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SORPTION AND TRANSPORT OF POLYNUCLEAR AROMATIC HYDROCARBONS IN LOW-CARBON AQUIFER MATERIALS

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Sorption studies of polycyclic aromatic hydrocarbons (PAH) on low-carbon aquifer materials are reported. Both column and batch partition coefficients (K_d) were affected by synthetic polymeric components, such as Teflon, in commonly used experimental apparatus. These influences include incorrect estimates for K_d and tailing of peaks in column studies. Both batch and column experimental methods are developed, using polymer-free systems, that allow accurate measurement of K_ds for hydrophobic PAHs in low carbon systems. Application of these methods shows that organic carbon contents below the commonly cited threshold level of 0.1 percent may dominate the partitioning and subsequent transport of phenanthrene in aquifer systems. Calculated K_d values from batch and column (temporal first moment) techniques did not agree. Reasons for the disparity in the results from these methods are discussed. Column results may be described using the batch K_d and two adjustable fitting parameters representing variables in a two-site kinetic model. However, the rate constant derived from such a fit differs with that which is independently predicted from an existing empirical

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correlation. Batch and column techniques were used to explore the potential of colloidal solids and macromolecules to enhance the transport of PAHs in porous media. Although a broad range of "carriers" was considered, none was found to be able to decrease the partition coefficient for phenanthrene onto a low-carbon sand. However, several of the materials tested increased phenanthrene partitioning. A column study with one such material verified that the increased batch partitioning of phenanthrene was manifested as increased retardation in a miscible displacement experiment.

PREFACE

The research described in this report was carried out at the U.S.A.F. Engineering Services Center, Engineering and Services Laboratory, located at Tyndall Air Force Base, Florida. During this investigation, Dr. Lion was supported by an Air Force Office of Scientific Research Interagency Personnel Agreement with Cornell University.

This research was performed as a collaborative effort with Dr. Thomas Stauffer of HQ AFESC/RDVW. Some of the central ideas which led to this research and made its conduct possible came from the fertile mind of Dr. William MacIntyre of the College of William and Mary. Portions of this report have been submitted for publication in a technical journal with Dr.'s Stauffer and MacIntyre as coauthors. The assistance of Kimberly Buggs, Edward Hougendobler and Don Wickman with the laboratory analyses is gratefully acknowledged. The author also thanks Dr. Suresh Rao, Mark Brusseau and Dr. David Burris for their helpful discussions of the research results.

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SECTION I
INTRODUCTION

A. OBJECTIVES

The goals of this research were to: (a) test and, if necessary, modify column techniques for measurement of the hydrophobic partition coefficients for polynuclear aromatic hydrocarbons (PAHs), (b) determine the importance of organic mater vs mineral surfaces in PAH partitioning on low-carbon aquifer materials, and (c) determine the capacity of selected colloidal solids and dissolved macromolecules to enhance the transport of PAHs in aquifers.

B. BACKGROUND

Aqueous sorption coefficients of hydrophobic organic compounds on soils and sediments are customarily measured by batch or column techniques. MacIntyre and Stauffer (Reference 1) recently proposed that use of synthetic hydrophobic polymers (ex.Teflon®) in measurement systems may produce incorrect results in experiments with low-carbon sorbates such as aquifer materials. Literature on the effect of Teflon® or other organic polymer surfaces on sorption measurement and on sorption of PAH by low-carbon aquifer materials is meager. Anderson and Pankow (Reference 2) and Abdul and Gibson (Reference 3) carried out batch measurements of PAH sorption on subsurface materials using bottles with Teflon® septa, but did not report on possible sorption by the Teflon®. Several workers (Reference 4, 5, 6, 7) performed PAH sorption studies on soils and sediments, but did not specify the container seal material or mention sorption by seals as a experimental problem. Nkedi-Kizza et al. (Reference 8) studied sorption of anthracene on soils from mixed solvents by the batch method, but did not use pure water in isotherms. Sorption coefficients in pure water were obtained by extrapolation from data in water cosolvent solutions. Sorption by polymeric container materials was not discussed. No literature was found that considered the effect of hydrophobic column system components on sorption coefficients of PAH on soils or aquifer materials determined by column methods, which is surprising considering the extensive use of Teflon® and other organic polymers in all commercially available columns.

The most abundant literature dealing with sorption of hydrophobic solutes on synthetic polymer surfaces relates to groundwater monitoring well construction and sampling. Miller (Reference 9) studied the uptake of chlorinated hydrocarbons on synthetic well casings and found significant sorption on both polyethylene and polypropylene well casings. Sykes et al. (Reference 10) measured volatile organic compound sorption on a variety of well casing materials including Teflon® (PTFE) and found that there was no statistical difference in the uptake of the materials but did not specify what that uptake was. Chlorinated hydrocarbons were sorbed onto various tubing, including Teflon®, in a study to assess effects of sampling tubes on groundwater samples (Reference 11). Teflon® (TFE) tubing again proved to be best, but it did sorb from 15-110 $\mu g/m^2$ of the saturated halocarbons from solutions initially ranging from 90-120 ppb. Benzene, toluene, and xylene (BTX) mixture sorption studies were conducted on Teflon® tubing by Patrick (as cited by Reference 12) An initial rapid loss was seen into the Teflon® followed by a slower sorption over 13 days. Sorptive losses over a 2 week period ranged from 17 percent for benzene to 58 percent for p-xylene from solutions of approximately 1000 µg/L. Controls containing no Teflon® tubing, but crimp-capped with Teflon® faced septa, decreased from 979 µg/L to 848 µg/L in BTX content.

Sorption results for PAH on synthetic polymers were not found, but larger and more hydrophobic chemicals with concomitant lower water solubility would be more likely to accumulate at the Teflon® surface. Permethrin, an insecticide, was shown to sorb from aqueous solution onto Teflon® surfaces; most ($\approx$ 70 percent) of the permethrin could be desorbed as well (Reference 13).

Because of the difficulty and cost associated with obtaining samples, there is insufficient published information on PAH sorption by low-carbon materials. Most investigations have focused on surface soils and sediments which have relatively high carbon contents. As a result, PAH sorption in aquifers (and consequent transport) must often rely on extrapolation of established empirical relations beyond the carbon contents for which they are applicable. The aquifer organic carbon content sufficient to dominate soil mineral surfaces in the sorption of PAHs is uncertain. Pertinent literature has been critically reviewed by Karickhoff (Reference 14).

Some batch equilibrium sorption data are available for sorption of PAHs on low-carbon sand from the Borden aquifer experimental test site in Canada (weight fraction of organic carbon = 0.0002) (Reference 3). The distribution coefficients (K_d) were low for the series of PAHs studied ranging from 0.13 for naphthalene to 6.2 for pyrene. The K_d for phenanthrene was reported to be 0.94 on the Borden sand. Stauffer (Reference 15) studied sorption of 1-methylnaphthalene on a series of low-carbon aquifer materials and reported K_d's ranging from 0.44 to 0.76 on materials with organic carbon contents < 0.1 percent. These results were generally supported by column measurements on the same materials by MacIntyre and Stauffer (1988). However, they observed disagreement between column and batch sorption coefficients by a factor of about 0.5. These differences may result from experimental artifacts and/or difficulties with data interpretation and have not been resolved..

PAH compounds share in common low water solubilities, high octanol-water partition coefficients and, consequently, relatively low mobility in soil. Recently, considerable attention has been given to factors which can enhance the transport of low solubility compounds (Reference 16, 17). This concern stems from studies in which hydrophobic chemicals are found to be transported to greater distances and at higher concentrations than is predicted based upon their sorptive partitioning (Reference 18, 19, 20). "Enhanced" transport may potentially result from physical or hydrodynamic processes such as fingering or the existence of macropores (ex. worm and root holes) in soils. In homogeneous isotropic porous media, other mechanisms must be invoked to explain enhanced transport. The presence of colloidal solids or dissolved macromolecules which may act as "carriers" for sorbed hydrophobic pollutants is one possible explanation (Reference 21). However the efficacy of carriers to simultaneously bind PAHs and to be mobile in low-carbon aquifers has not been demonstrated.

C. SCOPE

Experiments to determine the existence and magnitude of the effects of hydrophobic polymers on PAH sorption measurements are reported here. Batch and column techniques that avoid use of Teflon® or other synthetic organic polymers are described and demonstrated. Results from these batch and column methods are compared and reasons for differences are evaluated. The role of mineral surfaces vs organic matter in control of PAH sorption onto low-carbon aquifer materials is probed by batch equilibrium techniques before and after selective removal of organic matter. Batch kinetic studies and tailing of breakthrough curves from column experiments are used to illustrate the importance of sorption kinetics in PAH transport. Finally, both the batch and column methods developed in this research are applied to test the capacity of selected carriers to enhance the transport of PAHs through low-carbon aquifer materials.

SECTION II
MATERIALS AND METHODS

C^{14} radiolabeled naphthalene, 1-methylnaphthalene, and phenanthrene were obtained from Pathfinder Laboratories, Amersham International, and Sigma Chemical Co., respectively, and were assayed by liquid scintillation counting (Beckman Model LS 9800). Counts were corrected for quench. Chrysene and pyrene were analyzed by fluorescence spectroscopy using a Perkin Elmer Model MPF-66 spectroflurometer. The following excitation/emission wavelengths were used: pyrene (240/373.2 nm) and chrysene (265/360.8 nm).

Two different low-carbon sorbents were used. Samples of aquifer material were obtained from well borings at the Electric Power Research Institute's Macrodispersion Experiment test site located at Columbus AFB, Columbus MS (Reference 22). This material was passed through a 1.0 mm sieve and air-dried prior to use. The second sorbent was a graded filter sand (UniFilt Corp; Zelienlope, PA) with an effective diameter of 0.25 mm and uniformity coefficient of $\leq$ 1.5. Organic carbon contents for these sorbents were measured by IR analysis of the CO_2 evolved upon high-temperature combustion and were 0.036 percent and 0.005 percent for the Columbus AFB aquifer material and the graded filter sand, respectively.

A. BATCH ISOTHERM METHODS

Batch adsorption isotherms were measured in crimp-capped borosilicate glass vials as described by Stauffer and MacIntyre (Reference 23) with the modifications noted below. The procedure entailed equilibration of 2 grams of solids with varying sorbate concentrations in 6 mL amber-hypo vials (Pierce Chemical Co.) sealed with Teflon®-faced Silicone discs (Pierce Chemical Co.). Vials were filled to eliminate headspace and tumbled in a constant temperature chamber at 23 ± 1 °C for 24 hours. Solids were then separated by centrifugation at 2200xG and the aqueous phase sampled for analysis. The amount sorbed was calculated as the difference in dissolved sorbate mass in vials containing solids relative to that in control vials containing no sorbent. Duplicate samples and controls were analyzed at six sorbate concentrations to construct an isotherm.

The above procedure was also carried out with 10 grams sorbent (≈ 1:1 solids to solution weight ratio) to examine the effects, if any, of solids concentration on the sorptive partition coefficient. As a second check on the effect of solids concentration, replicate analyses were carried out with a constant initial sorbate concentration and variable solids concentration (2 grams to 10 grams). These data were reduced as described by Peterson, et al. (Reference 24). It may be shown that if the same sorbate mass is delivered to a control vial and to a vial containing a solid sorbent, and if a linear isotherm is obeyed:

$$(CoVo)/(C_sV_s) = 1 + K_d\,(M/V_s)$$

where C_o = equilibrium sorbate concentration in the control (no solids)
C_s = equilibrium sorbate concentration in the presence of solids
M = mass of sorbent
V_o = volume of aqueous solution in the control
V_s = volume of aqueous solution in contact with solids
and K_d = linear sorptive partition coefficient

A plot of the ratio $(CoVo)/(C_sV_s)$ versus (M/V_s) should yield a straight line with slope K_d and an intercept of one. This experiment, in which solids concentration is varied, serves as a check on the constancy of the sorptive partition coefficient with solids concentration. If the partition coefficient were to significantly decrease with increasing solids concentration as reported by DiToro, et al. (Reference 25), then the plot would be nonlinear.

As a check on the effect of sorption of the hydrophobic chemicals of interest by the Teflon®-faced discs, the isotherms described above were duplicated using 10 mL borosilicate glass ampules (Wheaton) which were flame-sealed to provide an all-glass reaction vessel. Sorption to the walls of the controls in both vials and ampules was calculated by subtraction of the sorbate mass at equilibrium in controls from the mass added, which was determined by direct addition of equal volumes of C^{14} labeled sorbates to liquid scintillation cocktail or by direct fluorescence analysis for the chrysene and pyrene stock solutions. Loss of the more volatile compounds (naphthalene and 1-methylnaphthalene) to the headspace in ampules was calculated from the Henry's Law Constant for each compound and shown to be negligible.

B. COLUMN METHODS

Column experiments were carried out with the system described by MacIntyre and Stauffer (Reference 1). Two ISCO LC-5000 syringe pumps were connected to a column through a six-way Valco valve (Supelco, Inc.). One column reservoir was filled with a solution of 0.005M $CaSO_4$ plus 0.02 percent NaN_3. $CaSO_4$ was employed as a background electrolyte to suppress clay mineral destabilization and NaN_3 was used to prevent biological degradation of the test compound. The second pump reservoir contained this same electrolyte solution plus either C^{14} phenanthrene or 0.01 M KCl. Switching from one pump to the other with the valve allowed a sharp step-function of Cl^- or C^{14} phenanthrene to be delivered to the column. For some column experiments a Waters Model 510 HPLC pump was used; pulses were introduced by switching the pump reservoir solution and repriming the pump at the appropriate time.

Chloride was assumed to behave as an inert tracer and was used to quantify pore water velocity and hydrodynamic dispersion. Cl^- in the column eluate was measured by the argentometric method (Reference 26). C^{14} phenanthrene was collected dropwise from the column into test tubes containing Ecolume liquid scintillation cocktail (ICN Biomedicals); samples were subsequently transferred to scintillation vials and counted.

Standard preparative LC columns commonly employed in laboratory studies of miscible transport are normally constructed with Teflon® tubing and end fittings. The apparatus used in this study was an Omni 25 mm preparative glass column which is described by the vendor as having PTFE end fittings, fluoroelastomer O-rings, polyethylene bed supports, and PTFE tubing. Also used was a Beckman/Altex 25 mm preparative glass column which is described by the vendor as having flurocarbon bed supports and inlets, Teflon® filters with a Tefzel® backing disc, and Teflon® tubing. As a check on loss of hydrophobic pollutant to the column and tubing, a second column was constructed by blowing a 25 mm filter assembly (Millipore Corp.) to a 25 mm threaded connector (Ace Glass, Inc.). This apparatus is illustrated in Figure 1. Capillary tubing was blown onto the fritted filter support to produce a low dead volume endpiece. Stainless steel HPLC tubing was used to connect the column to the pumps. Other than the Teflon® ferrule used in the threaded connector, this column assembly was entirely of metal or borosilicate glass and could therefore, be used to assess the influence of synthetic polymer column parts on measurement of hydrophobic pollutant transport.

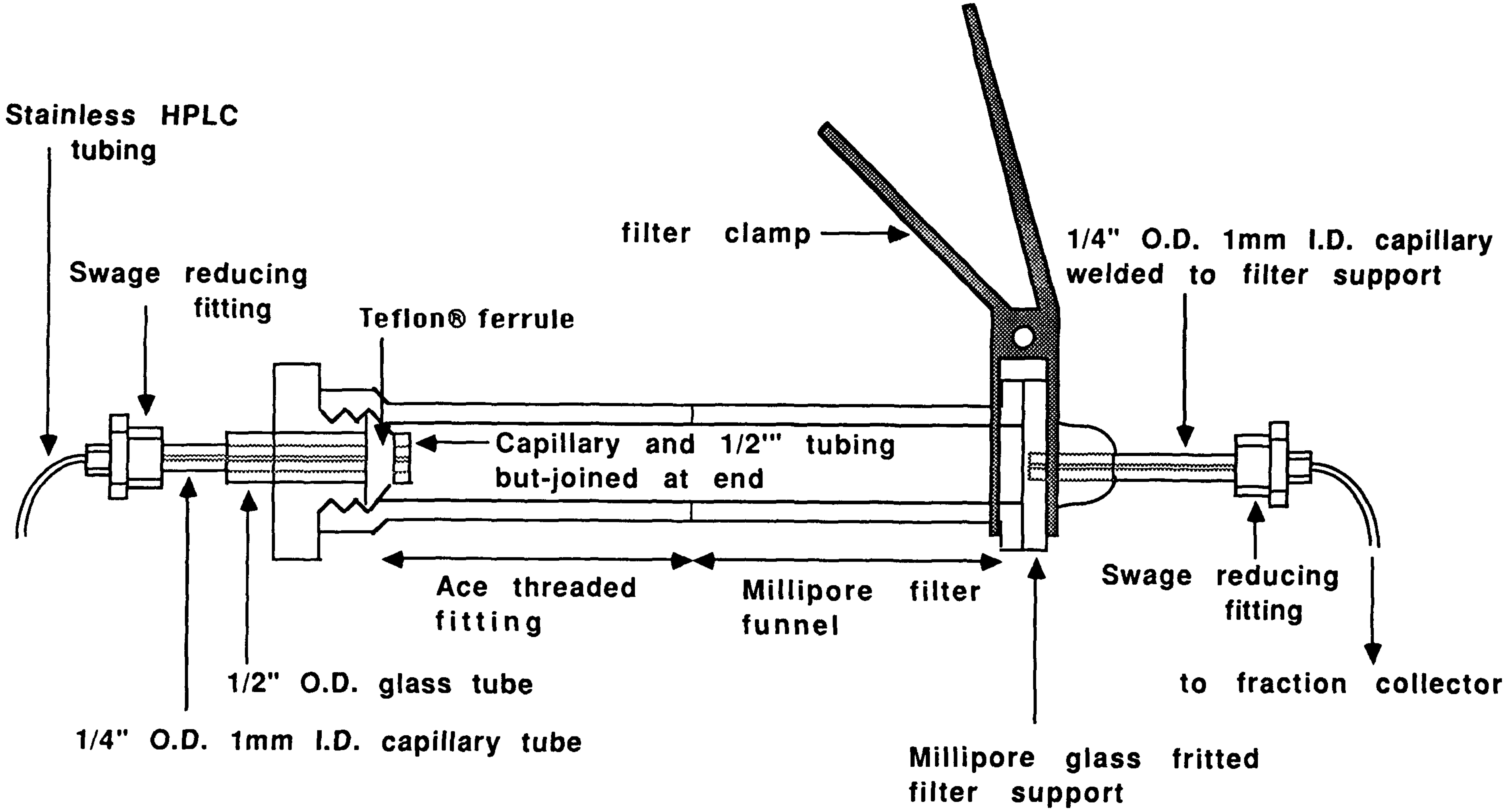


Figure 1. Schematic of "All-Glass" Column Assembly

SECTION III
RESULTS AND DISCUSSION

A. METHODS DEVELOPMENT

1. Batch Methods

Sorption isotherms for C^{14} phenanthrene on the walls of ampules and of Teflon®-sealed vials (in the absence of solids) are shown in Figure 2. [Note: the axes of these and other isotherms are shown in units of disintegrations per minute (DPM) since it is isotherm slope which is of interest. The manufacturer's reported specific activity for phenanthrene was 10.4 mCi/mmol]. It is apparent in Figure 2 that sorption of phenanthrene in bottles sealed with Teflon®-backed closures is greater than in the flame-sealed glass ampules. Sorptive losses to Teflon®-sealed vials were greater than to ampules for every other sorbate examined. Since each "empty bottle" isotherm was linear, the slope may be taken as a distribution coefficient (K_d). K_d values for each of the sorbates with the all-glass (ampule) and glass-plus-Teflon® (vial) systems are shown in Table 1.

TABLE 1. DISTRIBUTION COEFFICIENTS FOR SELECTED POLYNUCLEAR AROMATIC HYDROCARBONS ONTO FLAME-SEALED GLASS AMPULES AND TEFLON®-SEALED GLASS VIALS

Compound	Glass Ampules		Glass Vials with Teflon®		log K_{ow}*
	K_d	log K_d	K_d	log K_d	
Naphthalene	0.21	-0.68	0.93	-0.032	3.37
1-Methylnaphthalene	0.18	-0.74	1.09	0.037	4.11
Phenanthrene	0.51	-0.29	3.96	0.60	4.46
Pyrene	0.87	-0.060	2.87	0.46	5.32
Chrysene	1.02	0.0086	6.67	0.82	5.61

* all values taken from Callahan et al. (Reference 27) except for 1-methylnaphthalene. K_{ow} for 1-methylnaphthalene was assumed equal to the value for 2-methylnaphthalene reported by Karickhoff, et al. (Reference 28). This assumption is based on the similarity in structure and in water solubility of the two compounds.

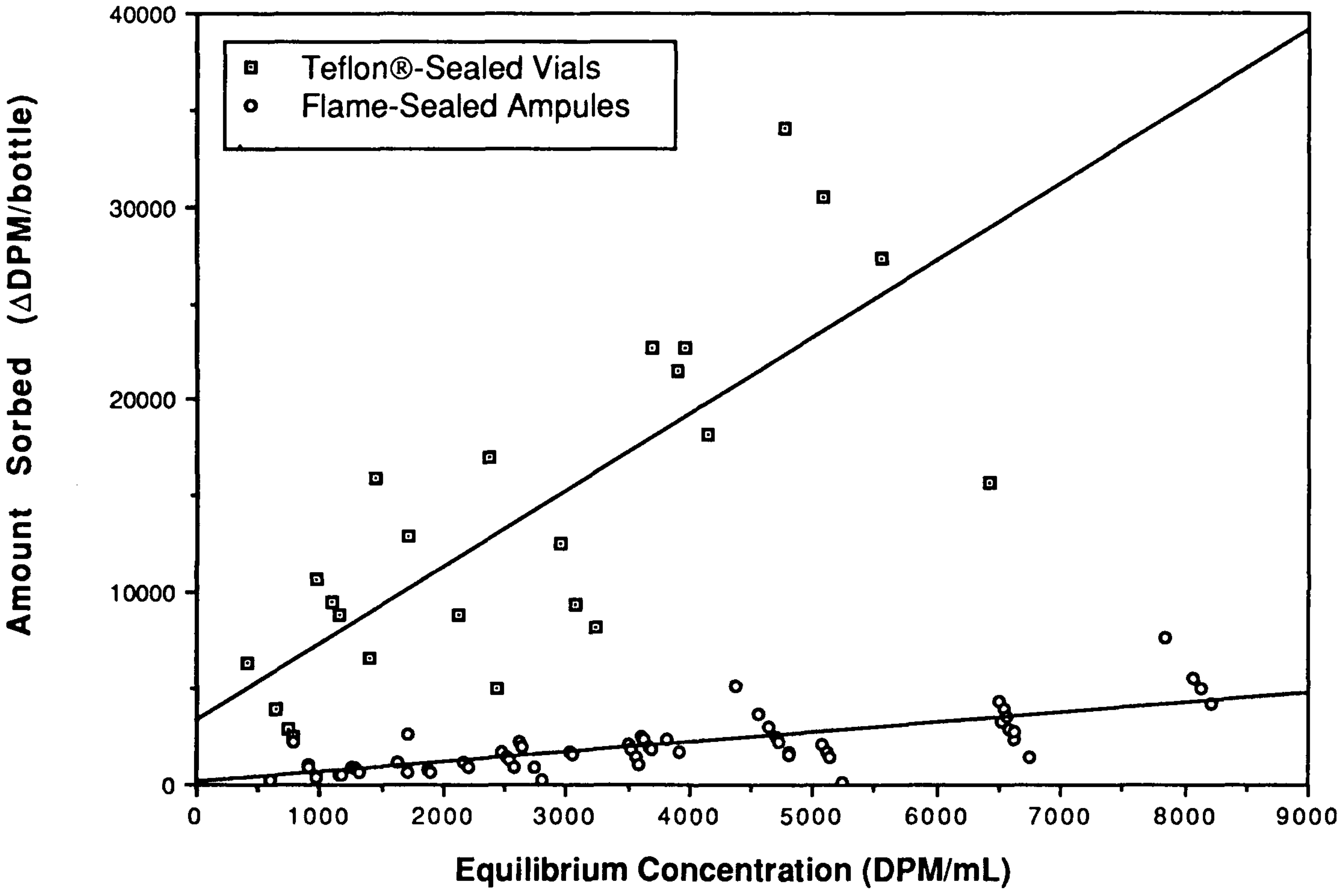


Figure 2. Comparison of "Empty" Bottle Isotherms for Phenanthrene in Teflon®-sealed Vials and Flame-sealed Ampules

It is not surprising that hydrophobic solutes sorb to Teflon® which is itself hydrophobic. The conventional assumption that Teflon® is an inert material, does not apply with respect to its interaction with polycyclic aromatic hydrocarbon solutes. In fact, Figure 3 illustrates that partition coefficients for both the all-glass and the Teflon®-capped containers display the commonly observed trend with solute octanol-water partition coefficient, K_{ow} (Reference 28, 29). Similar results for the sorption of substituted benzenes to Teflon® have recently been reported by Gillham and O'Hannesin (Reference 30). The slopes of the relationship between log K_d vs. log K_{ow} for both types of containers are very similar. However, the binding constant to the container with the Teflon® seal is, on average, a factor of 4.8 greater than that observed in glass. Generallv, the intended use of such containers is to measure the batch partition coefficient for a sorbent. In sorption studies with sediments and soils it has been shown (Reference 28, 31) that:

$$K_d = f_{oc}K_{oc}$$

where f_{oc} is the weight fraction of organic carbon in the sorbent and K_{oc} is a partition coefficient normalized for organic content.

This relationship expresses what is commonly assumed to be a partitioning phenomenon. K_{oc} values for sorbates were found by Karickhoff et al. (Reference 28) to be linearly related to K_{ow}. Therefore, the expected effect of an increase in sorbent f_{oc} is to proportionately increase the sorptive partition coefficient. By way of analogy, the Teflon® seal on the experimental container acts in a manner comparable to an increase in sorbent f_{oc}. Again, considering the hydrophobic nature of both the test compounds and Teflon®, this result is expected.

2. Column Methods

Results of column experiments using the commercial columns with synthetic fittings and tubing and the "all-glass" column assembly and are shown in Figures 4, 5 and 6, respectively. For testing purposes, columns were packed with 0.12 to 0.18 mm diameter glass beads (Thomas Scientific) which were precleaned by placing them in a muffle furnace at 650 °C to remove organic carbon. Since sorption of phenanthrene to the glass beads was negligible (K_d = 0.006 from batch isotherm), the glass bead column packing can be utilized to evaluate whether phenanthrene retardation or tailing was influenced by hydrophobic parts in the commercial column. For comparison, results are also shown for a chloride pulse of duration equal to that for C^{14} phenanthrene.

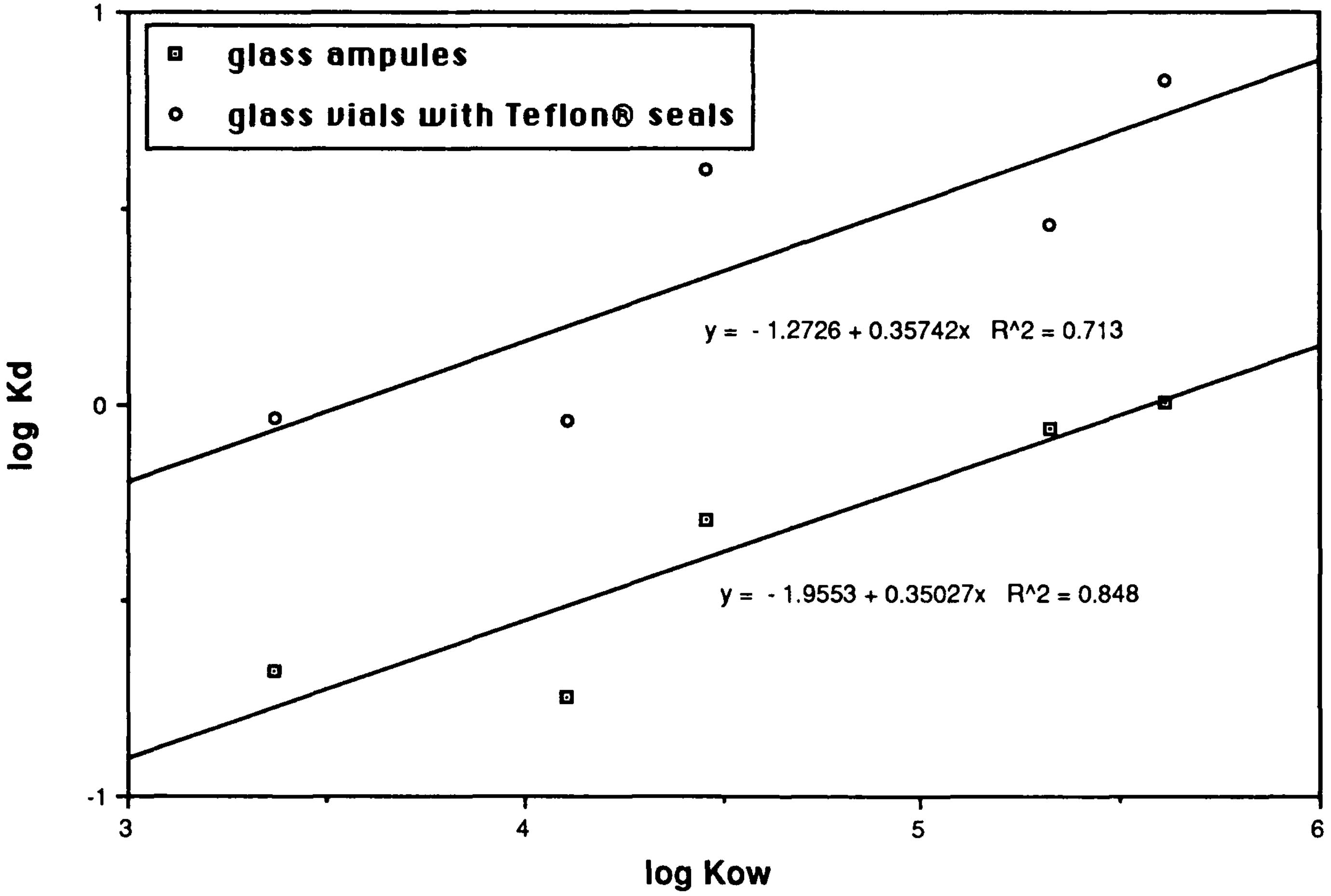


Figure 3. Distribution Coefficients for Polynuclear Aromatic Hydrocarbons on Glass Ampules and Teflon®-sealed Vials vs Compound Octanol-water Partition Coefficients.

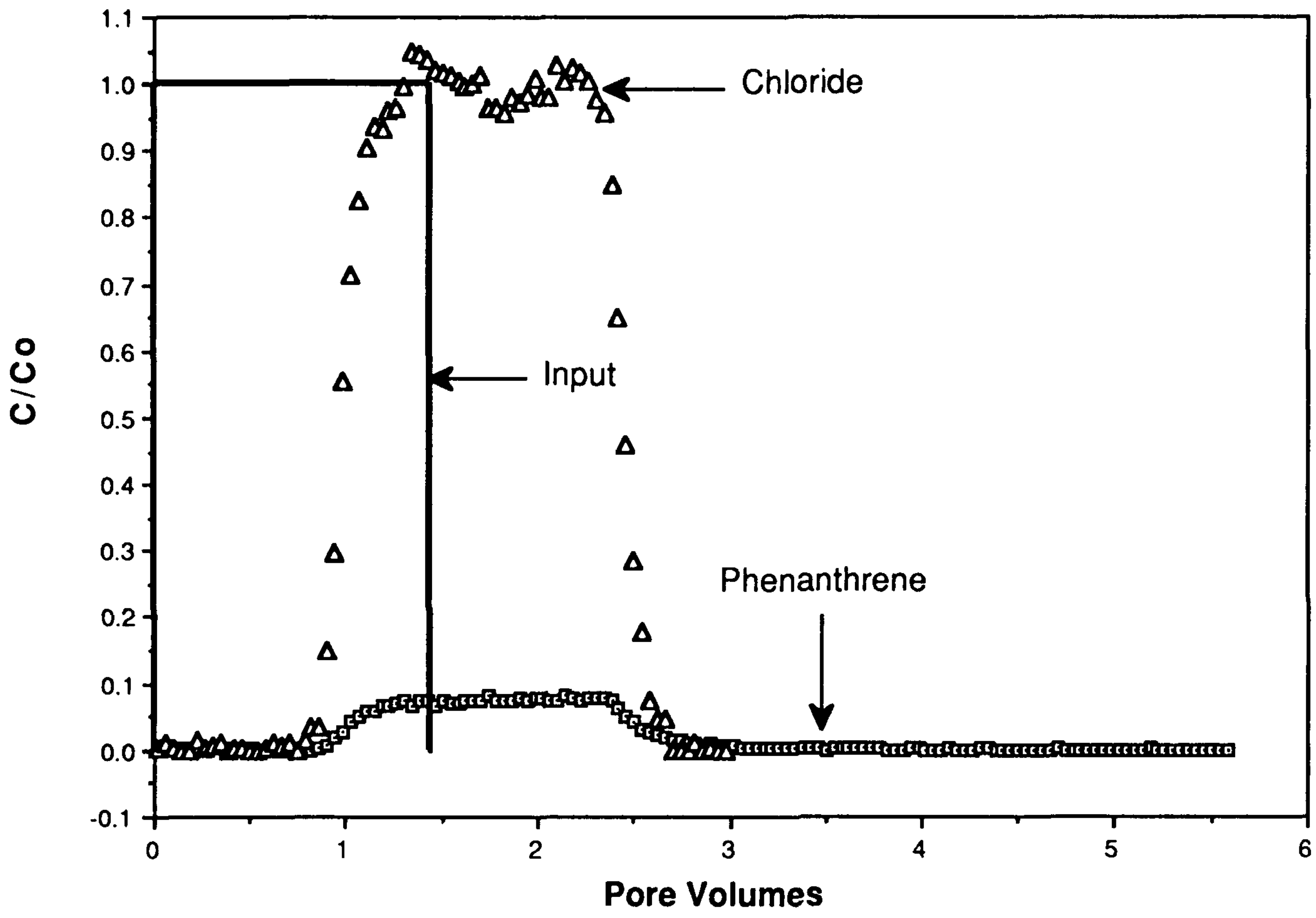


Figure 4. Elution of Step Inputs of Phenanthrene and Chloride from an Omni Commercial Column Assembly Packed with 0.12-0.18 mm Glass Beads.

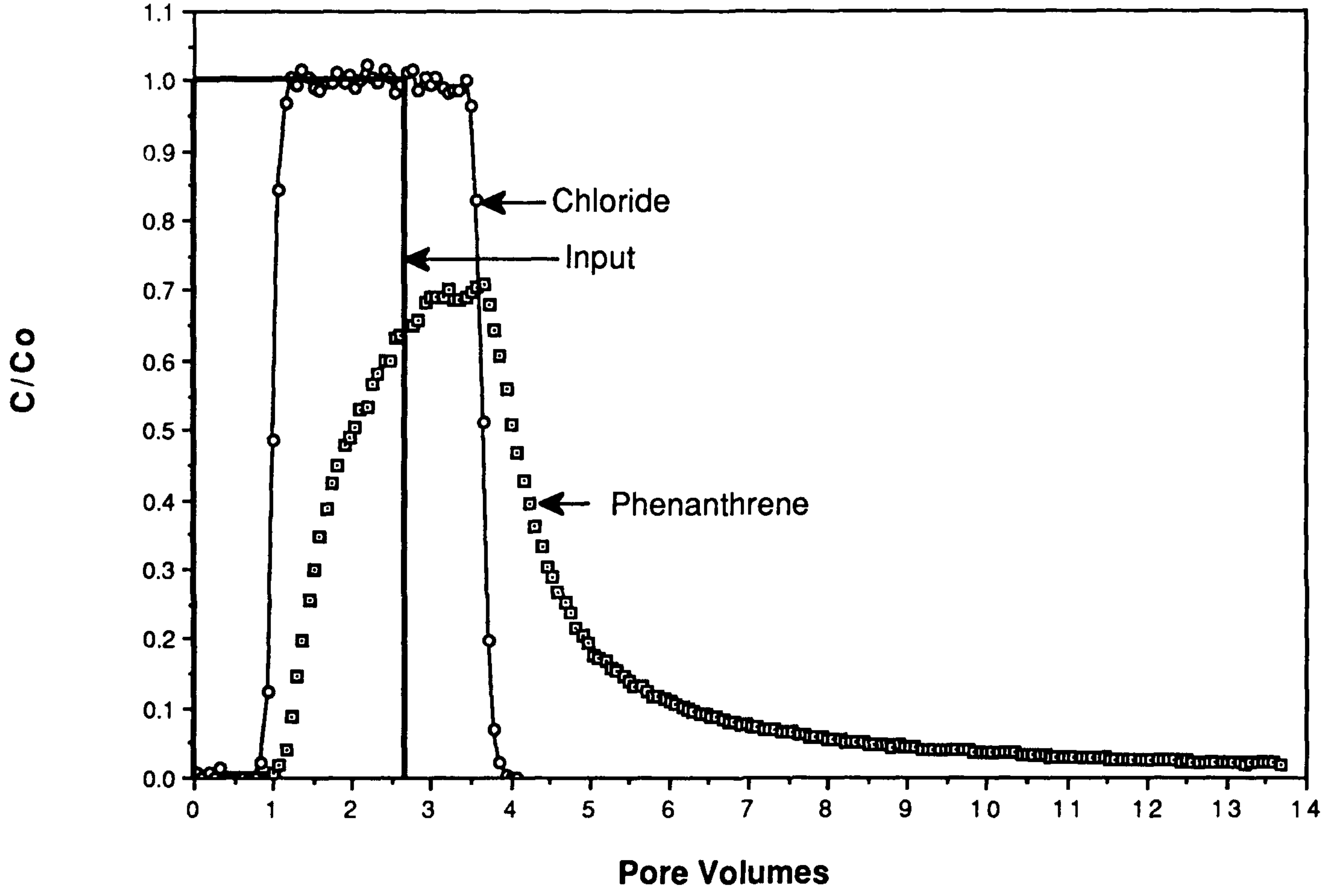


Figure 5. Elution of Step Inputs of Phenanthrene and Chloride from a Beckman/Altex Commercial Column Packed with 0.12-0.18 mm Glass Beads

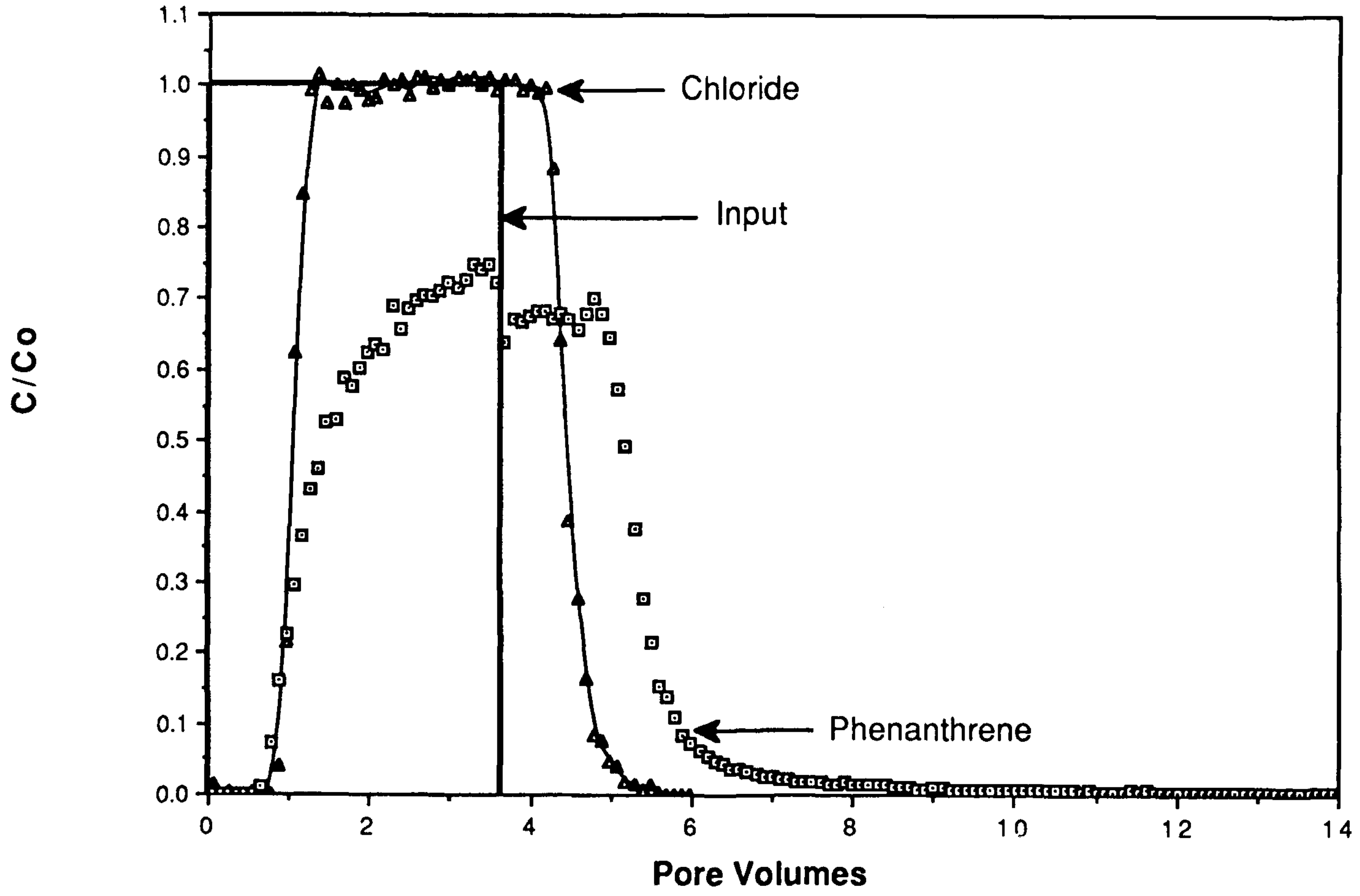


Figure 6. Elution of Step inputs of Phenanthrene and Chloride from a Custom "All-Glass" Column Packed with 0.12-0.18 mm Glass Beads.

Results for Cl^- elution from the columns were analyzed using CXTFIT, the nonlinear least-squares inversion method of Parker and van Genuchten (1984), to determine pore water velocity and dispersion coefficients. These results are summarized together with other pertinent parameters for the column experiments in Table 2.

Inspection of Figure 4 reveals a severe failure to achieve mass balance on the phenanthrene applied to the Omni commercial column. Only 8.5 percent of the input mass was recovered in the effluent. No attempt was made to isolate the possible source of the loss although, given the good recovery form the Beckman/Altex column (discussed below), irreversible binding or penetration of phenanthrene through polyethylene tubing used to connect the column to the pump and subsequent volatilization to the atmosphere are possible explanations. The polyethylene tubing used was a medical grade (Itramedeic tubing from Becton Dickinson and Co.) and was not provided as part of the Omni column apparatus

There was some evidence that nonglass column parts resulted in tailing of the phenanthrene elution peak from the Omni commercial column. Although the phenanthrene peak in Figure 4 appears coincident with that observed for the Cl^- tracer, expansion of the scale (Figure 7) reveals tailing of the phenanthrene breakthrough curve.

Phenanthrene recovery from the Beckman/Altex commercial column and the "all-glass" custom column was 88 and 82 percent,respectively. Since the column effluent was allowed to drip from the column exit tubing into scintillation cocktail, with subsequent transfer to a liquid scintillation counting vial, phenanthrene loss by volatilization or incomplete transfer may have occurred. Comparison of column effluent samples collected by manually submerging the column tubing into a counting vial containing cocktail verified that the loss of phenanthrene was ≈ 15 percent, sufficient to close the mass balance.

Inspection of Figure 5 reveals that nonglass column parts produce tailing and retardation of the phenanthrene elution peak from the Beckman/Altex commercial column. The column retardation coefficient, R, is defined as the velocity of a pollutant relative to that of water:

$$R = \frac{\text{Vwater}}{\text{Vpollutant}} = 1 + (\rho_b K_d)/\theta$$

where ρ_b = bulk density of the stationary phase

and θ = porosity

TABLE 2. CONDITIONS FOR MISCIBLE DISPLACEMENT COLUMN EXPERIMENTS

Parameter	Beckman/Altex-glass column with synthetic fittings and tubing	Fabricated all-glass column	
Packing	Glass beads precleaned in muffle furnace to remove organic carbon	Glass beads precleaned in muffle furnace to remove organic carbon	0.25 mm graded filter sand
Column length (cm)	14.2	14.0	14.0
Packing bulk density (g/cm^3)	1.79	1.72	1.58
Porosity	0.37	0.47	0.33
Pore water velocity (cm/hr)	3.41	8.45	7.65
Dispersion coefficient (cm^2/hr)	0.17	3.85	1.04

	Omni-glass column with synthetic fittings and tubing
Packing	Glass beads precleaned in muffle furnace to remove organic carbon
Column length (cm)	14.2
Packing bulk density (g/cm^3)	1.71
Porosity	0.37
Pore water velocity (cm/hr)	3.41
Dispersion coefficient (cm^2/hr)	0.17

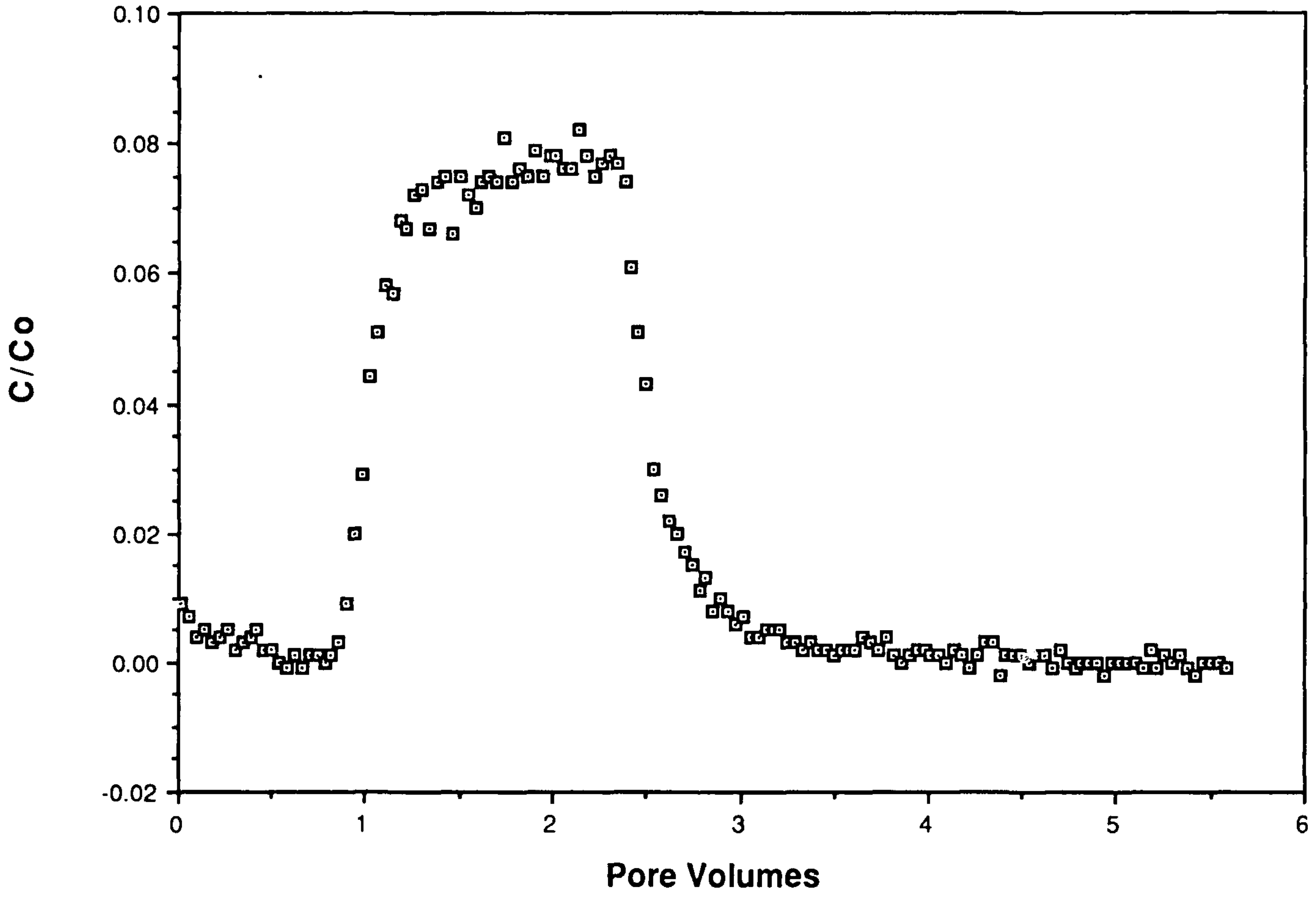


Figure 7. Elution of Phenanthrene from the Omni Column, Enlarged Vertical Scale.

The R value observed in the column study was taken as the first moment of the breakthrough curve minus half the input pulse width and equalled 2.73 for the commercial column. This value is well above the expected value of R = 1.03 calculated from the batch K_d of phenanthrene on the glass beads. Since the temporal first moment is used for the column R value, it should be independent of kinetic factors which resulted in the tailing of phenanthrene in the experiment (Reference 33, 34).

Comparison of Figures 5 and 6 shows that less tailing and retardation of phenanthrene was observed from the custom "all-glass" column. The R determined from the first moment of the phenanthrene breakthrough curve on the custom column was 1.65. Although this is still greater that the expected value of 1.02, the reduction in hydrophobic column parts substantially improved performance of the custom column relative to the commercial system.

B. APPLICATION OF METHODS TO LOW-CARBON SORBENTS

1. Batch Methods

The ampule and vial container systems were used to obtain batch partition coefficients for the graded filter sand and Columbus aquifer material. The graded sand is a commercial product that serves as an experimental surrogate for a very low-carbon aquifer material.

Prior quantification of the empty bottle isotherms for both types of container system allows experimental data to be corrected for wall losses. Normally, the amount sorbed is taken as the difference between dissolved sorbate mass at equilibrium in controls (with no sorbent) and samples containing experimental solids. However, since the equilibrium concentration is different with sorbent present, control bottle walls will have more compound sorbed than will bottle walls with sorbent (which have a lower equilibrium sorbate concentration). If sorptive binding to container walls is reversible, the difference in sorbate wall sorption must be included as uptake by the experimental solids. Since wall losses are normally low, this correction is usually negligible. However, wall loss can be significant for highly hydrophobic compounds such as those employed in this study. Sorption may be adjusted for wall losses as:

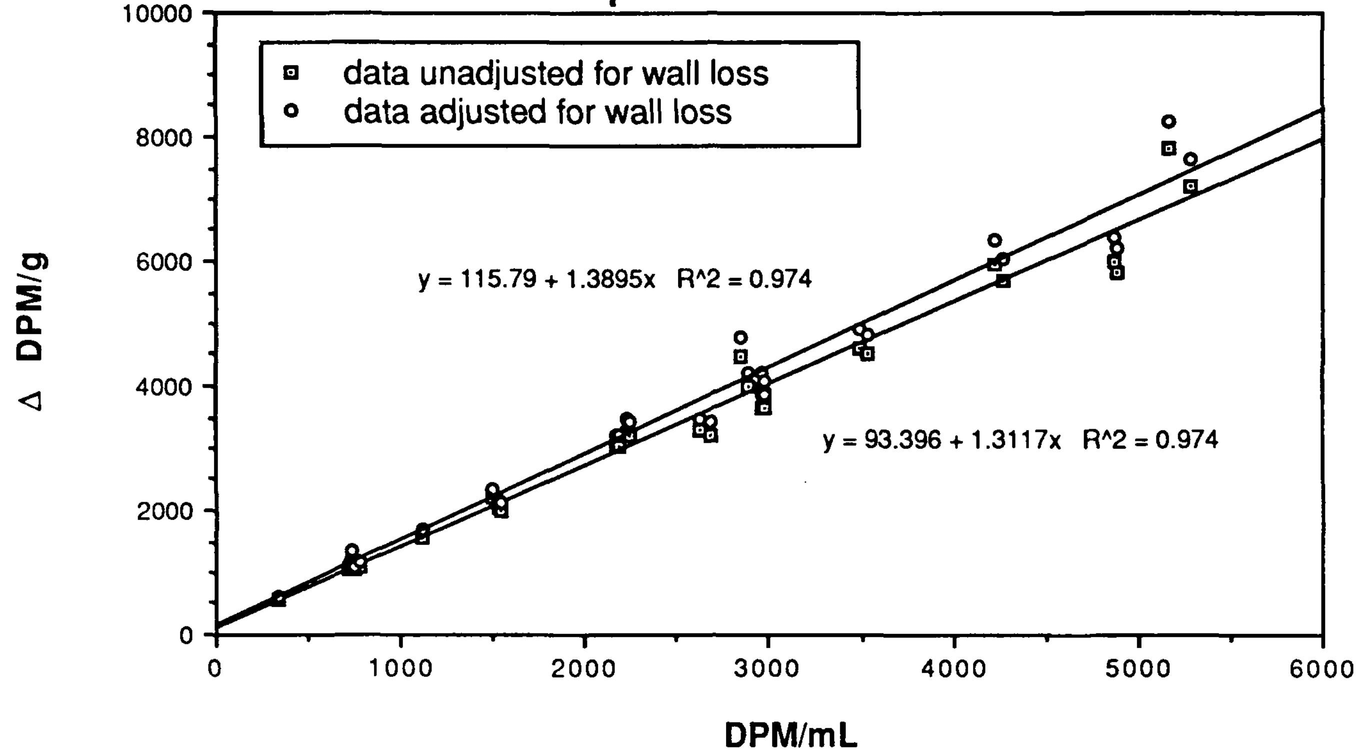
$$\text{amount sorbed} = \{(\text{Ceq control})(\text{Vcontrol}) - (\text{Ceq sample})(\text{Vsample})\} + \{(\text{Ceq control}) - (\text{Ceq sample})\} \times S$$

where: Ceq control is the equilibrium concentration in control bottles with no sorbent
Ceq sample is the equilibrium concentration in sample bottles containing sorbent
Vcontrol is the solution volume in the control bottle
Vsample is the solution volume in the sample bottle
S is the slope of the "empty" (with no sorbent present) bottle isotherm.

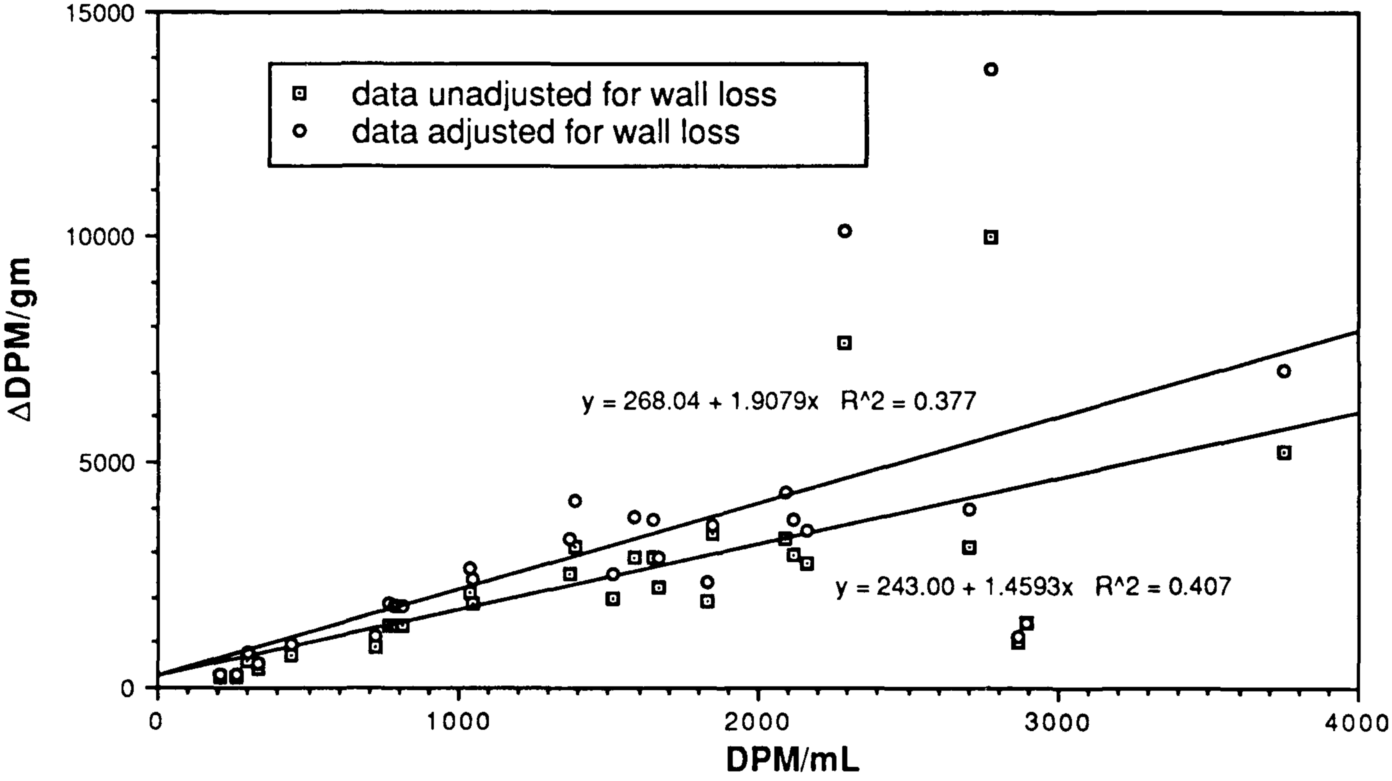
Example isotherms for the Columbus aquifer material and graded filter sand are shown for both types of sample containers in Figures 8 and 9. Data points and linear regression fits are given before and after adjustment to account for reversible loss of hydrophobic compound to the container walls. Inspection of data fits to data sets with 2 grams or 10 grams solids and the isotherm constructed from the variable solids data set revealed no observable solids effects. Therefore, the composite of the data from all these experiments has been pooled to calculate the isotherm slopes.

Comparison of the results for Teflon®-sealed vials vs. flame sealed ampules shows that, for phenanthrene on both sorbents, greater data scatter resulted from the vial system. Correction for reversible loss to container walls was relatively small in the flame-sealed ampules and may be neglected. However, the correction for the vial system appears important. Error in estimating hydrophobic partition coefficients may occur in experiments where Teflon®-sealed vials are employed and container effects are not taken into account. This error would be compounded if controls were not employed, permitting correction for any irreversible loss of sorbate to the bottle seal. If sorbate mass available was determined by an alternate means, such as direct measurement of a stock solution, the amount calculated as sorbed would be seriously overestimated.

The correction for loss to containers should be made only if the loss is reversible and the hydrophobic compound sorbed to walls in the control bottles is available for sorption to added solids. This appears to be a reasonable assumption for the interaction of glass container walls with nonionic sorbates. Interaction of a hydrophobic pollutant with a hydrophobic surface such as PTFE would be most likely to be reversible if it were a surface (i.e., adsorption) process. However, if the pollutant penetrates the structure of PTFE, reversibility may be kinetically constrained as is observed with pollutant interactions with soil organic matter (Reference 35, 36). Since the Teflon®-faced seal was bounded on one side by a silicone disc and the atmosphere, loss of hydrophobic material by volatilization from the experimental system is also possible. Comparison of the adjusted and unadjusted results for phenanthrene partition coefficients from the batch experiments indicates that better agreement is obtained if unadjusted results for sand in Teflon®-sealed vials are compared to the ampule results. This agreement would be anticipated result if loss to the Teflon® seal in the vials was irreversible. In the case of the aquifer material, better

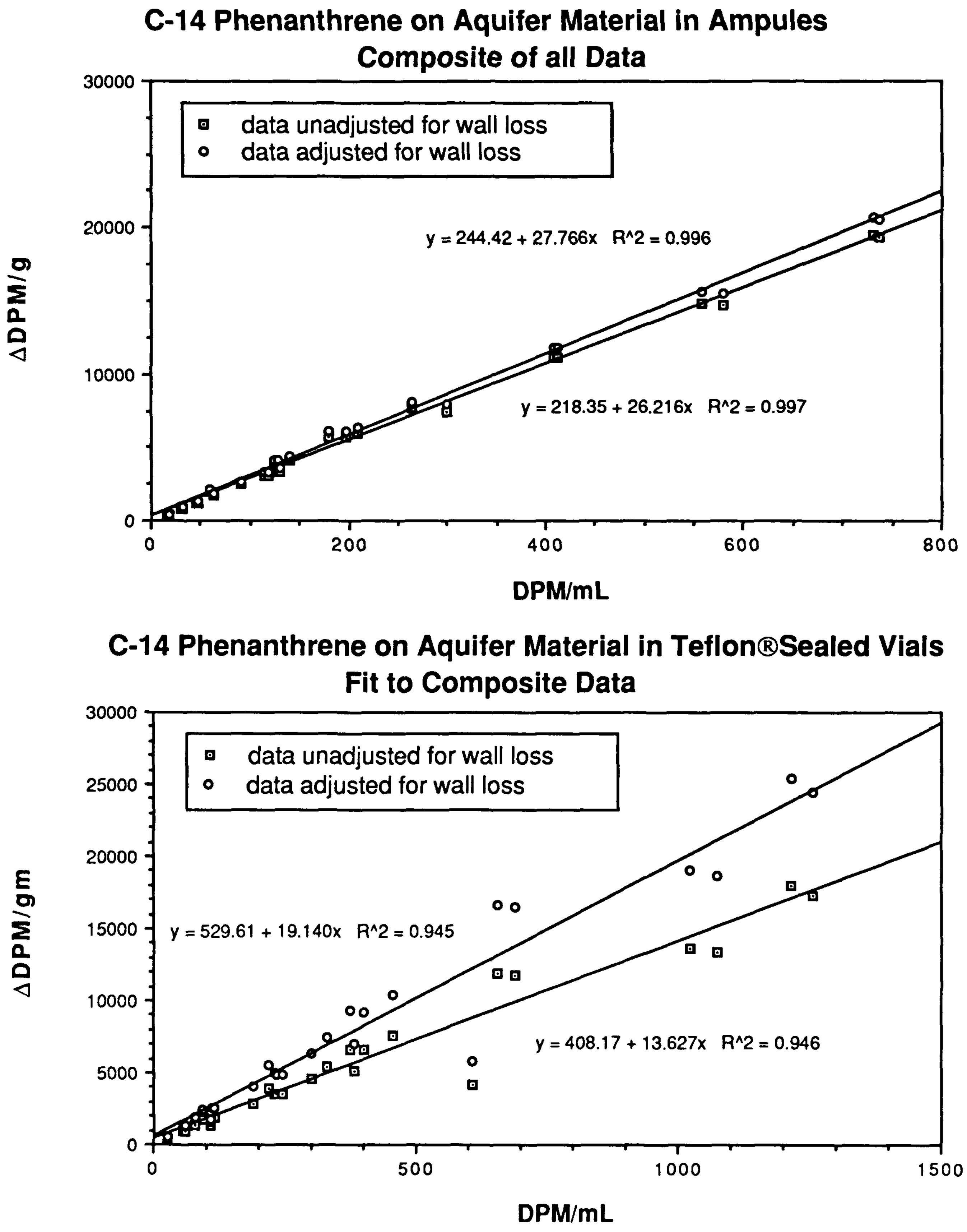


C-14 Phenanthrene on 0.25mm Sand in Ampules
Composite of all Data



C-14 Phenanthrene on 0.25mm Sand in Teflon®Sealed Vials
Composite of All Data

Figure 8. Batch Sorption Isotherms for Phenanthrene onto a Graded 0.25 mm Sand in Flame-sealed Ampules (Top) and Teflon®-sealed Vials (Bottom).


C-14 Phenanthrene on Aquifer Material in Ampules Composite of all Data

C-14 Phenanthrene on Aquifer Material in Teflon®Sealed Vials Fit to Composite Data

Figure 9. Batch Sorption Isotherms for Phenanthrene onto Columbus Aquifer Material in Flame-sealed Ampules (Top) and Teflon®-sealed Vials (Bottom).

agreement is also obtained if the fit to unadjusted vial data is employed. However, some reversibility in the reaction is indicated since the unadjusted vial results fall below those for the flame sealed ampules. These results demonstrate that the use of PTFE or other hydrophobic polymers should be avoided when dealing with low-solubility nonionic sorbates.

2. Column Methods

The breakthrough curve for phenanthrene from the graded sand in the "all-glass" column is shown in Figure 10. The column R was calculated from the temporal first moment and equalled 4.1 (K_d = 0.66). Using the batch value for K_d of phenanthrene on the graded sand (K_d = 1.4), the R value predicted for the column study is 7.7. This disparity in column and batch results is consistent with the trend observed by MacIntyre and Stauffer (Reference 1) in which column R values averaged approximately 0.5 times batch values.

The difference between the batch and column results for phenanthrene invites examination. Assuming the sorption isotherm is linear, there should in theory, be but a single partition coefficient which governs phenanthrene behavior in both experiments. Differences therefore suggest experimental artifacts which may ensue from one or both measurements. Common explanations for inconsistent batch and column values for partition coefficients include:

a. Equilibrium was not achieved in the batch experiment. If this occurred, then the true batch partition coefficient would be higher increasing the difference between batch and column results.

b. Solids effects existed in batch experiments. If colloidal solids were present in the batch equilibrations, the observed partition coefficient would be lower than the true value through failure to separate colloidal and dissolved sorbate. This would increase the difference between batch and column results.

c. Removal of fines, organic carbon, or other alterations in the solid phase occurred during column flow experiments. After the column experiment, a batch isotherm was performed on the sand packing removed from the column and this confirmed that the batch partition coefficient was unaltered (i.e., K_d still equalled 1.4). Therefore, the disparity between column and batch values of R cannot be attributed to washout of fine particles or organic matter from the column.

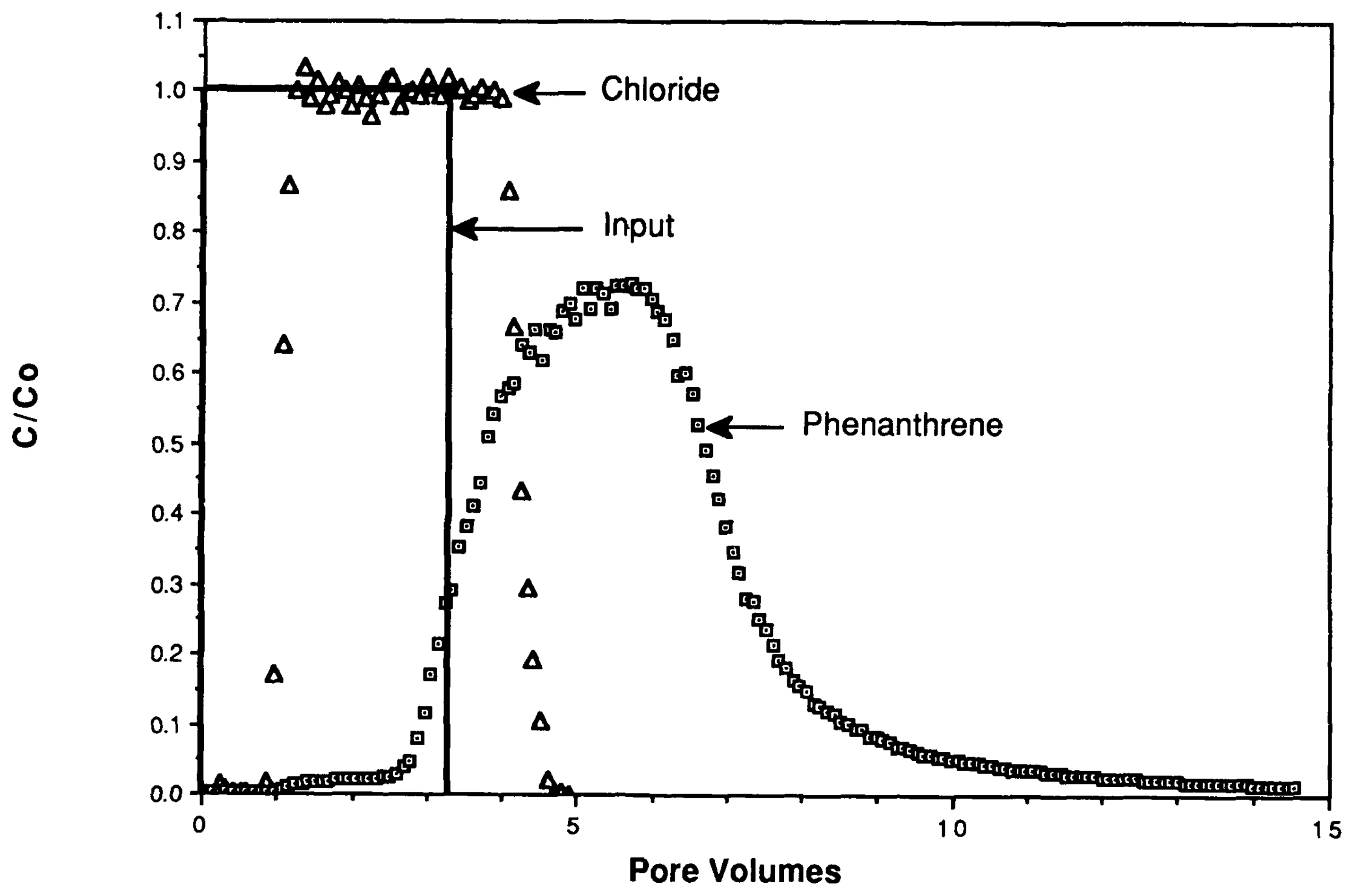


Figure 10. Elution of Step Inputs of Phenanthrene and Chloride from the "All-Glass" Column Assembly Packed with Graded Sand.

d. Column data was improperly interpreted. As noted by Brusseau and Rao (Reference 34), if tailing occurs, calculation of the column R values as the point at which C/Co = 0.5, or through use of a spatial first moment will result in erroneous values. The temporal first moment is independent of tailing phenomena; however, it is subject to analytical limitations. For example, it is difficult to accurately determine the contribution to the temporal first moment of peak tailing which is marginally greater than the analytical baseline. Such tailing may continue for very long time periods (as was observed in this study). Failure to include all of the phenanthrene peak in the first moment analysis would result in underestimation of the column retardation and may help to account for the discrepancy between the column and batch R values. Use of frontal analysis as employed by Nkedi-Kizza et al. (Reference 37) is also independent of the kinetic or mass transfer phenomena which result in tailing. This approach requires continuation of an experiment until the column effluent concentration equals that of the influent and was not possible with the data obtained in this study. The determination of the time at which C/Co = 1 is also subject to analytical constraints. Compounds which have slow sorption kinetics can approach C/Co = 1 very slowly.

The results of Karickhoff et al. (Reference 28), and Schwarzenbach and Westall (Reference 38) indicate that correlations between f_{oc} and K_d break down at $f_{oc} \approx 0.001$. This may be interpreted as indicating the onset of significant mineral contributions to K_d. Mingelgrin and Gerstl (Reference 39) review a number of studies in which mineral contributions to the adsorption of organic solutes appear significant. Given the low carbon content of the filter sand, which is an order of magnitude below that of the Columbus aquifer material and of values reported for other sandy aquifer materials (Reference 1, 40, 41), it is noteworthy that this sorbent has sufficient organic matter to dramatically alter phenanthrene transport.

The relative importance of organic carbon vs mineral surfaces in the graded sand may be examined in a variety of ways. As a first approximation, the relationship proposed by McCarty, et al. (Reference 42) may be used to estimate the critical fraction f_{oc}^* at which soil organic carbon will dominate sorption (vs a silica mineral surface with surface area, S). This relationship was derived under the assumption that soil minerals and organic matter act additively in their influence on sorption. Therefore,interactions such as organic coating of soil minerals to mask sorption sites are not considered. Given these assumptions, f_{oc}^* is:

$$f_{oc}^* = \frac{S}{200} \quad \frac{1}{(K_{ow})^{.84}}$$

Assuming $S = 1\ m^2/g$ for aquifer sand, then $f_{oc}^* = 8.9 \times 10^{-7}$ for phenanthrene. This suggests that the carbon content of the graded sand was well above that needed to dominate mineral contributions to sorptive behavior. This calculation is consistent with the findings of Karickhoff (Reference 14) who reviewed threshold values at which mineral contributions to sorption were expected to become important. He found that the threshold for mineral contributions to sorption of large (>C10) nonpolar organics was insignificant in natural sediments.

The sorptive role of organic matter in the graded sand was evaluated by measuring the batch K_d after treatment to remove organic carbon. Four alternative treatments were employed:

a. Organic carbon oxidation by reaction with 30 percent H_2O_2 (2:1 solution volume/volume sand) for 12 hours at room temperature.

b. Organic carbon oxidation with $K_2Cr_2O_7$ using the Walkey Black procedure (Reference 43) for measurement of soil organic carbon.

c. Organic carbon extraction with 1.0 N NaOH.

d. Organic carbon oxidation at 650°C in a muffle furnace for 6 hours.

Sand from the first three treatments was repeatedly washed with distilled water and centrifuged to remove excess reagents. As a control, an untreated sand sample was also washed to verify that the distribution coefficient was not altered by loss of small particles.

Measured K_d values for phenanthrene on the treated sand are summarized in Table 3. The first three treatments for carbon removal produced a sand with a distribution coefficient about 1/5 that of the unaltered material, while high temperature combustion removed virtually the entire sorptive capacity of the sand. The washed control showed that rinsing of the sand did not alter its K_d. The specificity of selective extraction techniques has been challenged (Reference 44), and it is possible that the treatments used here may have altered minerals in the sorbent. Nevertheless, the consistent effect of the alternative treatments suggests that even the very low amounts of soil organic matter in the graded sand are sufficient to regulate the transport of PAH.

To test the generality of this conclusion, organic carbon on the Columbus aquifer material was also removed by Treatments (a) and (d). Results are summarized in Table 3. The batch partition coefficient of the sand was reduced by a factor of ≈2.3 after oxidation with H_2O_2 and by a factor of ≈7.1 after combustion in a muffle furnace. Washing the aquifer material with 0.005 M $CaSO_4$ did not significantly alter the batch partition coefficient. The residual oxidized aquifer material had a sorption coefficient significantly higher than the oxidized sand indicating a contribution to phenanthrene sorption from mineral phases in the aquifer material (likely clay and iron oxide). However, as with the graded sand, the sorptive behavior of the aquifer material appears to be dominated by its small content of organic matter.

TABLE 3. DISTRIBUTION COEFFICIENTS FOR 0.25mm GRADED FILTER SAND AND COLUMBUS AQUIFER MATERIAL BEFORE AND AFTER TREATMENTS TO REMOVE ORGANIC MATTER

Material	Distribution Coefficient, K_d
unaltered graded filter sand	1.39
graded filter sand control, washed with distilled water	1.45
graded filter sand treated with H_2O_2	0.29
graded filter sand treated with $K_2Cr_2O_7$	0.31
graded filter sand extracted with NaOH	0.39
graded filter sand heated in muffle furnace	0.04
unaltered Columbus aquifer material	13.8
$CaSO_4$ washed aquifer material	14.1
Columbus aquifer material treated with H_2O_2	5.89
Columbus aquifer material heated in muffle furnace	1.93

3. Phenanthrene Sorption Kinetics

Tailing of phenanthrene was observed from the graded sand in the "all-glass" column (Figure 10). Recent reports (Reference 45, 46) indicate that, under circumstances in which immobile pore water is negligible (as indicated by the symmetric Cl^- breakthrough curve in this study), tailing of hydrophobic solutes may be attributed to kinetic hindrance of their partitioning into soil organic matter. A commonly employed model for kinetic limitations assumes two sorption site types (Reference 47). One site type is assumed to obey the assumptions of local equilibrium, while sorption at the other site type is governed by a first order dependence on the difference between the actual amount sorbed and that which would occur at equilibrium. The advection dispersion equation for reaction-rate limited transport in porous media has been solved by Parker and van Genuchten (Reference 32) and van Genuchten and Wagenet (Reference 47). In the absence of biodegradation, adjustable model parameters include: column length, pulse duration, pore water velocity, and the hydrodynamic dispersion coefficient. All of these may be measured directly or estimated from transport studies with an inert tracer. Additional model parameters are the pollutant retardation factor, R (which may be estimated from batch measurements of K_d as noted above), the fraction of sorption sites which are rate limited, F, and the rate constant for the kinetically limited sites, k. The parameters related to reaction kinetics are incorporated in the following model equations:

$$K_d = K_1 + K_2$$

$$F = K_1/K_d$$

$$R_1 = [1 + \rho_b F K_d/\theta]$$

$$\beta = R_1/R$$

and

$$\omega = \frac{k\,(1 - \beta)\,R\,L}{\upsilon}$$

where υ = pore water velocity

L = column length

K_1 = partition coefficient for sites which obey the assumption of local equilibrium.

K_2 = partition coefficient for kinetically-limited sites.

and R_1 = solute retardation by sites which obey the assumption of local equilibrium.

The rate constant, k, for hydrophobic solutes may be estimated from the empirical relationship proposed by Brusseau and Rao (Reference 36):

$$k = 2.0\ (K_d)^{-0.668}\quad (r^2 = .95)$$

Using this equation, k = 1.6/hr for phenanthrene based on the batch value of K_d, or k = 2.6/hr based on K_d calculated from the column R for phenanthrene.

The phenanthrene breakthrough curve was fit to the reaction rate-limited model using, CXTFIT (Reference 32). R, β and ω were allowed to be adjustable parameters while the pore water velocity and the hydrodynamic dispersion coefficient were fixed at the values determined from the Cl^- breakthrough curve (Table 2). This analysis gives R = 4.18, which is consistent with the R value calculated from the first moment of the breakthrough curve, β = 0.79 and ω = 0.59. The 95 percent confidence interval on the fitted R value from the column (R = 4.13 to 4.24) does not overlap the value estimated from the batch K_d (R = 7.7). From the fitted β value, the calculated F = 0.7 suggesting that a moderate fraction of the sorption sites in the graded sand (shown above to be organic carbon) could be kinetically limited. Since model fitting parameters do not necessarily bear any chemical significance, this implication remains highly speculative.

If the carbon in the graded sand were uniformly spread over the sand surface it would form a film on the order of one angstrom thickness. It is difficult to envision such a thin film behaving as a phase into which phenanthrene partitions. Kinetic limitations in desorption and tailing phenomena in transport of hydrophobic pollutants have been attributed to diffusion within soil organic matter (Reference 35, 36). Tailing of phenanthrene relative to chloride indicates slow reaction kinetics yet an angstom thick film of organic carbon could not act as a medium within which phenanthrene diffusion took place. It is therefore indicated that the sand organic matter exists as patches or porous blobs. This picture is consistent with what is seen in electron microscopic examination of soil organic matter (Reference 48).

To illustrate the limitations of model fitting parameters, the two-site kinetic model can be constrained to use values obtained through independent estimates. For example, the R and k values may be estimated from the batch K_d. This leaves one adjustable model parameter: the fraction of sorption sites which are rate limited, F. In the two-site model, the constants k and F are embodied in the terms β and ω. If k is fixed, then specifying the value of β determines the value of ω. Model predictions using the batch R and pairs of β and ω values interrelated by the k estimated form the batch K_d are shown in Figure 11. It is clear that no value of F, which can range between zero and one, is adequate to fit the actual column data. However, if both β and ω are allowed to be adjustable parameters it is possible to obtain a reasonable fit to the column data when R is constrained to equal the

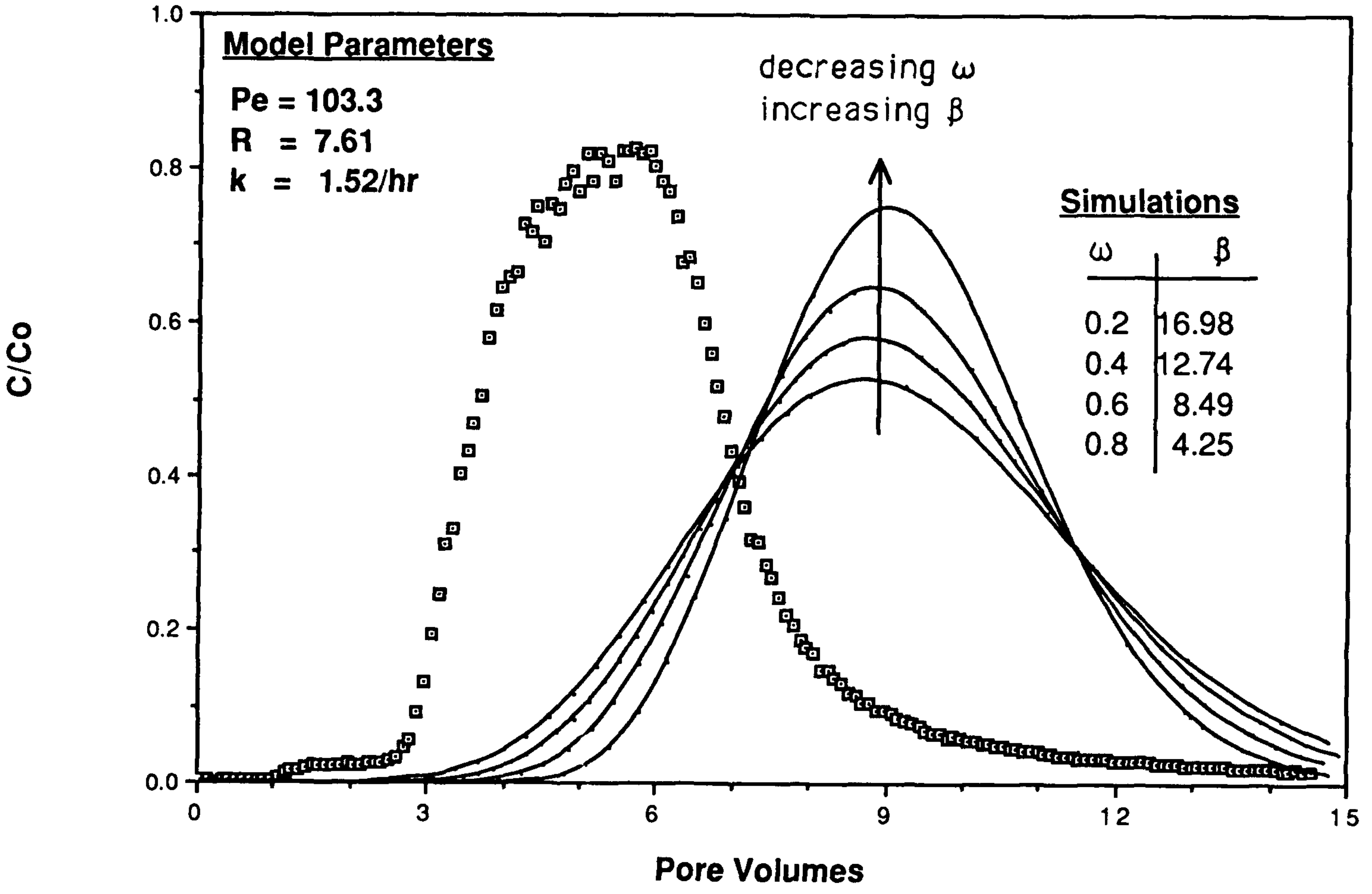


Figure 11. Phenanthrene Breakthrough Curve; Comparison of Data to Fits Obtained with One Adjustable Model Parameter.

value obtained from the batch K_d. The best fit is obtained with $\beta = 0.47$ and $\omega = 0.23$ and is shown in Figure 12. The best fit β and ω values yield an estimate of k (k = 0.31/hr) which is substantially lower than the values given above which were obtained using the empirical equation of Brusseau and Rao.

The kinetics of phenanthrene sorption were also examined directly by carrying out replicate batch sorption experiments on the graded sand over a time period ranging from 0.5 hours to 2 months. Duplicates of samples containing 2 grams and 10 grams sorbent and controls (no sorbent) were analyzed at each time interval for samples which were (a) suspended in distilled water and (b) suspended in 0.2 percent NaN_3 to inhibit biological growth. In the absence of azide, erratic results were obtained after 48 hours indicating the onset of biological degradation. Results for azide poisoned samples after the first 4 days of sampling and after a 2-month time span are shown in Figures 13, and 14, respectively. The results indicate the commonly observed fast initial sorption kinetics followed by a slow approach to equilibrium. Equilibrium is apparently obtained within 7 days, although the sorption reaction is 90 percent complete within 24 hours.

If the sorption reaction is considered as a single site process, then the reaction kinetics may be written as:

$$\partial S/\partial t = k(S^*-S)$$

where S is the amount sorbed at any popint in time t, and
S^* is the eventual equilibrium amount sorbed.

Integration gives: $(S^*-S)/S^* = e^{-kt}$

and a plot of $\ln(S^*-S)$ vs t would be linear if this simple kinetic model were obeyed.

The 10 gram data for the graded sand showed the least scatter and were analyzed using the single-site kinetic model. The fit to the data from the first 24 hours (n = 12) gave k = 0.11/hr ($r^2 = 0.77$) and the fit to the data from 24 to 400 hours (n = 10) gave k = 0.007 ($r^2 = 0.64$). Although these rate constants can not be directly compared to those which are arrived at uising the two site model, they do give a feel for the speed of the pheanthrene sorption process. By way of comparison, Karickhoff (Reference 6) reported rate constants for phenanthrene onto a sediment with K_d=250. For the slow sorption step, k = 0.24/hr and 0.29/hr at sedeiment to water ratios of 0.0025 and 0.005, respectively.

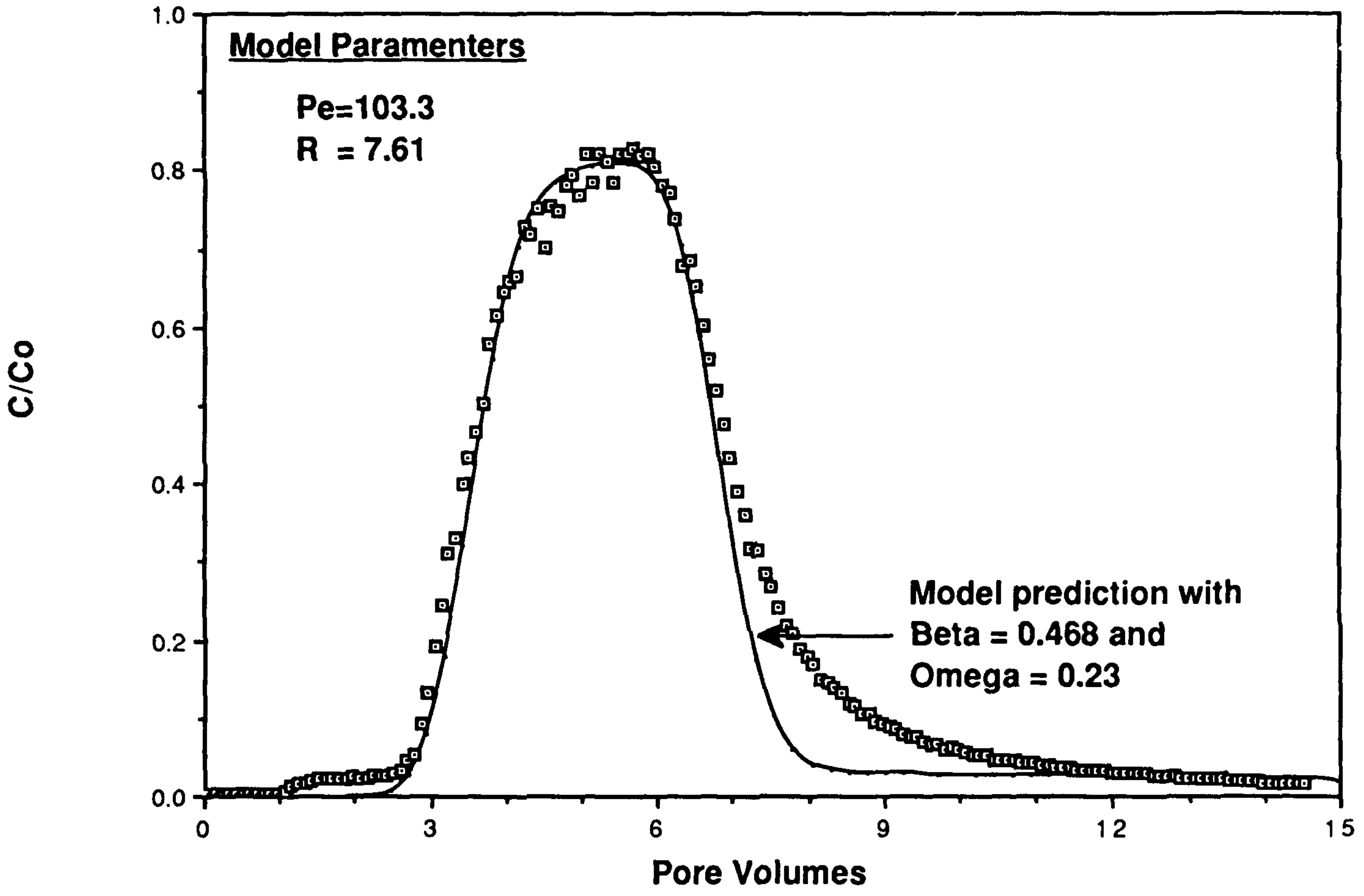


Figure 12. Phenanthrene Breakthrough Curve; Comparison of Data to Fit Obtained with Two Adjustable Parameters.

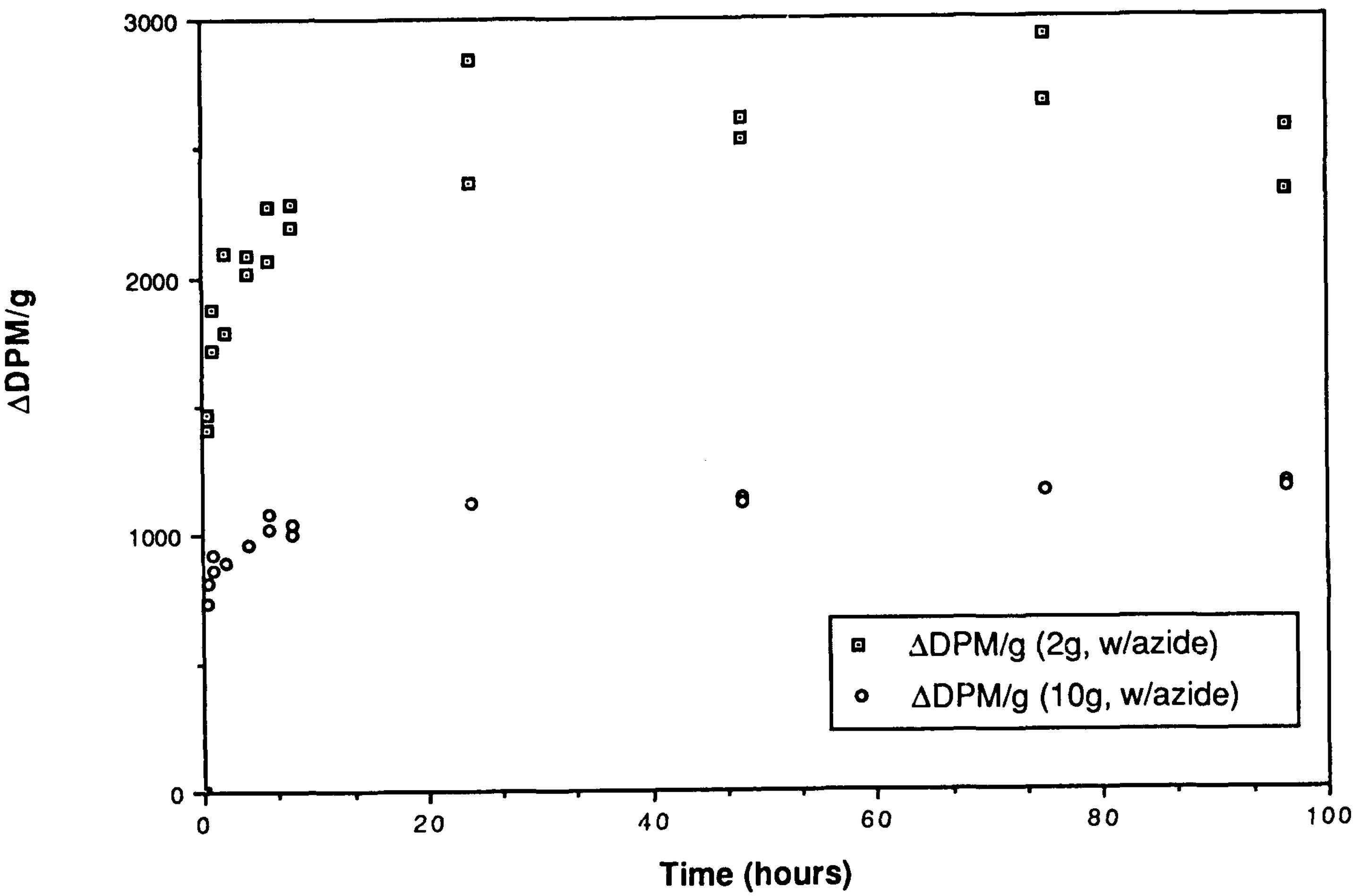


Figure 13. Phenanthrene Sorption Kinetics on 0.25 mm Sand; Results for a 4-Day Interval.

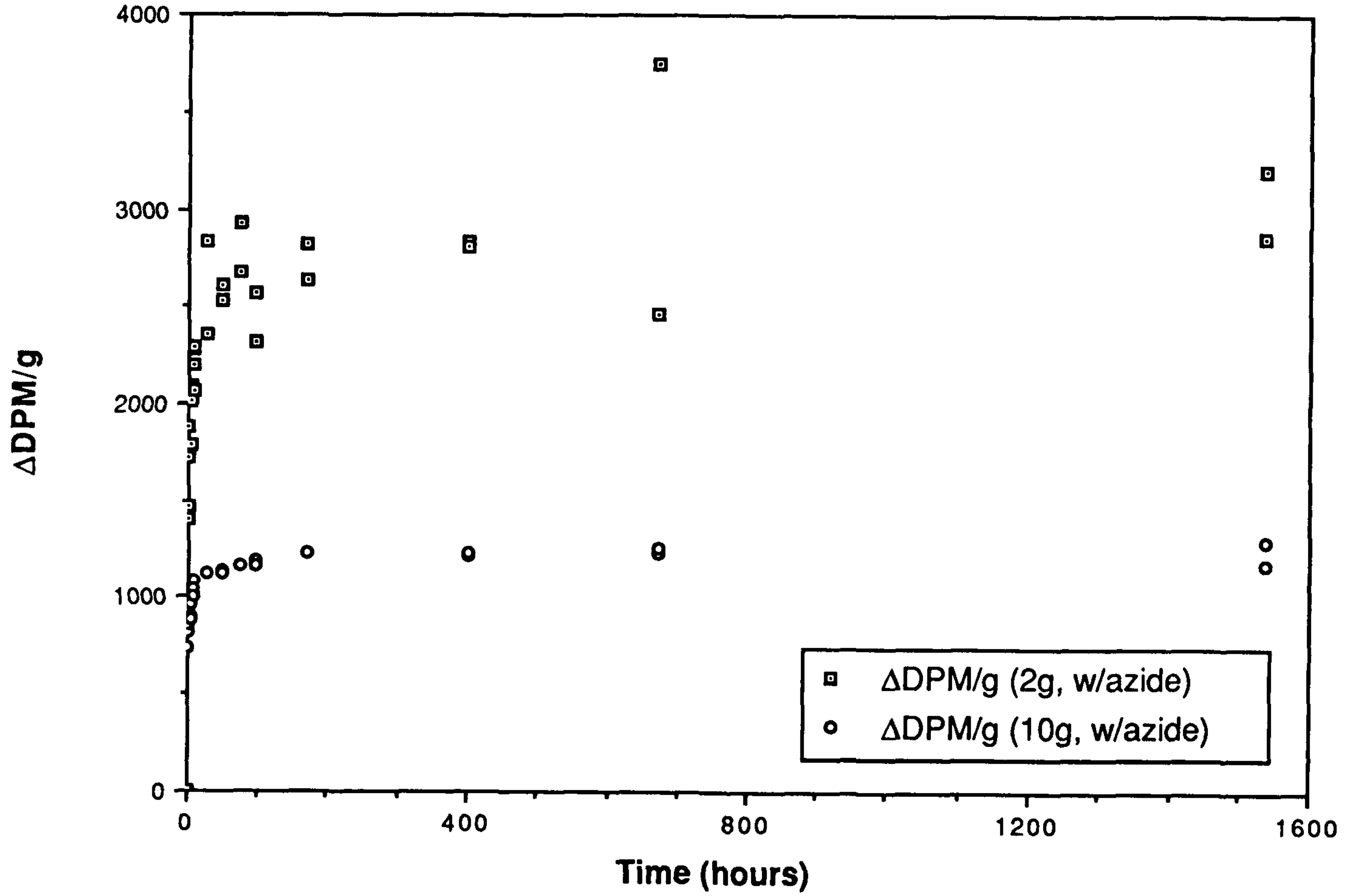


Figure 14. Phenanthrene Sorption Kinetics on 0.25 mm Sand; Results for a 2-Month Interval.

4. Studies of Enhanced Phenanthrene Transport

Because of their high sorptive partition coefficients PAHs are anticipated to move slowly in groundwater. Given their low mobility, the presence of PAHs is often neglected relative components of fuels with higher solubility such as benzene, toluene, and xylenes (BTXs). Nevertheless, some PAHs such as benzo(a)pyrene are carcinogens and their presence in groundwater poses a serious concern. Because of their low mobility it is likely that conventional pump and treat aquifer cleanup procedures may have difficulty removing PAHs. Innovative technologies such as soil venting are also unlikely to remove this class of pollutants because of their low vapor pressures. Factors which can increase the mobility of PAHs are therefore,of interest because:(1) it is imperative that PAH transport and fate be predicted accurately and not underestimated (2) any process which improves PAH mobility has the potential for application as an aquifer remediation technology and (3) given inevitable funding limitations, identification of waste sites with conditions which favor PAH mobility can aid in their prioritization for remediation.

Colloidal solids and dissolved macromolecules in soil pore water can potentially act as carriers for sorbed PAHs. For such a process to act to increase PAH mobility two conditions must be met: (1) the carrier must be able to bind PAHs to an appreciable extent and (2) the carrier must have a relatively greater mobility than the PAH molecule which it binds. Given these constraints, it is interesting that most studies of potential carriers have focused exclusively on either their binding properties or their mobility and have not coupled these properties. For example, extensive evidence shows humic type macromolecules can bind hydrophobic pollutants (Reference 49, 50, 51, 52, 53, 54, 55, 56) however, these studies do not reveal the extent to which humic-bound pollutants are mobile. In this regard one may generally anticipate that soil humic acids will be relatively immobile in soil under circumneutral pH conditions. Fulvic acids which are generally of smaller molecular size and contain more polar functional groups than humic acids will have higher mobility in soil, but the factors which make such molecules mobile also act to reduce their affinity for hydrophobic pollutants.

Movement of dissolved organic macromolecules presumably is subject to the same theory which governs the mobility of organic pollutants. Many naturally occurring organic macromolecules are polyprotic acids and have varying water solubility depending upon soil pH. At constant pH, the partition coefficient of a dissolved macromolecule should be approximated by:

$$K_d \approx f_{oc} K_{ow(pH)}$$

where f_{oc} reflects the weight fraction of bound soil organic matter and $K_{ow(pH)}$ is a measure of the organic macromolecule's hydrophobicity at the given pH. High macromolecule $K_{ow(pH)}$ favors interaction with PAHs but also increases the macromolecule's K_d, decreasing its mobility.

Most research on colloidal solids in groundwater has focused on factors which result in mobility (Reference 57, 58). This stems partially from reliance on filtration theory, in which particle removal is the chief concern. Filtration theory attained fundamental vs empirical status in the early 1970s when descriptions of basic process (i.e. particle transport to a media grain by brownian motion, interception, and sedimentation) were incorporated into models (Reference 59). Predictions indicate that particles of $\approx$ 1 µm diameter are most likely to be mobile in porous sandy media. This results from a minimum in the total collision efficiencies arising from the diffusion, interception and sedimentation transport mechanisms (η_D, η_I, and η_S respectively). These transport processes are proportional to particle size as follows:

$$\eta_D \propto (d_p)^{-2/3}$$

$$\eta_I \propto (d_p)^2$$

$$\eta_S \propto (d_p)^2$$

Although colloidal sized particles have been shown to be mobile in soils (Reference 60) their ability to sorb pollutants such as PAHs has not been demonstrated.

The distinction between dissolved macromolecules and colloidal solids is not a clear one and is often operationally defined by the use of filters. In this regard, both colloids and macromolecules are subject to the phenomena observed in size exclusion chromatography in which large-sized substances are excluded from entry into small pores. In such a case, larger-sized materials move with a higher velocity than an inert tracer such as ^3H_2O, which can enter all of the pore volume. The result of size exclusion in soils can be enhanced mobility of non-sorbing carriers relative to the nominal pore water velocity and concomitant enhancement of the mobility of carrier-bound pollutants (Reference 61).

The interactions between a hydrophobic pollutant, a carrier, and soil are illustrated in Figure 15. Conceptually, the influence of a carrier may be viewed as a competing sorption reaction for the PAH in which the competing sorbent may be mobile or may itself be sorbed. Sorption of the carrier is described through a separate partition coefficient which may be independently determined by either batch or column techniques. If a carrier is to enhance the transport of a hydrophobic pollutant, less of a pollutant will be sorbed in a batch experiment where both carrier and soil are present (subject to the experimental constraints discussed below). Mathematically this situation arises when the carrier-soil partition coefficient ($K_{dom}{}^{S}$) is less than the pollutant-soil partition coefficient ($K_d{}^{S}$) and the carrier is able to bind the pollutant to a significant extent ($K_d{}^{om} >> 0$).

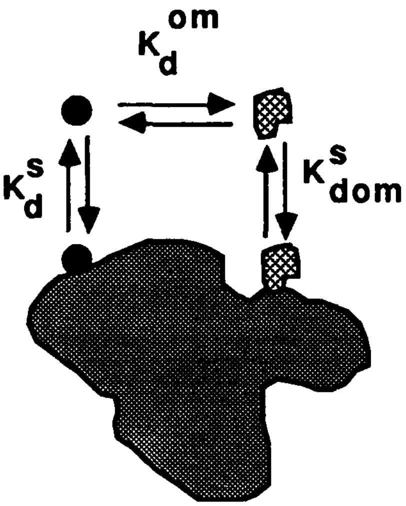


Figure 15. Schematic of interactions of a hydrophobic pollutant with soil and a colloidal solid or dissolved macromolecule. Binding constants are indicated for the pollutant with the soil, K_d^{s} ; for the pollutant with the carrier K_d^{om} ; and for the carrier with the soil, K_{dom}^{s}

The conventional one-dimensional form of the advection dispersion equation for solute transport (ie., without kinetic terms for sorption or mass transfer to regions of immobile pore water) may be solved assuming a pollutant is distributed as illustrated in Figure 15. The solution and parameter sensitivity analyses are given by Magee (Reference 62). The model also allows consideration of faster movement of carriers through size exclusion from pores. In general, model results were most sensitive to pollutant partition coefficients, $K_d{}^{om}$ and $K_d{}^{S}$ and to the concentration of the carrier. Experimental results with phenanthrene and a carrier (water soluble soil organic matter) showed the model to be capable of predicting enhanced transport in miscible displacement experiments. Model parameters were determined in independent batch and column studies (Reference 62 and 63).

The batch and column methods described above allowed the ability of selected carriers to enhance phenanthrene transport in low carbon aquifer materials to be assessed. Colloidal solids and and dissolved organic macromolecules were selected based upon their likely presence in soil pore water, or as experimental surrogates for colloid-sized particles and high molecular weight soil organic matter. Both natural and synthetic materials were used and are listed in Table 4.

TABLE 4. NATURAL AND SYNTHETIC CARRIERS USED IN LABORATORY EVALUATIONS OF ENHANCED TRANSPORT.

COLLOIDAL SOLIDS

Material	Source
Cellulose	Aldrich Chemical Co.
Iron Oxide	Pfizer Inc. (easy dispersing pure yellow oxide)
Kaolin	Wards Natural Science (colloidal powder, lab. grade)
Latex Microspheres	Curtin-Matheson Sci. (0.09μm and 1.1μm dia.)
Ca-Montmorillonite	Source Clay Minerals Repository (#STx-1)
Na-Montmorillonite	Source Clay Minerals Repository (#SWy-1)
Polystyrene	Aldrich Chemical Co.(2,000 and 47,500 M Wt.)

"DISSOLVED" ORGANIC MATERIALS

Material	Source
Methylsalicilate	Aldrich Chemical Co.
Polyethylene Glycol	Fisher, lab. grade, 400 M Wt. (PEG 400)
Polymaleic Acid	Types 1 and 2, synthesized as described by Spiteller and Schnitzer (Reference 64).
Tannic Acid	Aldrich Chemical Co.
Water Soluble Soil Organic Matter (WSSOM)	extracted using the procedure of Magee (Reference 62) from a peaty muck soil obtained at Belle Glade, Fl.

With the exception of the Latex spheres, all colloidal solid suspension concentrations were 100 mg/L in a 0.005 M $CaSO_4$ plus 0.02 percent NaN_3 electrolyte. Latex spheres were supplied by the manufacturer (Dow Chemical) as a concentrated suspension and were added to 0.005 M $CaSO_4$ plus 0.02 percent NaN_3 electrolyte until the suspension was turbid to the eye. Other than the Latex spheres, none of the colloidal solids considered formed a stable suspension in the $CaSO_4$, NaN_3 electrolyte. Iron, kaolin, and montmorillonite were selected for use because these mineral phases naturally occur in soils and are likely to exist, in part, as colloids. Cellulose particles can form stable suspensions under basic conditions. Use of polystyrene and Latex provided particles of known molecular weight and size.

With the exception of the Belle Glade water-soluble soil organic material (WSSOM), all dissolved organic solutions were 100mg/L in 0.005 M $CaSO_4$ plus 0.02 percent NaN_3 electrolyte. The WSSOM solution contained ≈80 mgC/L after centrifugation at ≈1400xG and filtration through a Whatman GFC filter. Tannic acid was selected for use because its acidic functional groups make it likely to be ionized and mobile in soil. Polymaleic acid has been suggested as a synthetic analog for soil fulvic acids (Reference 63). Polyethylene glycol (PEG 400) is polar and has a relatively high molecular weight. WSSOM extracted from the Belle Glade muck was soluble or formed a stable suspension in the experimental $CaSO_4$ plus NaN_3 electrolyte.

Results for batch experiments in which phenanthrene sorption onto the graded sand was compared for aqueous solutions (0.005 M $CaSO_4$ plus 0.02 percent NaN_3) with and without selected carriers are illustrated in Figure 16. The results indicate that methylsalicilate was the only material capable of substantially reducing the phenanthrene batch partition coefficient. Latex spheres and Belle Glade WSSOM actually acted to increase phenanthrene partitioning. Filtration of the WSSOM through a 0.45μ filter eliminated its effect on the phenanthrene K_d, indicating the increased removal was caused by > 0.45μ particles.

In batch experiments centrifugation was used to differentiate between sorbed and "dissolved" phenanthrene. Conceivably, colloidal solids (such as the Latex spheres) may be removed in this separation but may be stable in soil pore water. This is a limitation of the batch procedure to screen carriers for their ability to facilitate transport. In the case of the graded sand, adequate solid/solution separation could be achieved by simple sedimentation without centrifugation. Comparison of these two separation procedures revealed no effect on the observed phenanthrene K_d. Phenanthrene partitioning was still enhanced in the presence of Latex spheres when sedimentation was used to separate the

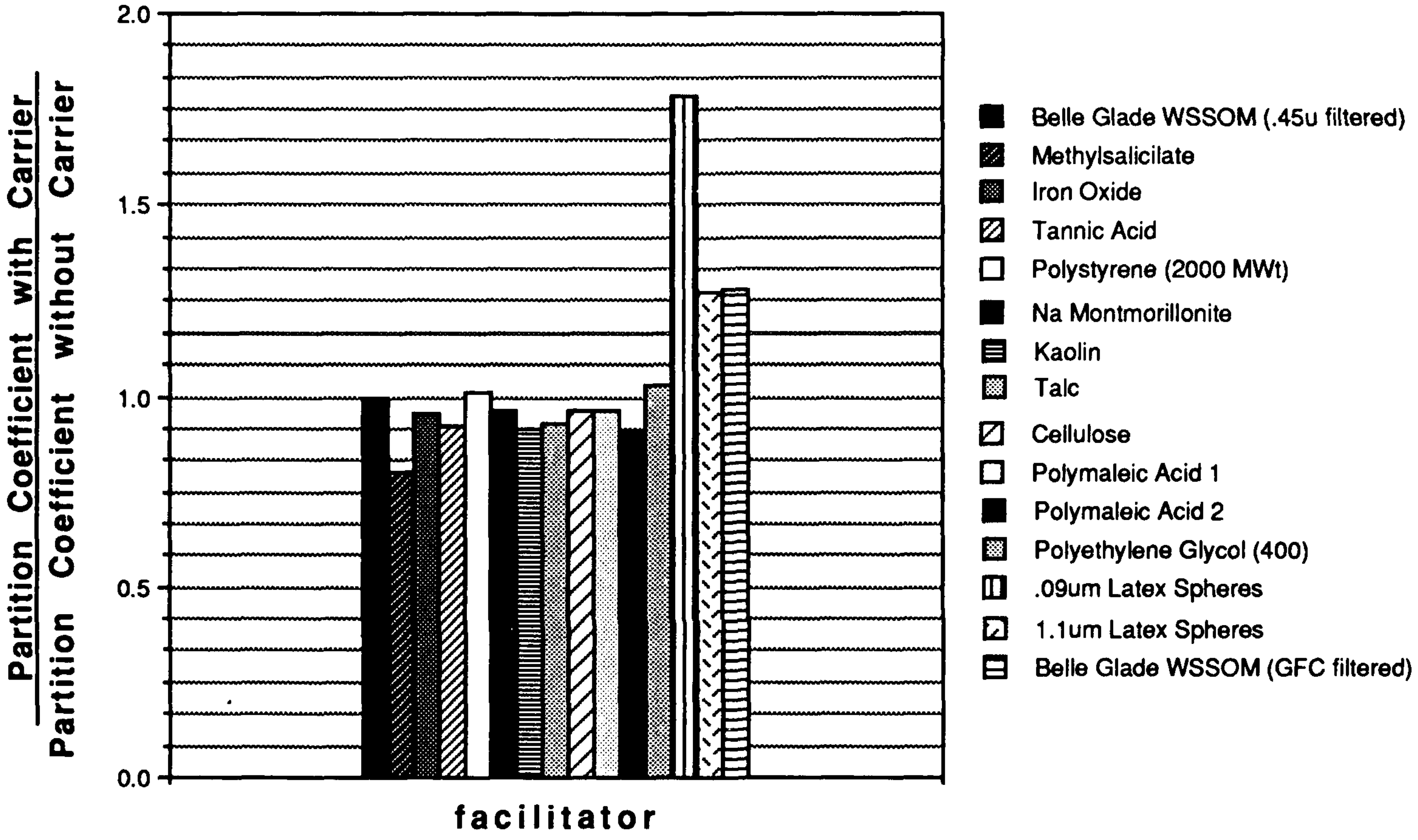


Figure 16. Phenanthrene Batch Partition Coefficients in the Presence of Carriers Relative to that Observed in their Absence.

solid phase. This result indicates that the increased phenanthrene removal occurred through binding of the Latex particles to the sand. This result was confirmed by performing a column experiment on the sand in which the phenanthrene pulse contained 0.09μ Latex spheres. The resulting phenanthrene breakthrough curve is shown in Figure 17 in comparison to phenanthrene breakthrough in the absence of the microspheres. The column R value (from the temporal first moment) for the sand increased to 5.0 in the presence of the Latex spheres vs 4.1 in their absence. This corresponds to a 27 percent increase in K_d which is in qualitative agreement with the 78 percent increase observed in the batch experiments.

The above results indicate that batch experiments can indeed be used to deduce the influence of various carriers of interest. More importantly the results show that PAH mobility can be decreased in low-carbon aquifers if colloidal solids are introduced which strongly bind to the aquifer matrix and also bind PAHs. Thus, it is possible to "defacilitate" as well as to facilitate the transport of hydrophobic pollutants, depending upon the nature of the pollutant, the "carrier", and the aquifer media.

Carriers may occur in soil pore water through several mechanisms:

a. They may be introduced by the aquifer recharge region which has been shown to be of major importance in determining groundwater composition (Reference 65). In such cases it is possible that even low carbon aquifer media may have a pore water with relatively high dissolved organic carbon (DOC) content. Typically, DOC levels are highest near the soil surface and decline with depth below ground (Reference 65).

b. Carriers may be introduced directly or indirectly through waste disposal practices. Direct introduction of carriers would occur when the waste itself contains macromolecular or colloidal material. Land application of sewage sludge or municipal wastewater serves an an example. Indirect introduction of carriers may occur when a waste application induces carrier producing reactions in the aquifer such as mineral dissolution/precipitation or solubilization of bound soil organic mater. The colloidal ferrous phosphate mineral observed by Gschwend and Reynolds (Reference 60) may represent an example of carrier induction.

In initial experiments with the Columbus AFB aquifer material, formation of an orange colloidal suspension was observed when the solid was equilibrated with deionized water (Millipore, Milli Q system). The colored matter could not be removed by centrifugation, and was not formed when the aquifer material was equilibrated with 0.005 M $CaSO_4$ plus 0.02 percent NaN_3 electrolyte. Based on its color and resistance to removal

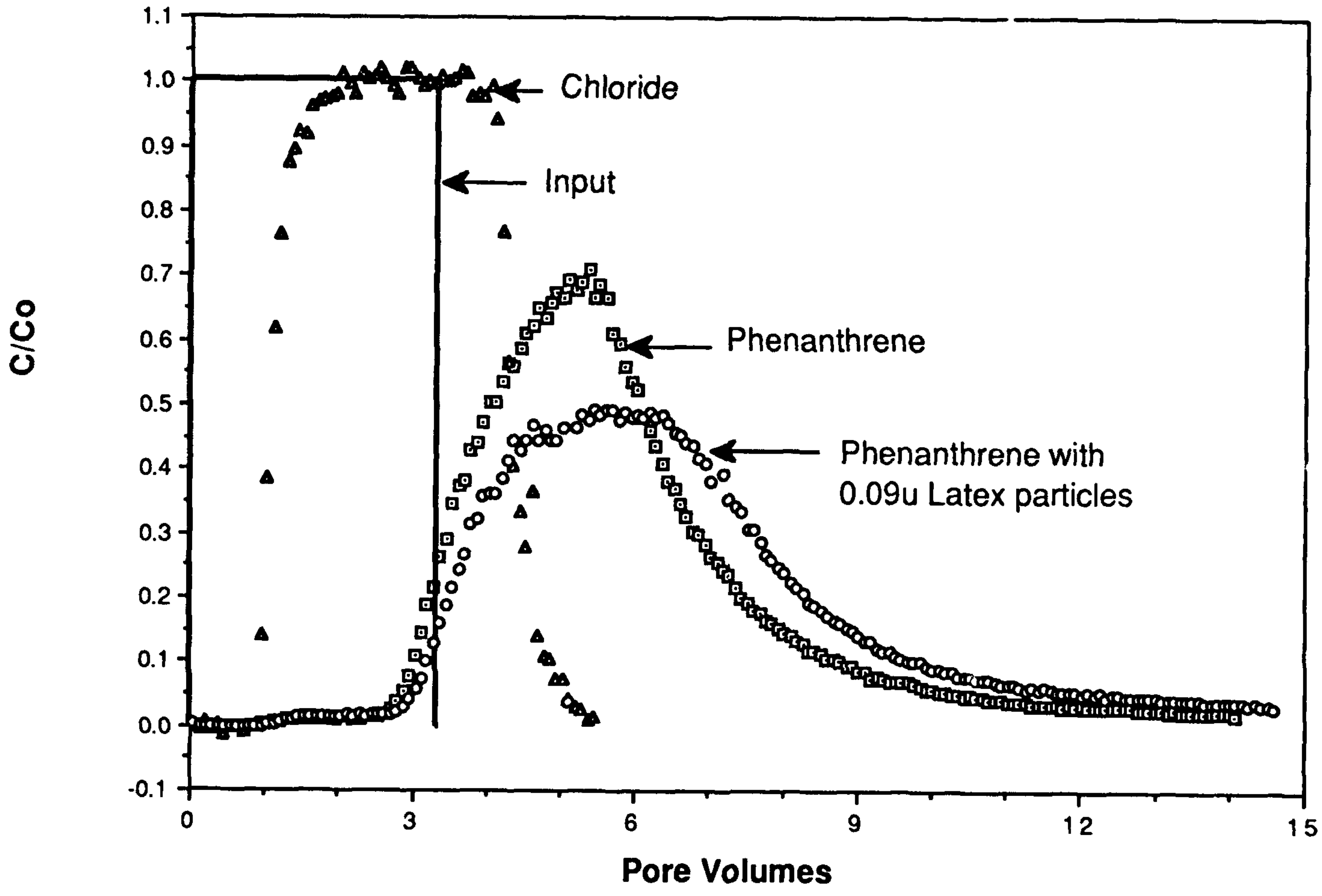


Figure 17. Phenanthrene Breakthrough Curve in the Presence and Absence of Latex® Microspheres

by centrifugation the suspended material is assumed to have been dissolved or colloidal Fe/Mn oxides, Fe and/or Mn bound to colloidal or dissolved organic matter, or colloidal clay minerals which were destabilized in the absence of a weak electrolyte. Formation of this colored suspension by the Columbus aquifer material illustrates the potential for changes in the soil solution composition to induce carriers.

The ability of the suspended colored material to act as a carrier was evaluated by carrying out parallel sorption experiments in deionized water vs the 0.005 M $CaSO_4$ plus 0.02 percent NaN_3 electrolyte. The isotherms are compared in Figure 18. It is clear that less phenanthrene is sorbed (as defined by the solid separation procedure) from the deionized water. This likely results from phenanthrene binding to the colloidal materials or dissolved macromolecules which were not removed by centrifugation. Comparable results have been previously reported and termed "solids effects" in which observed partition coefficients are reduced through the presence of colloidal solids or macromolecules (Reference 66, 67).

C. SUMMARY AND CONCLUSIONS

The results indicate that sorption behavior of hydrophobic PAH onto low carbon sorbents should not be assessed in the presence of competing hydrophobic materials such as PTFE septa or column parts. The weak sorption of low carbon aquifer materials necessitates experimental methods in which interferences are minimized.

Using the methods developed here, the sorption behavior of PAHs (as exemplified by phenanthrene) is seen to be driven by the organic content of the sorbent even at carbon contents below those commonly occurring in low carbon aquifer materials. Fractional carbon contents less than 0.001 are sufficient to dominate the partitioning of phenanthrene and are likely to result in kinetic hindrance of its movement in low carbon aquifers.

Breakthrough curves for phenanthrene in column studies reveal considerable tailing which is interpreted as evidence for slow sorption kinetics. Slow reaction kinetics were confirmed through batch experiments. The breakthrough of phenanthrene from columns can not be predicted based on equilibrium and kinetic parameters estimated from batch results. This may result, in part, from analytic limitations in the analysis of the long tails which occur in miscible displacement experiments.

Transport of phenanthrene in low-carbon aquifers can be retarded by the introduction of selected colloidal solids. This result is in contrast to the concept of facilitated transport, in which colloidal carriers are postulated to increase hydrophobic pollutant transport.

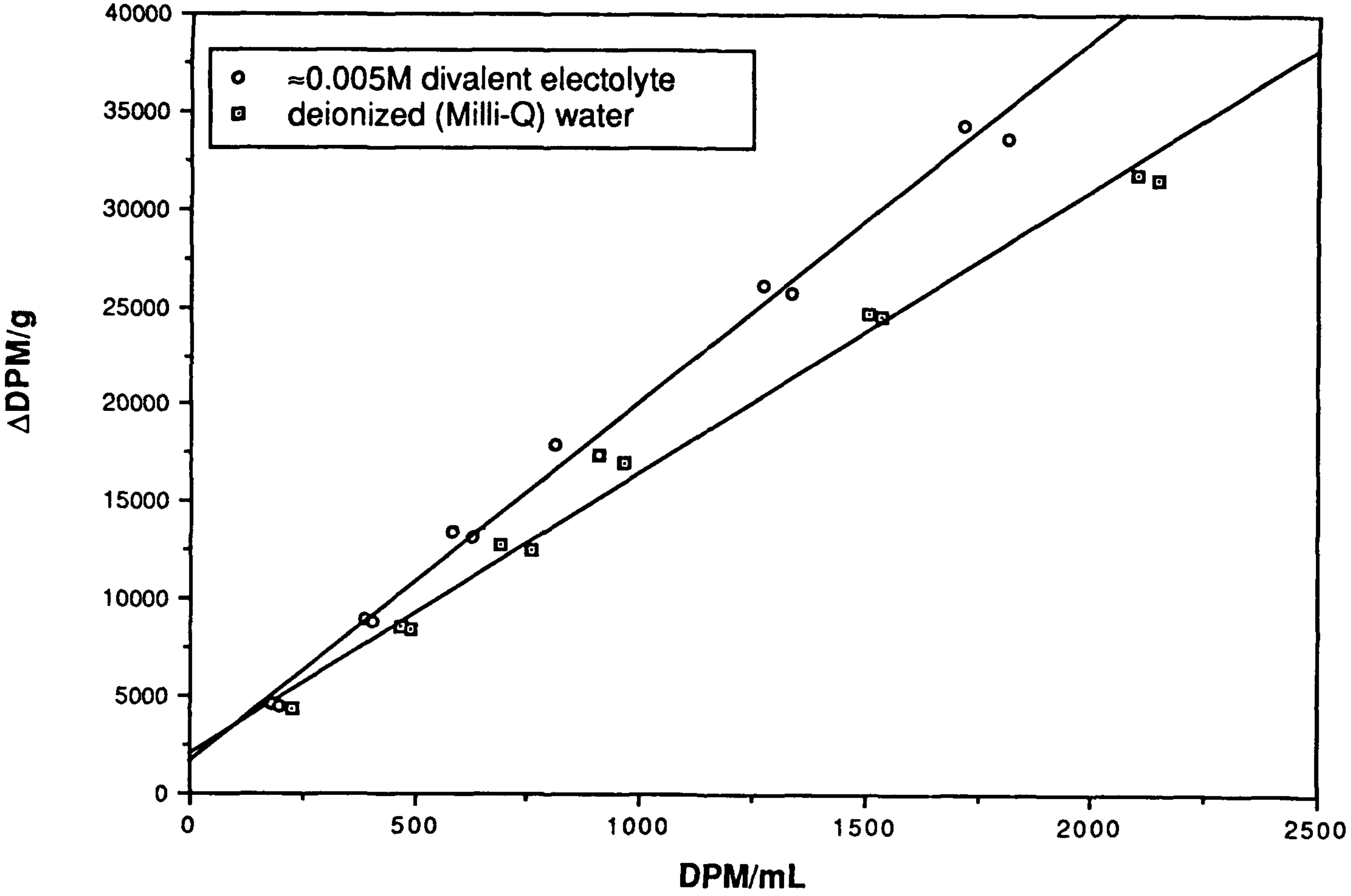


Figure 18. Phenanthrene Sorption Isotherms on Columbus Aquifer Material in the Presence and Absence of Colloids Induced by Deionized Water.

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