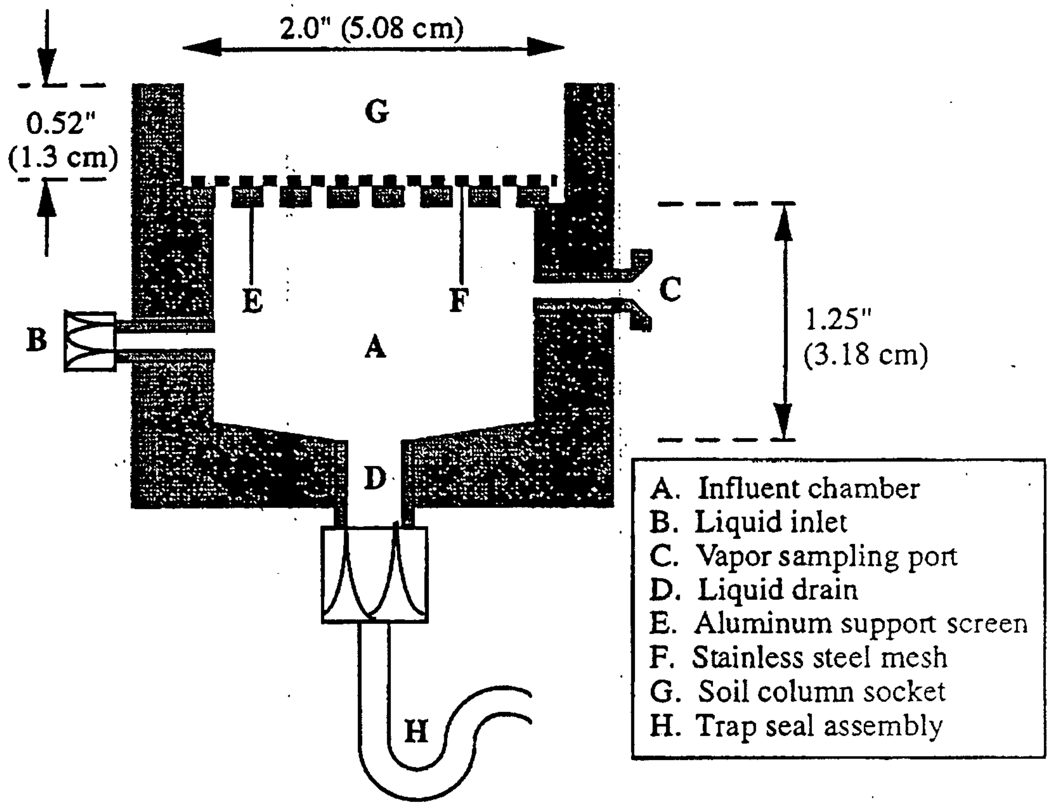


Figure 3. Diffusion Column Assembly: Influent Chamber, Elevation View.

Figure 4 shows both plan and elevation views of the exit or effluent chamber. This component of the diffusion assembly provided a means for maintaining low VOC concentrations, relative to influent concentrations, at the downstream end of the soil column. A thin stream of air at 100 percent relative humidity was directed through the sweep gas passage (B) at a nominal flow rate of 100 mL/min. This "sweep flow" carried contaminants emerging from the upper face of the soil column out of the cell through the gas outlet at point D. VOC concentrations in the effluent sweep gas were monitored over time via syringe extraction of 0.5 mL to 1 mL of effluent gas at a sampling port downstream of the chamber. These time-varying effluent concentration profiles, or breakthrough curves, were used to assess transient transport behavior in a number of different experiments.

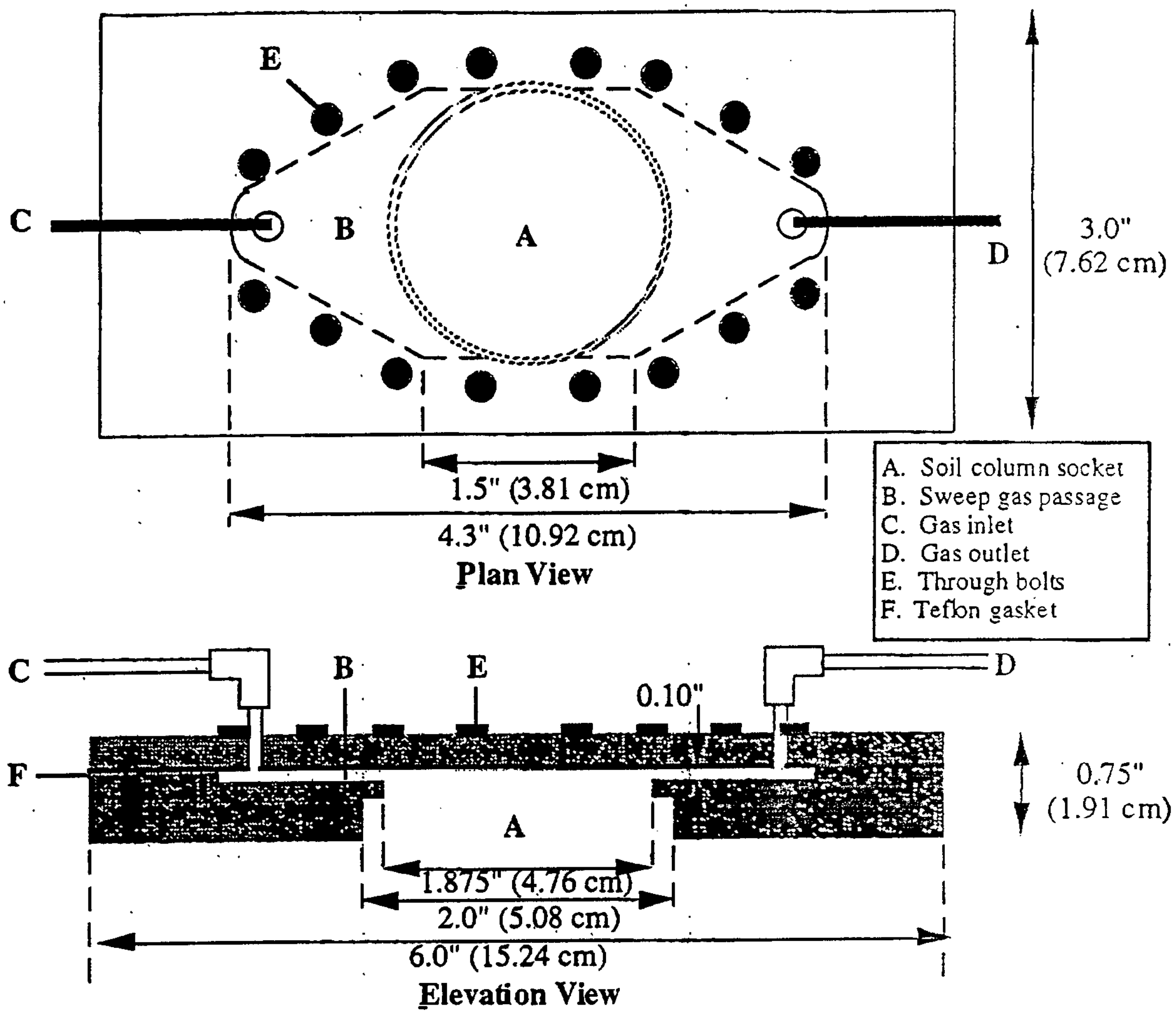
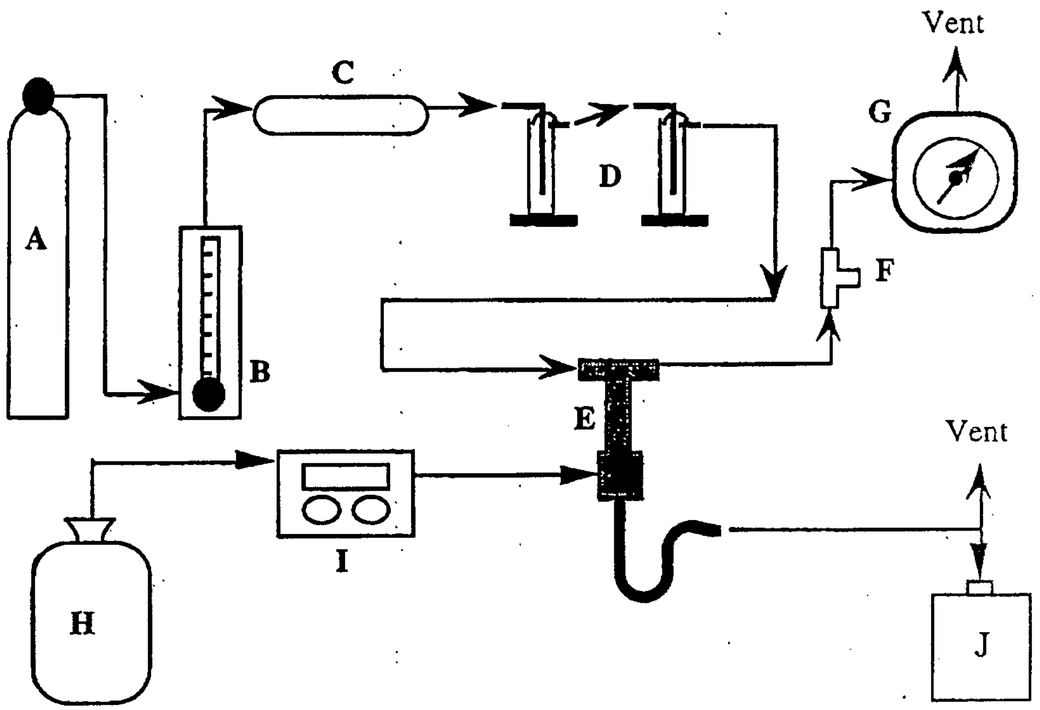


Figure 4. Diffusion Column Assembly: Effluent Chamber, Plan and Elevation Views.

A schematic diagram of the entire diffusion apparatus appears in Figure 5. With the exception of the compressed air source tank (A), all components of the experiment were maintained at 25 ± 0.2 °C within a constant temperature chamber.



→ = Gas flow path
➤ = Liquid flow path

A. Compressed air and regulator
B. Flow meter and needle valve
C. Hydrocarbon trap
D. Gas washing bottles (water)
E. Diffusion cell assembly
F. Gas sampling tee
G. Wet-test flow meter
H. Solvent source reservoir
I. HPLC solvent pump
J. Liquid waste container

Figure 5. Schematic of Diffusion Test Cell Assembly (after Peterson *et al.* 1988).

At steady state, the diffusive flux of a compound through a soil column of length L (cm) is described by Fick's first law:

$$J = -D_{eff}\frac{(C-C_0)}{L}$$

where J is the vapor flux (g/cm^2/min), C is the concentration of the compound in the effluent sweep gas (g/mL), C_o is the concentration of the compound in the source vapor (g/mL), and D_{eff} is the effective diffusion coefficient for the VOC under the experimental conditions (cm^2/min).

At steady state, the vapor flux through the soil column may also be determined via mass balance at the upper surface of the soil. The rate of contaminant mass flux through the soil surface, J, is equal to the rate of mass exiting the diffusion cell with the sweep gas flow:

$$J = \frac{QC}{A},$$

where Q is the sweep gas flow rate (mL/min), C is the concentration of the compound in the effluent sweep gas (g/mL), and A the cross-sectional area of the soil column (cm^2).

Setting the above two equations equal to one another and solving for D_{eff} gives:

$$D_{eff} = \frac{QCL}{A(C - C_0)}.$$

In analyzing the results of the diffusion experiments, values of source concentration, effluent sweep gas concentration, and sweep gas flow rate data were used to compute values of D_{eff}. Data points from times near the end of each experimental run were selected for these calculations based on evaluation of the data and allowed adequate time for the diffusion process to reach steady state.

Advection experiments

As the primary means for investigating VOC mass transfer, advective transport experiments were conducted using TCE in a bench-scale column reactor. Experimental details are described by Lorden (1996) and are briefly summarized here. All experiments were conducted at 25 °C. A stainless steel column (2.36 cm. I.D. x 38 cm. long) was filled with the aquifer sand and allowed to equilibrate to constant weight with with a flowing gas stream at 90% relative humidity. Glass saturators containing either water or liquid TCE were used to prepare the gas stream to be used in experiments. By adjusting the temperatures of the saturators and the gas flow through each, it was possible to control the relative humidity, vapor phase VOC concentration, and total gas flow upstream of the column. Experiments were conducted at two relative pressures of TCE [10% P/P_0 (52.5 mg/L), and 90% P/P_0 (472.5 mg/L), designated LC and HC for low and high concentration, respectively] and two different gas flow rates (40 and 80 mL/min, designated LF and HF for low and high flow, respectively). Of the two TCE relative vapor pressures used, 90% P/P_0 is considered representative of the "near-field", close to a nonaqueous liquid phase VOC source, while 10% P/P_0 is more representative of the "far-field", at contaminated sites. The gas flow rates were chosen so that the resulting pore velocity of the gas would fall within the range of 0.001 m/s to 0.008 m/s. This range is thought to be representative of the range of velocities attained during the soil vapor extraction remediation process (Grathwohl and Reinhard, 1993). A schematic of the experimental apparatus for the column experiments is given in Figure 6. In the first section of the apparatus, the gas flow rate, relative humidity, and partial pressure of TCE were established. The middle section contained sand-filled column through which the gas flow traveled. Provisions were made to measure the pressure drop across the column and the relative humidity of the gas. Figure 7 shows a detailed schematic of the column end fittings. The third section of the apparatus consisted of a gas chromatograph with an auto sampling valve that was used to measure effluent TCE concentrations.

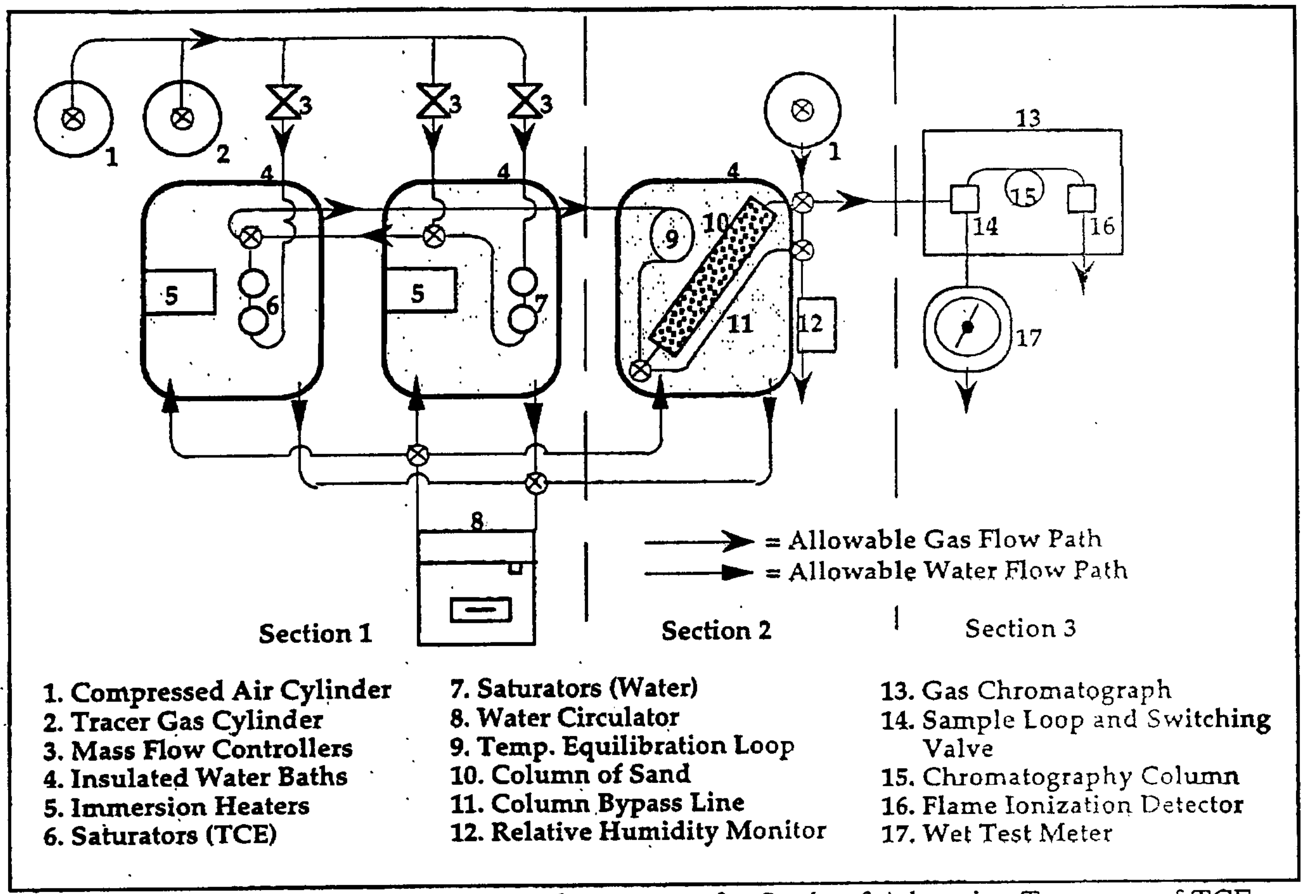


Figure. 6. Schematic Diagram of Apparatus for Study of Advective Transport of TCE.

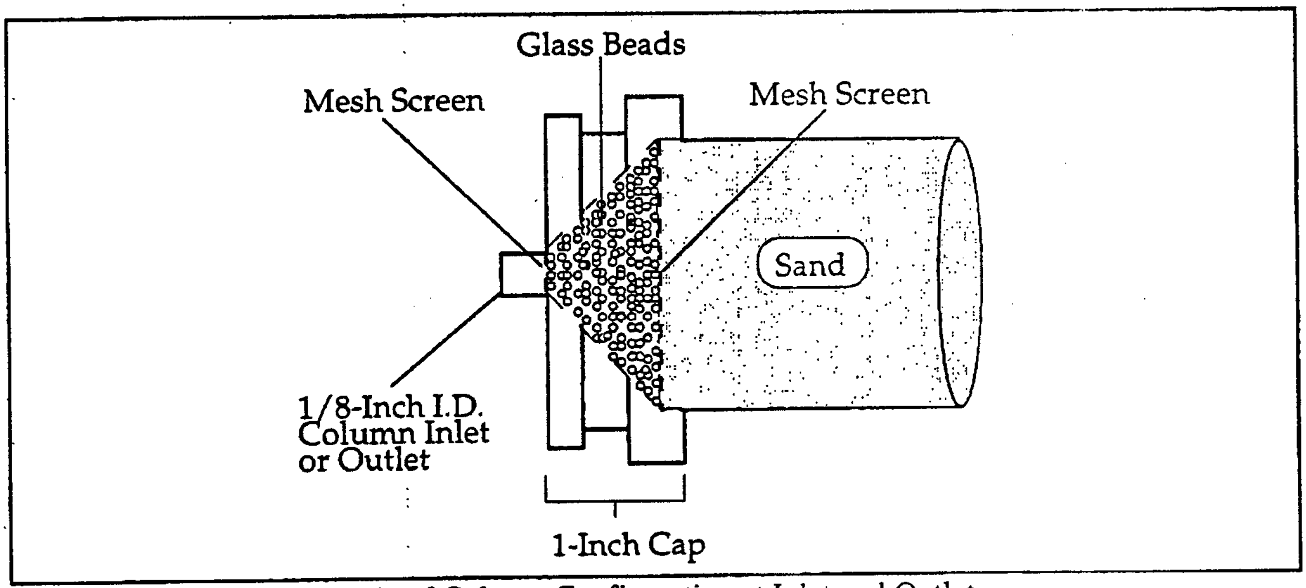


Figure 7. Schematic of Column Configuration at Inlet and Outlet.

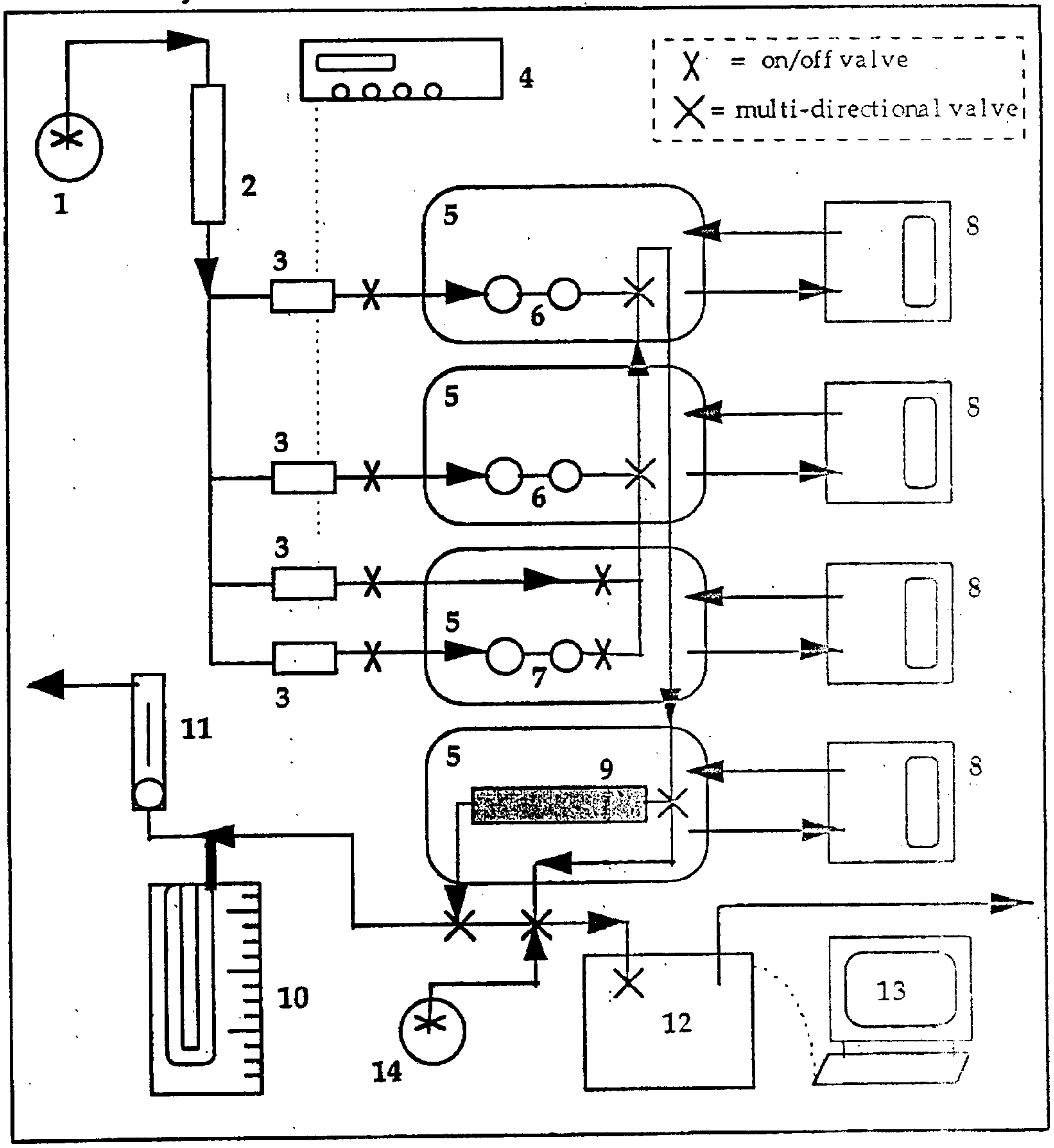
Once desired experimental conditions had been established, a breakthrough profile (BP) was generated by introducing gas flow to the column. After the relative TCE concentration (C/C_0) in the column effluent reached 0.99, the column was allowed to equilibrate with the flowing gas for an additional 7 days, during which conditions were periodically monitored to verify stability. The column was then isolated from gas flow for 1 to 2 hours while TCE concentrations upstream of the column were reduced to negligible levels. The gas flow was then re-directed through the column and a TCE elution profile (EP) was generated. Effluent concentrations were monitored until C/C_0 was less than or equal to 0.001.

Mathematical modeling of the data was performed by Dr. W. Chen using a transport model that invoked a Gamma distribution of sorptive rate constants. The reader is referred Chen and Wagenet (1995) for a derivation and description of the model governing equations. Methane breakthrough profiles were used to determine porosity, gas pore velocity, and mechanical dispersion for subsequent use in mathematical modeling of the TCE experiments. The TCE breakthrough profile at low flow and low TCE relative pressure (LC-LF-BP) was fit to obtain the parameters that described the Gamma distribution of rate constants, α and β. Predictions were then made of all remaining TCE breakthrough profiles (BP) and elution profiles (EP) at both low and high gas flow with no adjustable parameters. The TCE sorptive distribution coefficient used in the model computations was calculated directly from the experimentally measured TCE adsorption isotherm.

To accommodate multiple sorbates, the advective flow apparatus was modified as shown in Figure 8. The modifications permitted the presence of a second vapor (CF), increased temperature (and consequently concentration) control, and computerized data acquisition.

Two types of experiments were conducted and compared: single sorbate experiments with TCE, designated by "T," and binary experiments with CF and TCE, designated by "CT". The experimental designations below also include a number to indicate the relative pressure of the sorbates. Higher numbers signify higher concentrations of TCE in the single sorbate experiments and of CF in the binary experiments, in which TCE concentrations were held constant. An exception was experiment CT5, which replicated experiment CT4.

All concentration data was collected using a gas chromatograph (GC) equipped with a air-actuated sampling valve. A computer program designed for this research allowed full control over sampling interval and peak area integration parameters (Weber-Shirk, 1996). The experimental protocol, in general, was as follows. First, the desired VOC vapor concentrations at 90% relative humidity were established by varying both the temperatures and the carrier gas flow of the gas washing bottles containing reservoirs of TCE, CF, and water, respectively. The column of aquifer sand was then exposed to the vapors for two hours. VOC breakthrough typically occurred within the first 10 minutes. At the end of the two hour equilibration the column was isolated and the plumbing purged to remove any residual VOCs. Clean, humidified air was then used to elute the column in three stages, separated by intervals 18 and 6 hours, respectively. In each stage the effluent peak areas were monitored until the gas concentrations approached the GC peak area detection limit. The interval between elutions allowed VOC concentrations in the column to rebound by slow desorption from the stationary phase. Tests indicated that this procedure permitted the recovery of more than 99% of the VOC mass sorbed onto the column.



1. Source Air or Tracer Gas Cylinder
2. Dessicator
3. Mass Flow Controller Transducer
4. Mass Flow Controller
5. Constant Temperature
6. VOC Gas Washing
7. Water Gas Washing
8. Constant Temperature Circulator
9. Soil Column
10. Manometer
11. Flowmeter with Restrictor
12. Gas Chromatograph (GC)
13. Computer
14. Purging Cylinder (N_2 Gas)

Figure 8. Schematic of the Modified Advective Flow Apparatus.

Results and Discussion:

VOC Sorption

At low relative pressures, TCE adsorption was described by a linear isotherm (see figure 9).

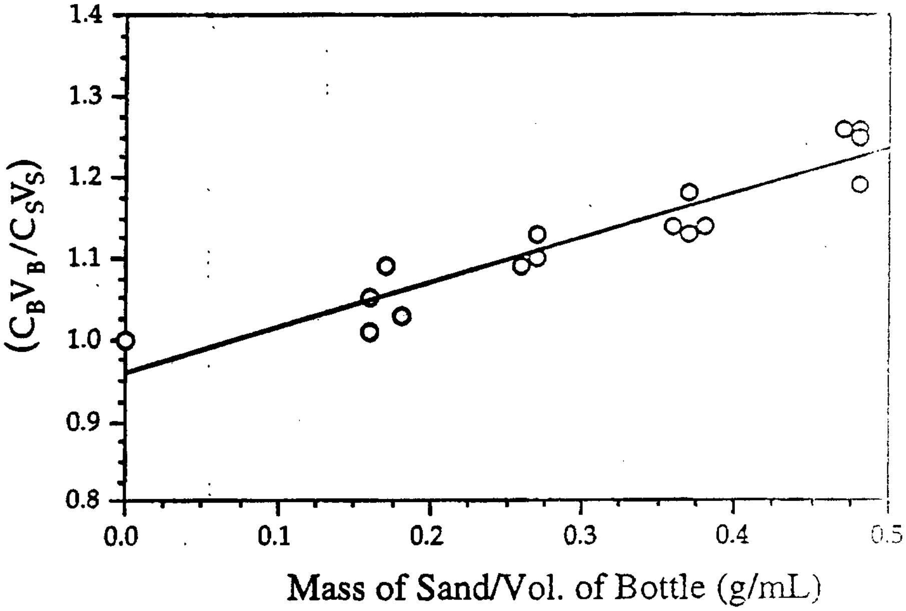


Figure 9. Linear Isotherm for Sorption of TCE Vapor on Moist (M.C. = 4%) Aquifer Sand.

The soil-vapor distribution coefficient, K_d', was determined from the following equation derived from mass balances by Ong and Lion (1991):

$$\frac{V_B C_B}{V_S C_S} = K_d' \frac{M}{V_S} + 1$$

where C denotes concentration, V denotes volume, and the subscripts B and S denote control (blank) and sample vials, respectively. M is the mass of a moist soil sample minus the mass of associated water.

The value of K_d' is given by the slope of a plot of $V_B C_B / V_S C_S$ versus M/V_S, as shown in Figure 9 and equaled 0.60 ± 0.11 ml/g at the 95% confidence interval.

Ong and Lion (1991) developed the following predictive equation for K_d' which is applicable when the average number of bound molecular layers of water exceeds five, the soil water behaves ideally, and when VOC condensation and sorption at the gas-water interface are negligible:

$$K_d' = K_d / K_H + (\text{M.C., }\%)/(100\ K_H)$$

where K_H is the Henry's constant for the compound, K_d is the saturated distribution coefficient for sorption from the aqueous to the solid phase and M.C. is the sorbent's moisture content.

Substituting $K_d = 0.20$ ml/g (Lorden, 1996), M.C. = 4.0%, and $K_H = 0.397$ (Garbarini and Lion, 1985) yields $K_d' = 0.60$ ml/g. At this level of significant figures, the predicted value is the same as the experimentally determined value. The excellent agreement between experiment and theory suggests that the value of K_d' determined in this research is accurate, and that model of Ong and Lion (1991) can be used to estimate K_d' for a given moisture content.

Non-linear adsorption isotherms were developed for both water and TCE (Figures 10 and 11) using the gravimetric apparatus described by Ong and Lion (1991). The adsorption of water on oven-dried sand yielded an isotherm with characteristics fitting the Type I BET isotherm described by Gregg and Sing (1982).

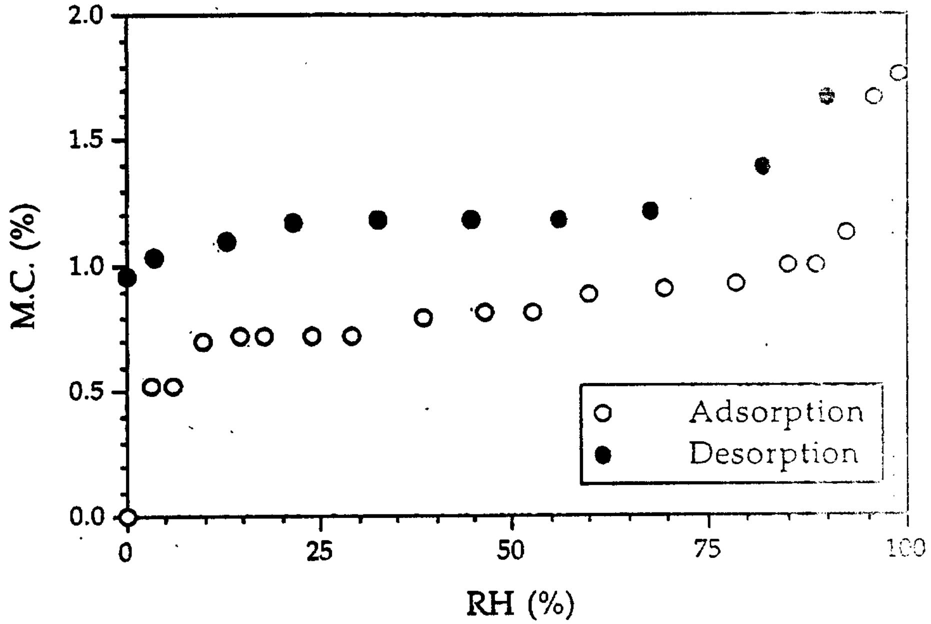


Figure 10. Water Sorption on Oven-Dried Aquifer Material.

The TCE isotherm on the moist sand (Figure 11) has characteristics comparable to those of the Type V isotherm as defined by Gregg and Sing (1982). The aquifer sand sorbent had additional capacity for TCE even at a relative humidity of 90%, suggesting that condensation of TCE could occur even in nearly saturated soils. The TCE adsorption isotherm also indicates that condensed vapor can constitute a high fraction of the TCE sorbed at high relative pressures of TCE.

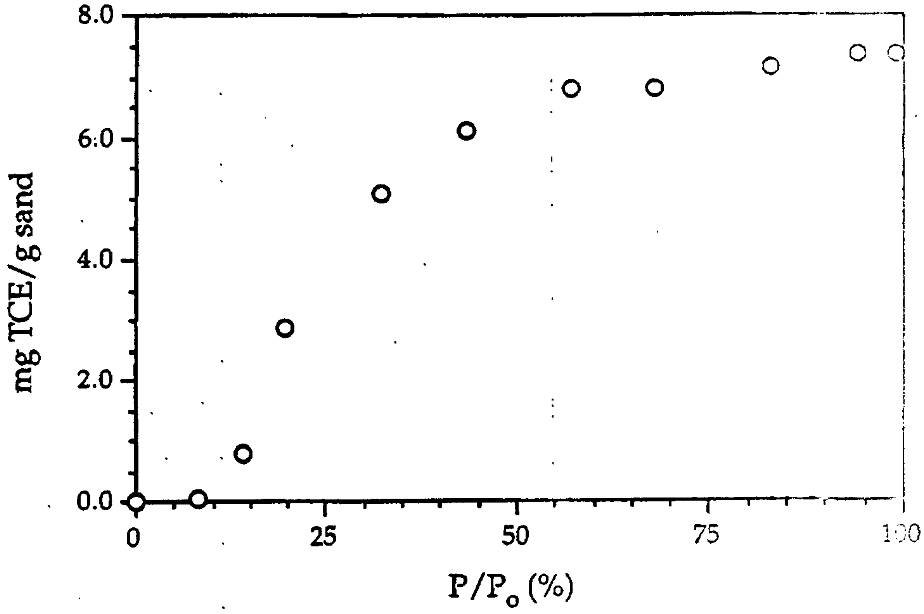


Figure 11. TCE Sorption on Aquifer Material at 90% Relative Humidity.

Competitive sorption between VOCs at high relative vapor pressures was also observed. For example, this was evident in the case of PCE in the presence of CF. As illustrated in Figure 12 the PCE isotherm was non-linear and PCE sorption was suppressed in the presence of CF.

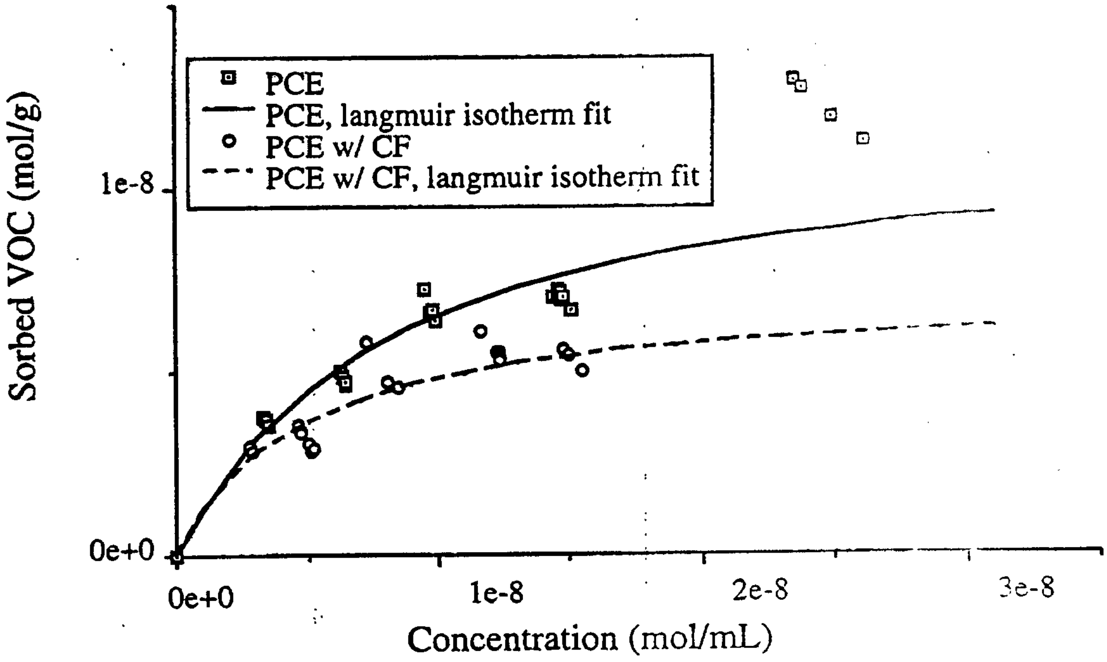


Figure 12. Sorption Isotherms for PCE on Moist Aqufer Material in the Presence and Absence of CF.

Advective Transport

The breakthrough curves shown in Figure 13 demonstrate the reproducibility of replicate column experiments.

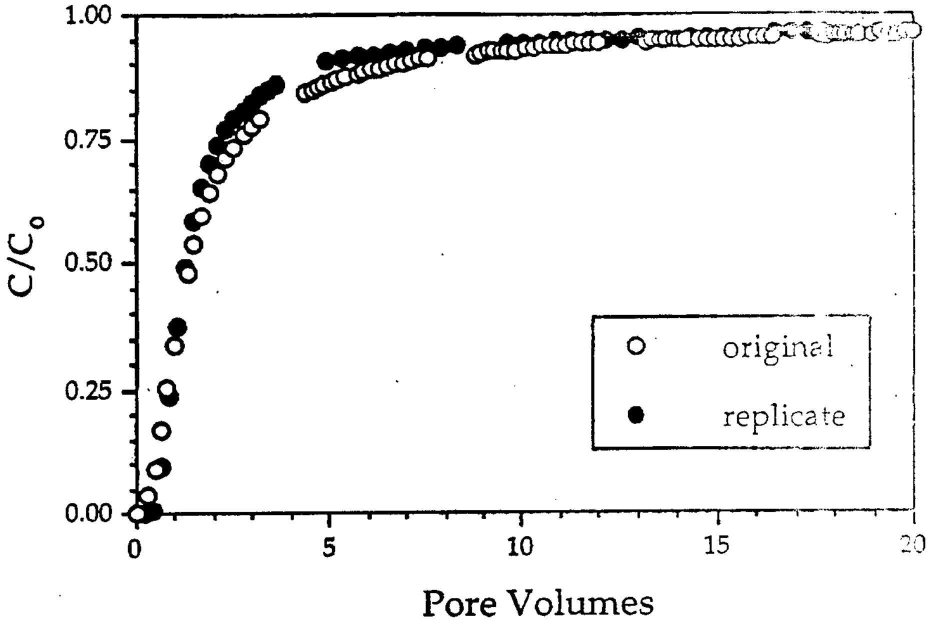


Figure 13. Replicate Breakthrough Profiles for TCE $P/P_0 = 0.90$, Q = 40.0 mL/min

Previous research has suggested that a Gamma distribution of desorption rates can serve as a robust tool for characterization of contaminant mass transfer (Connaughton *et al.*, 1994; Chen, 1994; Culver, *et al.* 1997). Gamma model parameters of $\alpha = 1.85$ and $\beta = 2.22 \times 10^4$ minutes were obtained from a fit of the LC-LF-BP column experiment. The value of the distribution coefficient used for the fit was 11.8 ml/g, and was calculated directly from the TCE adsorption isotherm at a relative pressure of 10% P/P_0 (see Figure 11). The fitted values obtained for α and β suggest that slow sorption sites predominated in the advective transport experiments. The mean first order rate transfer coefficient, $\bar{k}$, was equal to 8.33×10^{-5} min^{-1}. A probability density function generated from the fitted values of α and β is shown in Figure 14. Note that a peak in the distribution occurs at k 4.0×10^{-5} min^{-1}, and that the mean k value lies slightly to the right of this value.

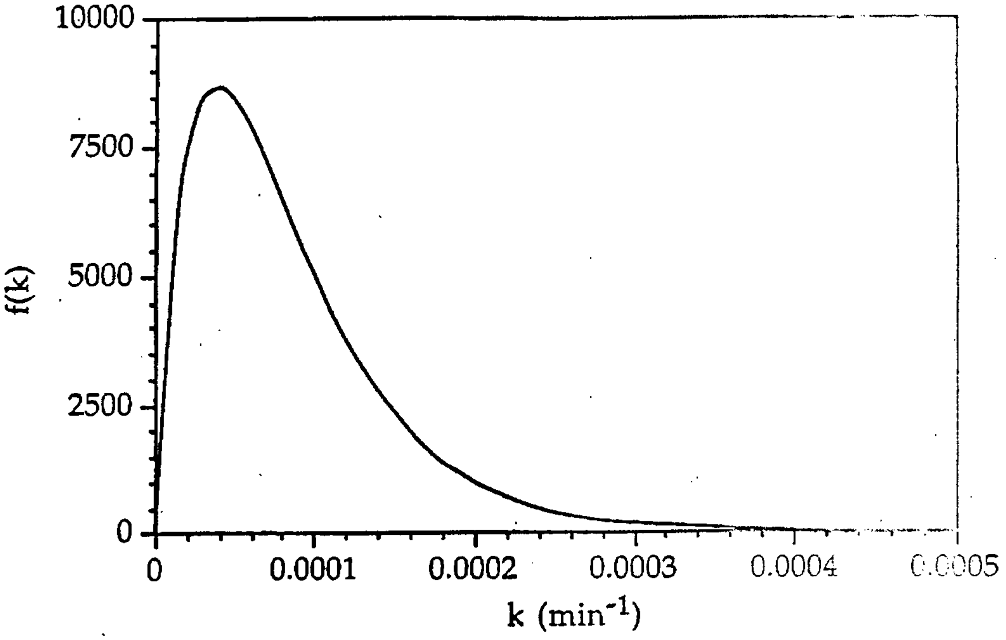


Figure 14. Experimentally Determined Gamma Distribution of First Order Rate Constants Applicable to Sorption and Desorption of TCE over a Wide Range of Relative Pressures and at Two Gas Flow Rates.

Figure 15 illustrates the the predictions of the Gamma site model for the breakthrough profile (BP) of the LC-HF experiment. Figure 16 provides a comparison for the predictions of the Gamma model to the elution profile (EP) from the LC-HF experiment. The agreement between the model and the observations is excellent. Model predictions were also obtained with the same values of α and β for all other experimental conditions including those at a high gas concentration and high gas flow velocity and agreed well with the data [see Lorden (1996) for additional comparisons of the model and experimental data]. Additional calculations (in progress) suggest that the Gamma model predictions are significantly superior to those of two other commonly invoked paradigms: the two site/two region model and a pore diffusion model.

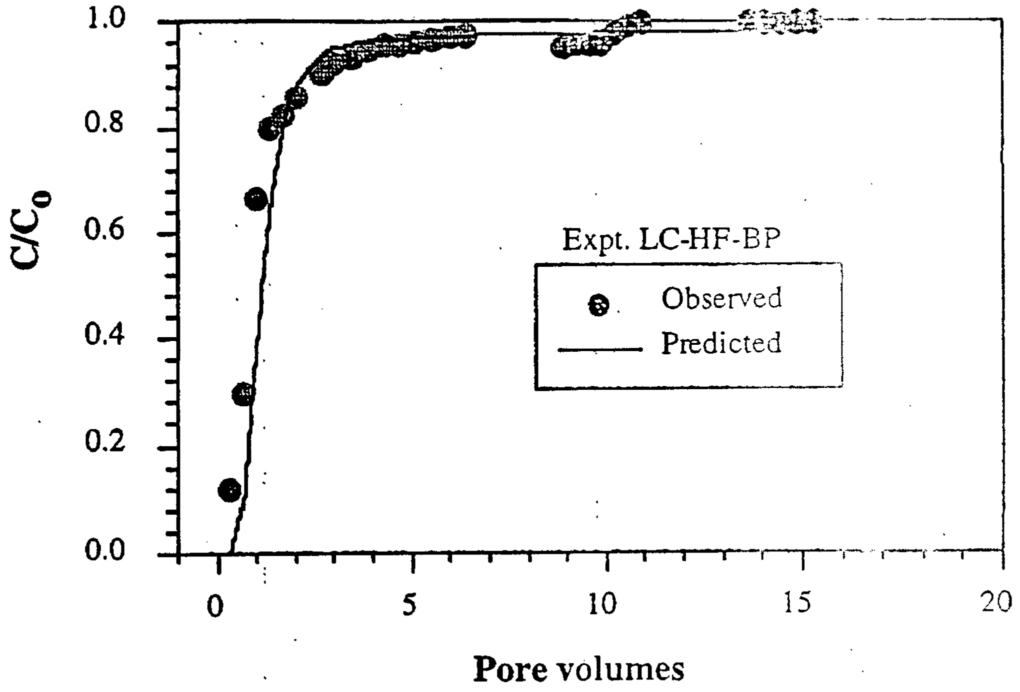


Figure 15. Comparison of Experimental Data with the Predictions of the Gamma Model for the Breakthrough Profile of the Low Concentration, High Flow Column Experiment.

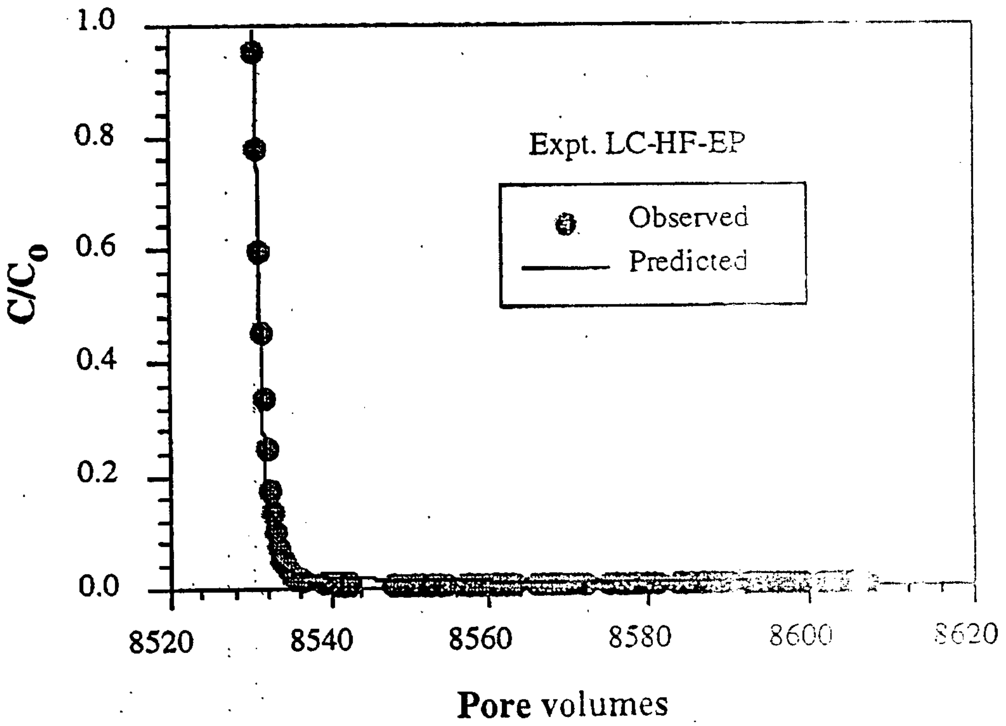


Figure 16. Comparison of Experimental Data with the Predictions of the Gamma Model for the Elution Profile of the Low Concentration, High Flow Column Experiment.

A listing of the experimental conditions from column experiments in which the behavior of mixtures was considered is given in in Table 1.

Table 1: Experimental Conditions for Comparison of TCE and TCE with CF Elution Profiles

Experiment	*Relative Vapor Pressure*		*Mass Sorbed (mg/kg wet sand)*	
	TCE	CF	TCE	CF
T1	0.10	-	0.0574	-
T2	0.10	-	0.0616	-
T3	0.10	-	0.0557	-
T4	0.23	-	0.1037	-
T5	0.33	-	0.1815	-
CT1	0.10	0.03	0.0666	0.0413
CT2	0.10	0.06	0.0518	0.0693
CT3	0.10	0.10	0.0527	0.1299
CT4	0.10	0.21	0.0546	0.2635
CT5	0.10	0.21	0.0531	0.2500
CT6	0.10	0.37	0.0510	0.4580

Based on the observations from the column studies listed in Table 1, pseudo isotherms for TCE and CF may be developed as shown in Figures 17 and 18, respectively. These isotherms display the amount of vapor uptake on the column for a given influent VOC concentration and are subject to possible mass transfer limitations that may have restricted vapor contact with the stationary phase within the 2 hour equilibration period that was used.

The sorption data for both compounds in the range of concentrations examined were best fit to linear isotherms. However, the data may also be fit to BET type-III isotherms, which are linear at lower vapor concentrations, with virtually identical R^2 values. This observation is consistent with the results obtained by other researchers for VOC sorption under conditions of advective flow and 90% relative humidity (Pennell *et al.*, 1992; Thibaud *et al.*, 1993).

The TCE vapor concentration was held constant at a relative vapor pressure (P/P_0) of 0.10 at 25 °C in experimental runs T1-T3 and all the mixture experiments (CT runs 1-6). The mean of TCE sorbed in the single sorbate experiments was 0.0582 mg TCE/kg wet sand, compared to 0.0526 mg/kg in the binary runs (see Table 2). [Note, the mass of TCE sorbed in experiment CT1 is considered an anomaly due to a temperature-induced problem with the TCE vapor flow.] A non-parametric statistical analysis, the Wilcoxon rank sum test, was applied to the TCE sorption data.

The results indicate that the average mass of TCE sorbed is significantly different in the binary experiments to the 95% confidence level.

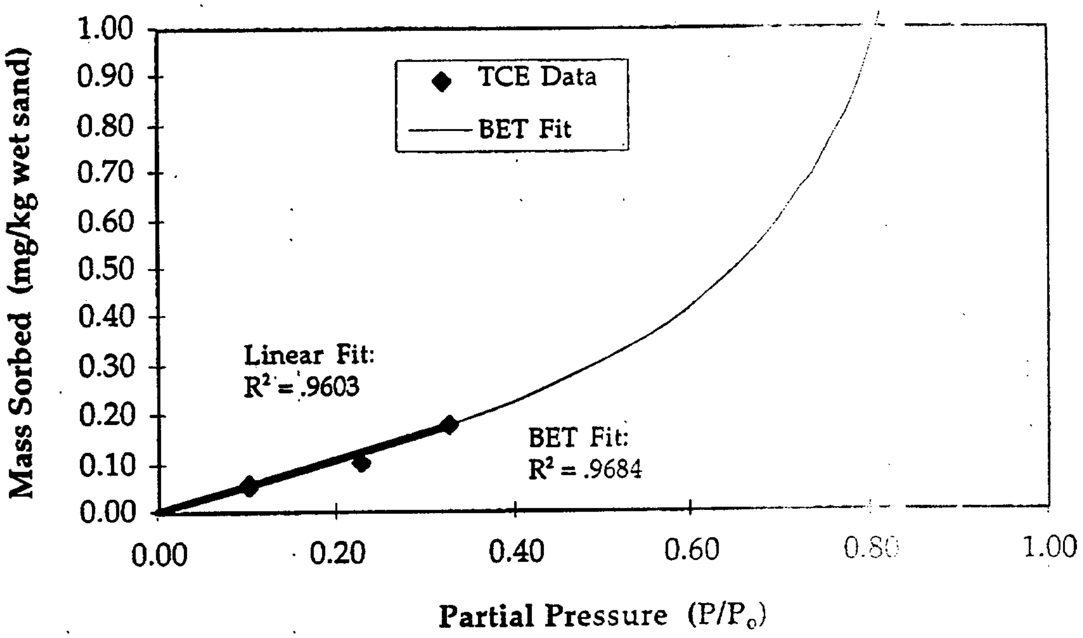


Figure 17. TCE Isotherms Based on Column Experiments.

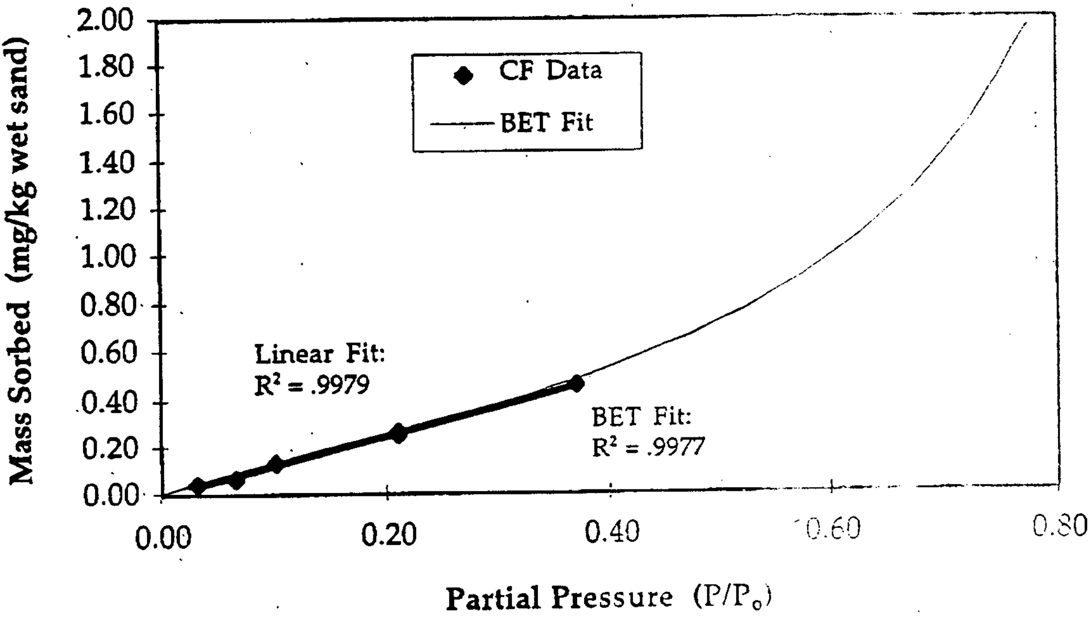


Figure 18. CF Isotherms Based on Column Experiments.

The results indicate that the average mass of TCE sorbed is significantly different in the binary experiments to the 95% confidence level.

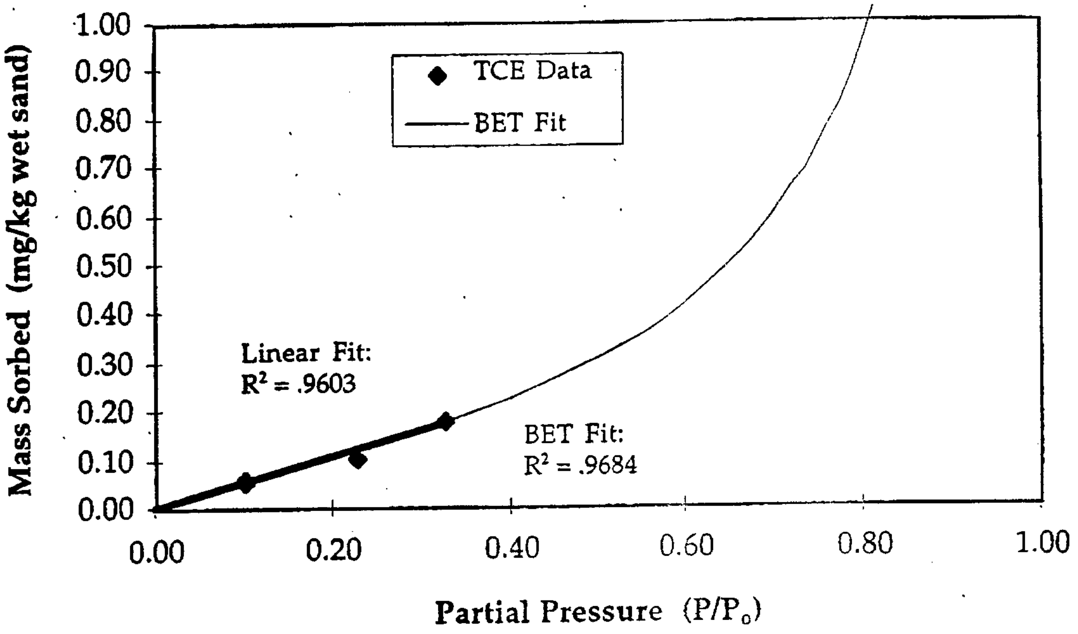


Figure 17. TCE Isotherms Based on Column Experiments.

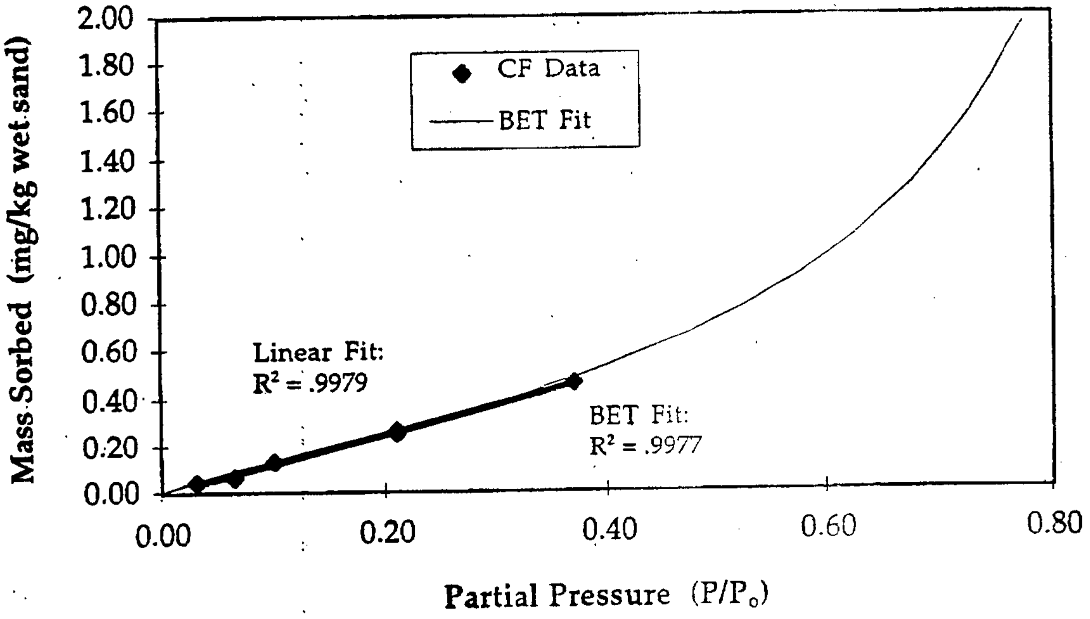


Figure 18. CF Isotherms Based on Column Experiments.

The effect of CF on TCE sorption was not dependent on the CF vapor concentration, but rather a presence/absence relationship. CF concentrations spanning an order of magnitude reduced TCE sorption by approximately the same amount, an average of 0.0056 mg/kg. This finite, quantifiable effect suggests that CF completely may effectively compete with TCE for a particular class of sorption site(s).

There are five types of sorption "sites" (or uptake mechanisms) that are generally considered applicable to vapor-phase sorption in the vadose zone: 1) VOC dissolution in soil moisture; 2) VOC partitioning from soil moisture into soil organic matter; 3)VOC adsorption at mineral surfaces; 4) VOC diffusion into the pores of soil grains; and 5) VOC sorption at the gas-water interface. Both VOC dissolution and partitioning are typically linear processes and are not subject to competitive interactions between VOCs. Since water effectively out-competes nonionic organics such as TCE and CF for polar mineral surface sites, any competitive VOC sorption at the mineral surface would be expected to be of a negligible magnitude. Migration of VOCs into intraparticle pores is governed by aqueous diffusion, a slow transport mechanism. Given the experimental equilibration time of two hours, coupled with the fact that over 99% mass recovery of sorbed VOC was accomplished in three elution phases spanning 24 hours, it seems extremely unlikely that a significant amount of VOC mass was located in intraparticle pores. Therefore, it is deemed likely that the observed competition between CF and TCE must have occurred at the gas-water interface.

Some researchers have determined that sorption at the gas-water interface may be significant, and perhaps as much as 50% of the total under certain conditions (Pennell *et al.*, 1992). Karger, *et al.* (1971a) found vapor-phase, interfacial adsorption to be important under advective conditions. In another report, Karger and colleagues (1971b) suggested that it was possible for compounds sorbed at the gas-water interface to form hydrogen bonds, and that interfacial adsorption increased with increasing polarizability of the adsorbing species. Valsaraj (1994) advanced this concept further by demonstrating that adsorption at the interface was thermodynamically favorable for hydrophobic compounds.

Given the similar experimental conditions in this research to those of the other investigators noted above and the hydrophobicity of TCE and CF, it seems likely that significant sorption at the gas-water interface occurred. Corley (1996) found that the fraction of the total mass sorbed that was attributable to adsorption at the gas-water interface declined with increasing water content. Since the ratio of interfacial area to volume (of water) decreases at higher moisture contents, VOC dissolution into soil moisture becomes increasingly important. Hoff *et al.* (1993) determined that the fractional mass adsorbed at the gas-water interface declined with increasing equilibration time. This is not surprising given that sorption into intraparticle pores is diffusion-limited and thus becomes increasingly important at longer equilibration times. While neither of these prior findings definitively prove that the gas-water interface has a relatively small, finite number of sorption sites, they do suggest that this is likely. If this is true, then competition between CF and TCE for interfacial sorption sites seems probable. Since CF has both greater polarizability and has twice the hydrogen bond electron donor basicity as TCE, it should be an effective competitor for interfacial sorption sites, as the data from this research suggests.

In order to examine competitive effects on the relative removal rates of the VOCs, the mass removed from the soil column over time during the first elution phases of each experiment was normalized by the total mass removed over all three elutions. This allowed for column experiments with different total masses of VOCs sorbed to be compared on a the basis of percent mass remaining in the column. The transformed data was plotted against the number of pore volumes of clean air passed through the column. The removal of TCE in experiments at which TCE was held at a constant vapor concentration of $P/P_0 = 0.10$ is shown in Figure 19.

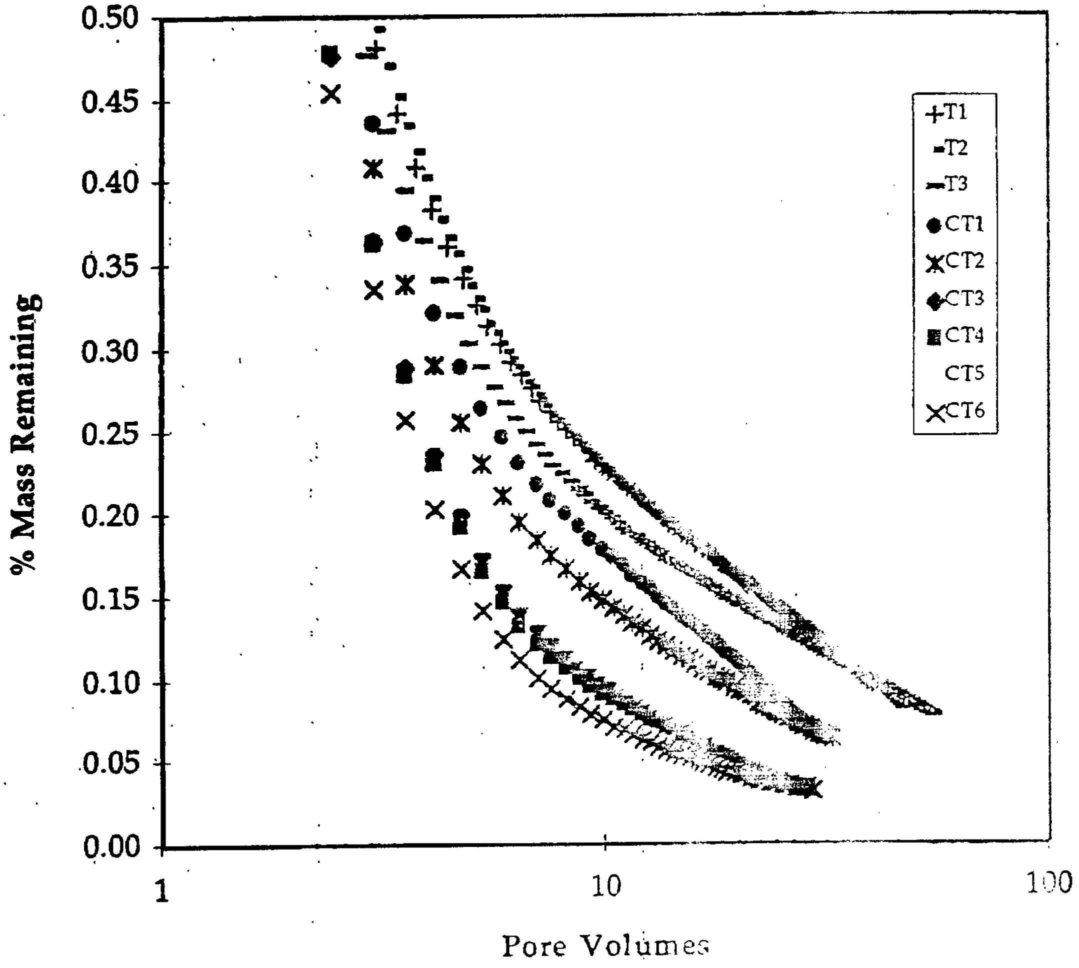


Figure 19. TCE elution in experiments with TCE $P/P_0 = 0.10$.

Figure 19 suggests that the sorbed TCE sorbed was removed faster in the presence of CF, and that increasing the amount of CF further increased the removal rate. Since the number of moles of TCE sorbed was roughly constant in each case, there also appears to be a trend that indicates that the removal rate of TCE was dependent on the total number of moles of both VOCs sorbed (see Table 2). This trend is also seen in the data for the removal of CF in the binary experiments. As shown in Figure 20, CF removal increased, on a percentage basis, with an increasing number of total moles of VOC sorbed. This same trend is seen in the single sorbate experiments involving only TCE (Figure 21). Thus the effect of the presence of CF on the desorption removal rate of TCE can not be discerned from the apparent effect of the increase in the total number of moles of VOCs sorbed to the sand.

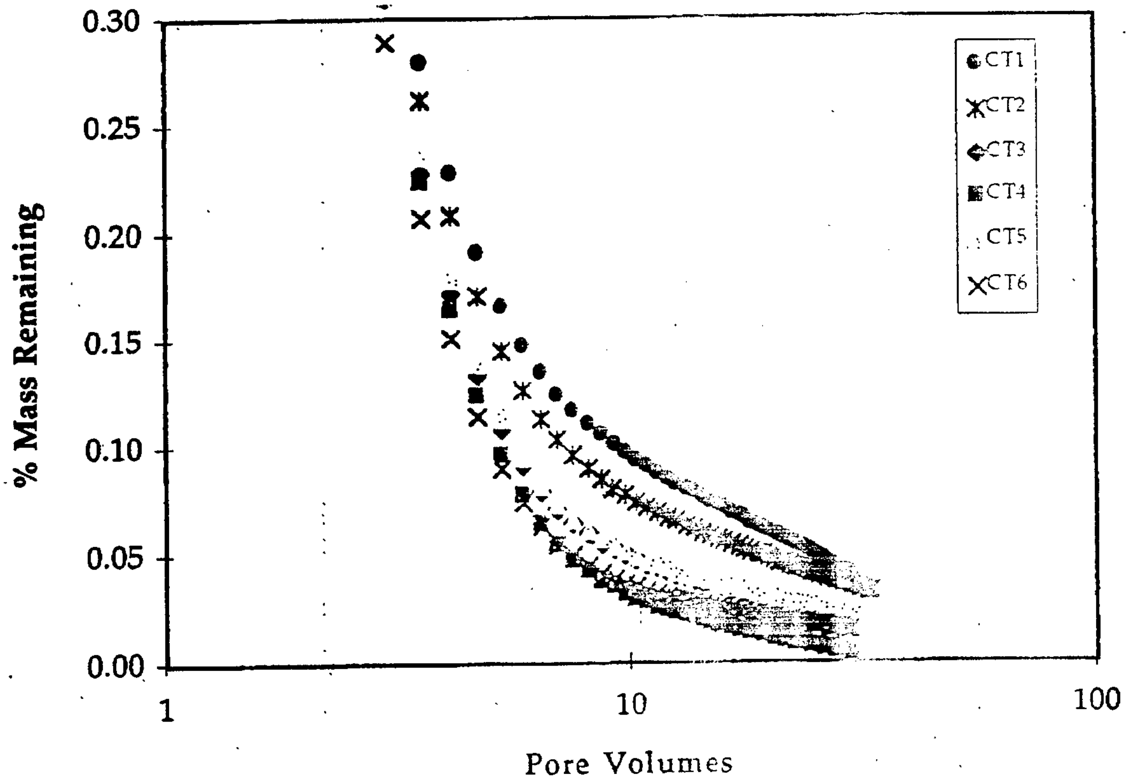


Figure 20. CF Removal in Column Experiments.

Table 2. Total Number of Moles Sorbed in Each Experiment.

Experiment	*Partial Pressure*		*Moles Sorbed (mmol)*		*Total Moles Sorbed (mmol)*
	TCE	CF	TCE	CF	
T1	0.10	-	2.190	-	2.190
T2	0.10	-	2.350	-	2.350
T3	0.10	-	2.124	-	2.124
T4	0.23	-	3.954	-	3.954
T5	0.33	-	6.922	-	6.922
CT1	0.10	0.03	2.538	1.431	3.969
CT2	0.10	0.06	1.976	2.402	4.378
CT3	0.10	0.10	2.009	4.501	6.509
CT4	0.10	0.21	2.084	9.131	11.215
CT5	0.10	0.21	2.025	8.663	10.688
CT6	0.10	0.37	1.944	15.872	17.816

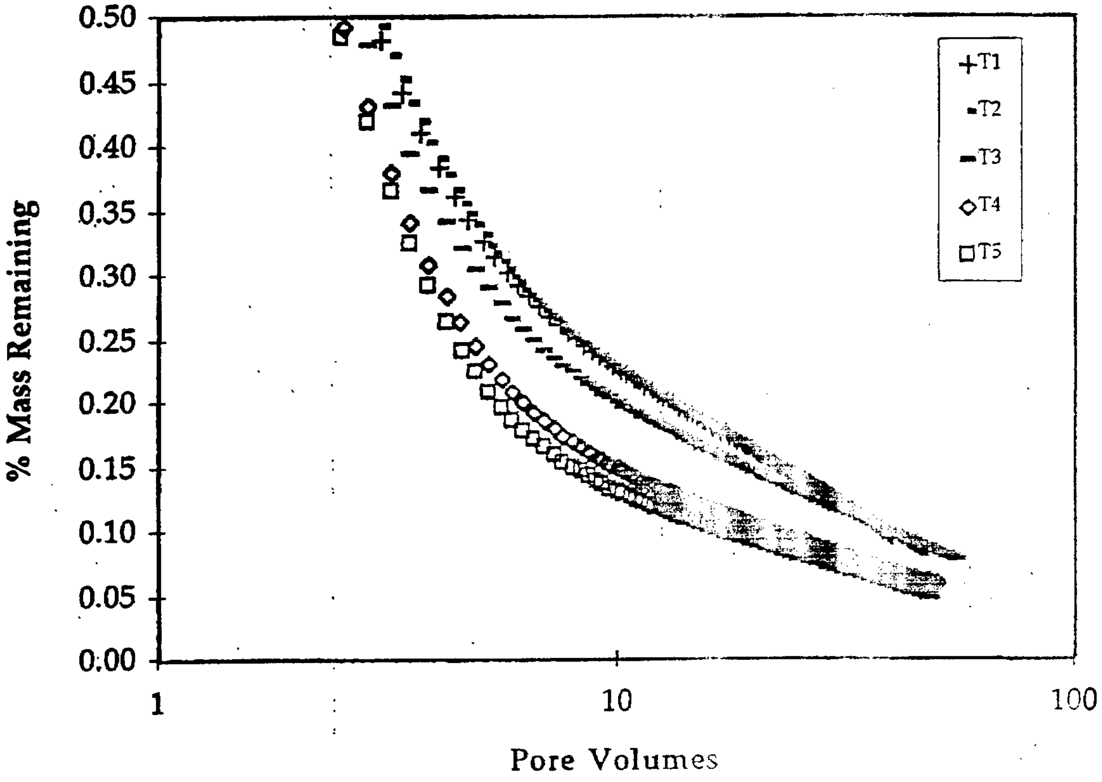


Figure 21. TCE Removal in Experiments in which TCE was the Sole Sorbate.

Diffusive Transport of VOCs

Diffusion experiments involving a number of different VOC concentrations and combinations were conducted. For convenience, each experiment is described with reference to maximum influent concentrations measured for each compound. A brief summary of concentration conditions is shown in Table 3. In the table, and subsequently in this report, experiments will be referred to by listing the first letter of each compound involved, in alphabetical order, followed by the run number. For example, the sixth experiment involving TCE and CF is designated CT-6.

An example of raw data collected during experiment CT-7 is displayed in Figures 22 and 23. The CF and TCE influent profiles shown in Figure 22 display a gradual approach to a maximum concentration which was a function of the influent liquid flow rate and the mass transfer of VOCs from the liquid phase to the gas phase in the influent chamber. Corresponding effluent profiles in Figure 23 show a 1 to 2 hour lag between the initiation of the experiment and the appearance of VOCs in the effluent sweep gas. This delay is consistent with retardation of the diffusive vapor flux by the aquifer sand medium.

Table 3. Diffusion Experiment Concentration Summary

Experiment	**CF Influent Concentration (% of P_{sat})**	**PCE Influent Concentration (% of P_{sat})**	**TCE Influent Concentration (% of P_{sat})**
C-3	2.37	--	--
C-4	21.05	--	--
CT-5	2.20	--	1.67
CT-6	19.93	--	1.44
CT-7	18.64	--	3.28
CT-8	16.04	--	13.56
PT-5	--	2.78	1.36
T-15	--	--	3.78
T-16	--	--	1.54
T-18	--	--	1.46
T-19	--	--	13.00

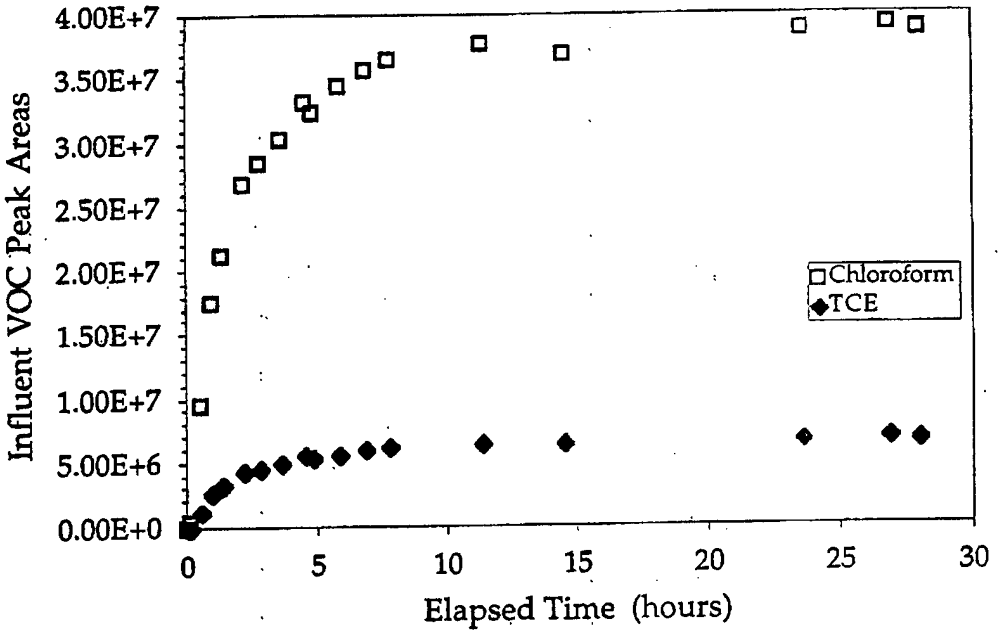


Figure 22. Experiment CT-7 Influent Concentration Profiles.

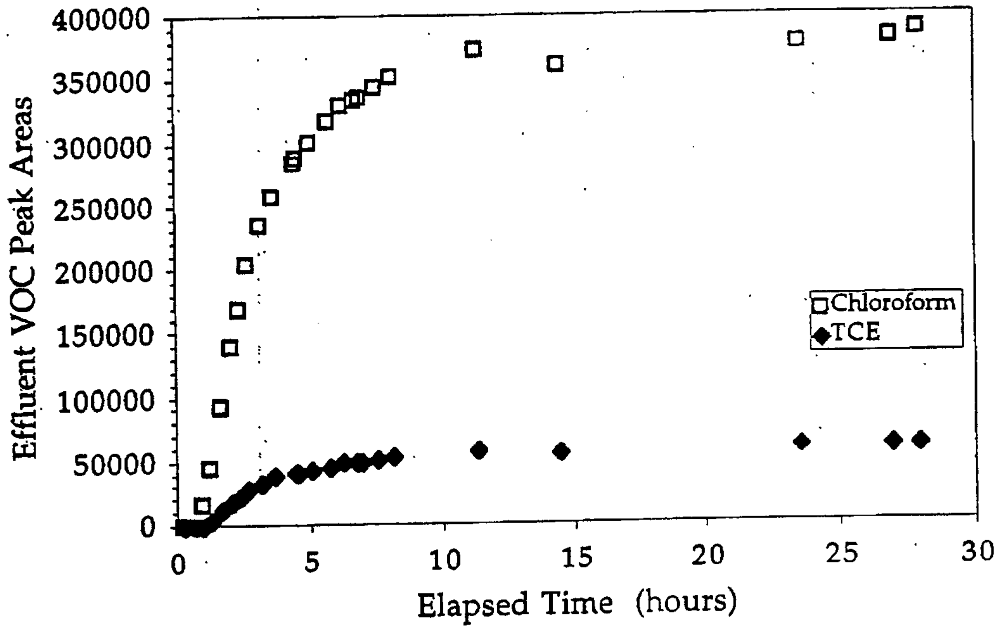


Figure 23. Experiment CT-7 Effluent Concentration Profiles.

A number of studies have been conducted to determine the relationship between physical characteristics of porous media and vapor diffusion rates. One widely accepted model which accounts for physical impedance to diffusion was proposed by Millington and Quirk (1961). The model, based on the concept of porosity and the probability of connected pores, provides a relationship between vapor diffusion coefficients in air and in a porous media. The form of the Millington-Quirk model is:

$$D_{eff} = D_o\left[\frac{\alpha^{(10/3)}}{\phi^2}\right]$$

Were, D_o is the free air diffusion coefficient (cm^2/min), α is air-filled porosity, ϕ is total porosity, and D_{eff} is the "effective", or physically hindered, diffusion coefficient. Values of D_{eff} are independent of sorption or any other reaction.

As described above under methods, the effective diffusion coefficient for a vapor can be calculated from steady state diffusion data using Fick's first law. Concentration gradients observed during the late stages of several diffusion experiments (after influent and effluent concentrations stabilized) were used to compute D_{eff} values. These values were compared to predictions made using the Millington-Quirk model. The experimentally derived and empirically predicted D_{eff} values showed very close agreement.

Since the Millington-Quirk model was shown to serve as an accurate means for describing the physical hindrances to VOC diffusion, it was possible to look more closely at sorption phenomena. This was accomplished using a numerical simulation to predict the transient behavior or vapor breakthrough in the diffusion experiments. For the purpose of this report, a very brief description of the model is presented. Details pertaining to the numerical model, along with a complete analysis of model output, may be found in Gilbert (1997, M.S. thesis, in preparation).

In general, the transient diffusive transport of a vapor through porous media is described by Fick's second law:

$$\frac{\partial C}{\partial t} = -D_{app}\left(\frac{\partial^2 C}{\partial x^2}\right)$$

where D_{app} is the "apparent" diffusion coefficient and t is time.

In contrast to the effective diffusion coefficient, the apparent diffusion coefficient includes sorption related retardation effects. Fick's second law is often expressed as:

$$\frac{\partial C}{\partial t} = -\frac{D_{eff}}{R}\left(\frac{\partial^2 C}{\partial x^2}\right)$$

where R is a dimensionless retardation factor. The value of R is always greater than or equal to 1, with larger values corresponding to more significant sorption and correspondingly slower diffusion. An investigation of VOC sorptive behavior in this study required an analysis of R. Consequently, a solution to the above equation was necessary.

Many analytical solutions to Ficks second law have been documented for particular boundary conditions (Carlslaw and Jaeger, 1959; Crank, 1975). The combination of boundary conditions encountered during this study, however, made it necessary to utilize a numerical solution. This was accomplished by developing a finite difference model that simulated the diffusion experiments. Input parameters for the model included D_{eff} (determined using the Millington-Quirk expression), α, ϕ, Q, the length of the soil column, and an expression for the influent VOC vapor concentrations as a function of time. Given these known parameters and an estimated value for R, the model provided a prediction, using no adjustable parameters, of the expected effluent VOC concentration profile.

Figure 24 shows the measured influent TCE data from experiment T-18, and a curve used to represent to the data. A curve fitting application was used to identify an equation which best represented experimental measurements. In all cases, an expression of the following form was used:

$$C_o = A[1-\exp(-Bt)]$$

where A and B are adjustable fitting parameters. In all cases, this curve fitting process yielded R^2 values of 0.98 or greater. Influent expressions determined in this way were used as input to the diffusion computer model.

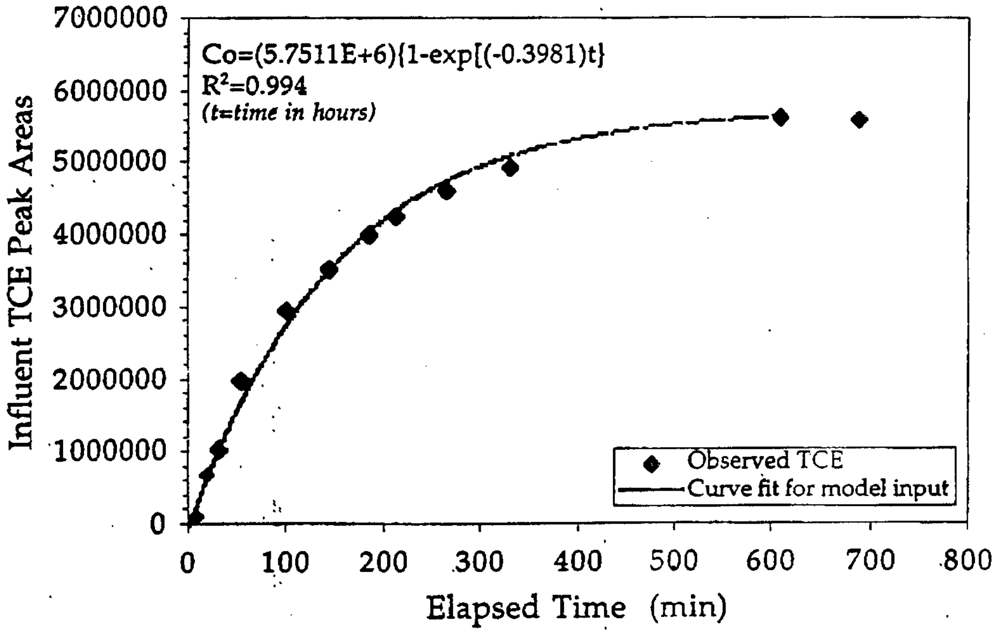


Figure 24. Experiment T-18 TCE Influent Data and Best Fit Curve.

The output from the numerical simulation of the experiment T-18 TCE diffusion is shown along with the measured effluent concentration profile in Figure 25. The value of the retardation factor, R, which appears in Figure 24 is based upon the assumption of a linear sorption isotherm for TCE.

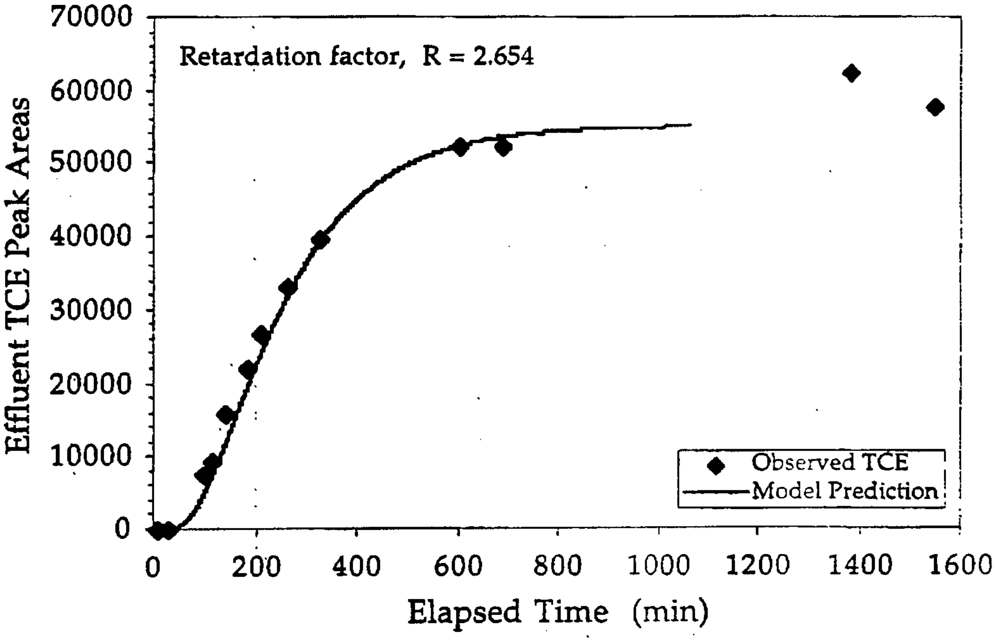


Figure 25. Experiment T-18 effluent TCE; Data and Model Prediction.

Referring to Table 3, it may be seen that the maximum influent concentration for TCE during experiment T-18 was relatively low, 1.46% of P_{sat}. Sorption isotherms displaying linearity at low sorbate vapor concentrations have been observed by several researchers (Chiou and Shoup, 1985; Ong *et al.*, 1991) With the assumption of a linear sorption isotherm, an expression for the retardation factor may be written as:

$$R = 1 + \frac{\rho K_d'}{\alpha}$$

where ρ is the sorbent bulk density (g/cm^3), α is the air-filled porosity and K_d' (mL/g) is the overall partition coefficient describing equilibrium between the vapor phase and the sorbed phase. As noted above, a method for predicting K_d' from easily measured parameters has been documented in the literature (Ong and Lion, 1991) and was confirmed by this research.

$$K_d' = \frac{K_d}{K_H} + \frac{\theta}{100K_H}$$

where K_d is the liquid phase or saturated partition coefficient, K_H is the dimensionless Henry's constant, and θ is the soil moisture content expressed as a percentage of dry soil mass. The value of K_d is both compound and sorbent specific, and was measured for TCE and the sorbent used in this study (Lorden, 1996). Henry's constant is readily available for a large number of compounds. Sorbent moisture content was directly measured in this research. Knowledge of all variables on the right-hand side of the above equation allowed for computation of K_d'. This K_d' value was then used to calculate an expected retardation factor for each experiment.

The retardation coefficient used for the model prediction in Figure 26 was calculated as described above. Consequently, the numerical model had no fitting parameters, and never-the-less displayed excellent agreement with measured effluent data. This suggests that the numerical model employed is a valid predictive tool for TCE at low influent concentrations. This procedure was employed to model TCE data from all experiments. It was observed that use of independently determined R values yielded excellent model predictions of breakthrough behavior for TCE at low concentrations, but gave less accurate estimates of effluent profiles at high TCE concentrations or for experiments involving more than one VOC.

The diffusion apparatus designed for this research permitted introduction of VOC mixtures to the influent chamber, and therefore examination of the impact of potential competition among VOC vapors on transport behavior. Experiments were conducted using binary vapor mixtures of CF and TCE. Experimental procedures allowed for manipulation of the relative concentrations of each compound in the mixture. By comparing observed VOC transport behavior from binary experiments with profiles from independent TCE or CF experiments, assessments of presence/absence or concentration dependent impacts of a co-sorbate were possible.

Plots such as the one displayed in Figure 26 allow for qualitative comparisons of VOC behavior under varying mixture or concentration circumstances. Generally speaking, experiments were conducted using different maximum influent, and consequently effluent, vapor concentrations. Since it was desirable to compare the time dependent effluent profiles from different experiments, it was necessary to normalize the effluent breakthrough graphs for each experiment. This was accomplished by dividing each measured effluent data point by its respective maximum observed influent concentration. The result, as shown in Figure 26, was a vertical axis which had been "normalized", allowing for direct visual comparison of breakthrough trends from multiple experiments.

Figure 26 shows normalized effluent CF profiles from experiments with varying amounts of TCE in the influent vapor. As the graph legend indicates, experiment CT-8 had an influent TCE concentration approximately four times greater than that in the influent of the other experiments shown in the figure. The departure of the CT-8 data from the other curves suggests more rapid breakthrough of CF (and hence reduced CF retardation). It is possible to explain this breakthrough behavior in terms of competition between CF and TCE in sorption reactions. If CF sorption is inhibited by TCE, less retardation of CF would be expected, leading to more rapid transport and breakthrough of CF. The breakthrough curves in Figure 25 are also consistent with what may be a concentration dependent effect, with higher levels of TCE having a more pronounced impact on CF behavior.

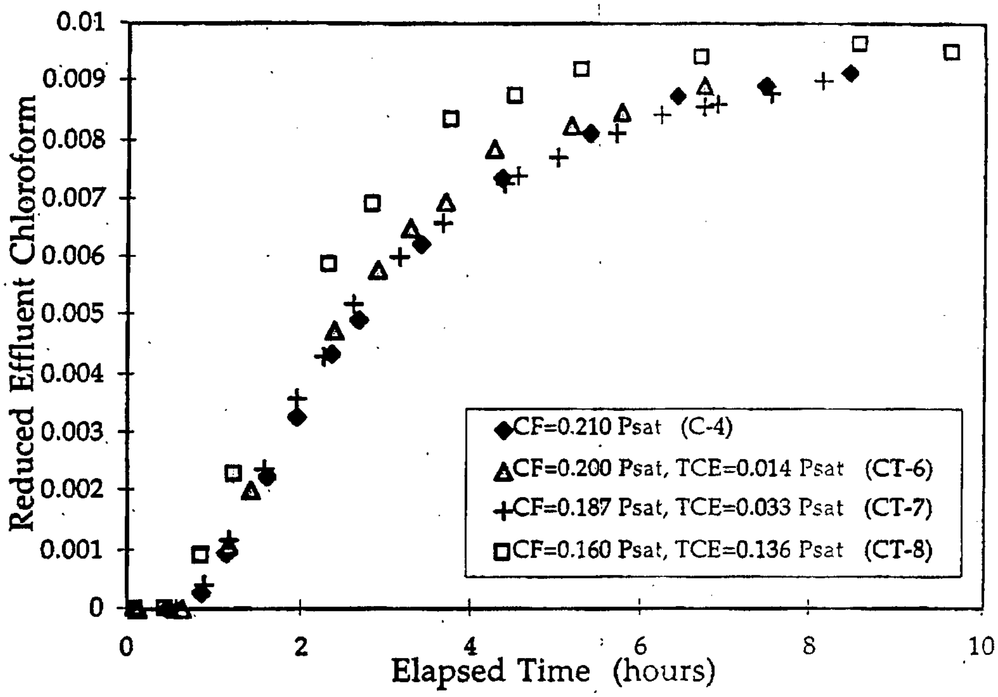


Figure 26. CF Breakthrough with Varying TCE Concentration

Several relationships of the type depicted in Figure 26 were observed upon normalization of the experimental data. However, since the normalization procedure did not account for small differences in soil conditions (e.g. porosity, moisture content) or time dependent influent profiles, these visual observations were not deemed to be conclusive proof of competitive interactions between VOCs. A more detailed examination of the experimental results is still underway, the results of which will be included in the thesis associated with this ongoing research (Gilbert, 1997, M.S. thesis, in preparation).

Conclusions

The research described in this report is continuing under the auspices of a DOD augmentation grant "Augmentation for Basic Research on Vapor Transport in Soil" (AFOSR project no: F49620-94-1-0316). As a result, the full analysis of the data and its implications has not been completed. Nevertheless, several conclusions can be drawn at this stage as follow.

At low relative vapor pressure, the sorption of TCE on a moist sandy aquifer material displayed a linear isotherm that could be predicted using the model of Ong and Lion (1991). At higher relative pressures, the TCE sorption isotherm was non-linear, in accordance with BET theory and indicating vapor uptake occurs at the gas-water interface.

The Gamma model, which employs a statistical distribution of mass transfer rates, has now been successfully employed to describe the advective transport of VOCs in unsaturated porous media. Model parameters obtained from a single column experiment and from equilibrium sorption measurements were capable of predicting, with no adjustable parameters, the breakthrough and elution of TCE vapor over a wide rage of relative pressures and gas flow velocities.

Column experiments comparing TCE vapor sorption individually and as a mixture with CF show mild but significant suppression of TCE sorption in the presence of CF. Both TCE and CF elution rates appeared to be enhanced when greater amounts of vapor were sorbed. This result is consistent with the expectation that increases in vapor uptake may occur at the gas water interface and that the release rate of this material is faster that that of dissolved VOC or VOC that is sorbed to soil organic matter. However, since vapor sorption was generally less than that at equilibrium based on gas-water and water-sand distribution coefficients, the occurrence of VOC uptake at the gas-water interface can not be definitively established in the column experiments. To the extent that VOC condensation occurs in the field, an expected consequence would be that gas phase soil clean up technologies, such as soil vapor extraction, would to be most efficient in removing at high levels of VOC contamination, but the mass transfer rate for removal would decline after removal of VOC at the gas water interface.

The Millington-Quirk formulation for calculation of the effect of soil tortuousity on the steady state diffusion coefficient of vapors has been shown to give accurate predictions. At low relative pressures, the transient diffusion coefficients of vapors show the expected retardation attributable to linear sorption processes. However, vapor diffusion in mixtures appears to be enhanced in some cases, as does vapor diffusion at high relative pressures. Both of these observations suggest non-linear isotherms for vapor uptake are operative and that vapor competition and/or condensation at the gas water interface can act to enhance diffusive transport. A consequence of this observation is that diffusive spread of vapor mixtures in the near field close to source materials should happen somewhat more rapidly than would be expected based on models that employ linear VOC phase distribution processes would predict.

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