Environmental Toxicology and Chemistry, Vol 9, pp 253-263, 1990
Printed in the USA Pergamon Press plc

0730-7268/90 $3 00 + .00

Environmental Chemistry

GROUND WATER TRANSPORT OF HYDROPHOBIC ORGANIC COMPOUNDS IN THE PRESENCE OF DISSOLVED ORGANIC MATTER

AMY T. KAN* AND MASON B. TOMSON
National Center for Ground Water Research,
Department of Environmental Science and Engineering,
Rice University, Houston, Texas 77251

(*Received* 8 *November* 1988; *Accepted* 24 *May* 1989)

Abstract—The effects of dissolved organic matter (DOM) on the transport of hydrophobic organic compounds in soil columns were investigated. Three compounds (naphthalene, phenanthrene and DDT) that spanned three orders of magnitude in water solubility were used. Instead of humic matter, molecularly well-defined DOM represented by Triton X-100, a nonionic industrial detergent, and bovine serum albumin protein were used. In batch isotherm studies, the sorption of naphthalene to both model DOMs appeared to be hydrophobic in nature and quantitatively similar to the binding to humic materials. Equations were derived to model the enhanced transport of organic compounds by DOM based on octanol/water partition coefficients, K_{ow}. For a specific soil and DOM level, it was shown theoretically and experimentally that all organic compounds with K_{ow} values above a specific value should move at the same rate in ground water. In some situations, DOM can increase the movement of highly hydrophobic compounds, such as DDT, by a factor of a thousand or more. This enhanced transport in the presence of DOM can either be a problem, as with ground water contaminant spreading, or a benefit, as with contaminated aquifer cleanup.

Keywords—Facilitated transport Soil column Dissolved organic matter

INTRODUCTION

In recent years, the effect of naturally occurring dissolved colloidal materials on the fate of contaminants in the environment has attracted much attention. The significance of dissolved colloidal material to the fate of contaminants depends on the following factors: (a) the identity and concentration of dissolved colloidal matter; (b) the nature of the interaction between the contaminants and the dissolved colloidal matter; and (c) the mobility of the colloidal matter in an aquifer.

Dissolved humic and colloidal materials have been isolated from various aquatic sources [1-4]. Ground water typically contains a few mg/L dissolved organic matter, but the dissolved organic matter may reach a few hundred mg/L in surface water and in ground water near a dump site. Wershaw [5] has proposed a membrane or micellar double layer structure for humic materials wherein the thermodynamic affinity for contaminants is similar to that with surface active micelles.

The partitioning of neutral organic compounds into dissolved humic materials can enhance the apparent solubility of contaminants and reduce the apparent partition coefficient to the soil [2,6-15]. West [1] has reported that the sorption of hexachlorobenzene, bis(2-ethylhexyl)phthalate and DDT to dissolved humic materials isolated from pristine ground water to be of similar magnitude as the sorption of these contaminants to soil humate. Similar results were reported by Leo et al. [16] for the interaction of neutral organic compounds with numerous biological macromolecules. Baker et al. [4] evaluated the sorption of polychlorobiphenyls to sediments from Lake Superior and concluded that the apparent partition coefficient was inversely related to the suspended colloidal concentration.

The mobility of dissolved colloidal materials is more difficult to assess. Thurman et al. [17] observed the movement of alkyl benzene sulfonate (ABS, a surfactant) at a field site that had been previously polluted with surfactants and found that ABS moved at about the same rate as that for a conservative tracer. Gschwend and Reynolds [18]

---

*To whom correspondence may be addressed.

Although the research described in this article has been supported by the United States Environmental Protection Agency through assistance agreement No. CR-812808 to Rice University, it has not been subjected to Agency review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred.

detected mobile ferrous phosphate colloidal materials in ground water and suggested that contaminants associated with the colloidal materials will travel at the velocity of water. Enfield and Bengtsson [19] proposed that some of the dissolved organic matter might be excluded from small pore structure and move faster than water. Using ideas from chromatography theory discussed by Said [20], scientists at Rice University [1,9–10] proposed the concept of "facilitated transport" of neutral organic compounds by dissolved humic matter and derived the corresponding equations to predict contaminant transport in the presence of dissolved organic matter.

In this work the potential importance of dissolved organic matter (DOM) to the fate of organic contaminants is assessed using abiotic soil columns. For humic substances, DOM is generally proportional to dissolved organic carbon (DOC) by the relationship DOM = 1.724 DOC [21]. Model compounds were used as dissolved organic matter because ground water humic materials are not readily available and because commercial humic materials (e.g., Aldrich humic acid) may not be representative of soil or ground water humic materials [22]. Two surrogate materials, i.e., bovine serum albumin (BSA) protein and Triton X-100 surfactant, were used as models for natural dissolved organic matter because these materials are molecularly well defined and their physical chemical properties are well known, as opposed to natural humic materials. Both BSA and Triton X-100 have similar affinity (probably hydrophobic in origin) for small molecular weight neutral organic compounds as do naturally occurring ground water humic materials [5,16]. In addition, the use of surfactants in aquifer restoration has attracted much interest in the field and the following research may provide some mechanistic prediction for the effectiveness of Triton X-100 in mobilization of organic contaminants.

THEORY

The transport of contaminants in soil columns is generally modeled using a one-dimensional advective dispersion equation (ADE) [23]:

$$R(\partial C/\partial t) = D(\partial^2 C/\partial x^2) - v_w(\partial C/\partial x) \qquad (1)$$

with

$$R = 1 + (\rho_b/n) * (dq/dC), \qquad (2)$$

where C (μg/ml) represents contaminant concentration in the flowing water, t (s) is time, x (cm) is distance, D (cm^2/s) is the dispersion coefficient, v_w (cm/s) represents the linear velocity of the water, ρ_b (g/ml) is the solid bulk density, n is porosity and q (μg/g) is the amount of contaminant sorbed on the soil per gram of soil. R is called the "retardation factor." If the contaminant in the aqueous phase sorbs to aqueous DOC, then C in Equations 1 and 2 refers to the total contaminant concentration in solution, i.e., that bound to aqueous DOC (C_{DOC}) plus that free in solution (C_{free}):

$$C = C_{DOC} + C_{free}. \qquad (3)$$

The concentrations in Equation 3 are in units of μg contaminant per unit volume of water. q in equation 2 for the present research is assumed to be given by the following isotherm:

$$q = K_{soil} * (C_{free})^N. \qquad (4)$$

When $N = 1$, Equation 4 is called a linear isotherm, and when $N \neq 1$ Equation 4 is called a Freundlich isotherm. For most soil samples, N is found to be less than one. The significance of the constants in Equation 4 has been discussed by numerous authors [24–27]. To differentiate q in Equation 4 with respect to C, Equation 2, it is necessary to express C_{free} in terms of C. This can be done by using the contaminant/DOC partition coefficient, K_{DOC}, defined as follows [1,10]:

$$K_{DOC} = \frac{\mu\text{g compound-bound/g DOC}}{\mu\text{g compound-free/ml water}}, \qquad (5)$$

where g DOC refers to the mass of DOC in a milliliter of water. Combining Equations 3 and 5 for a corresponding volume of water, V_w, and simplifying, Equation 4 can be written explicitly in terms of C:

$$q = K_{soil} C^N/(1 + K_{DOC}\text{DOC})^N, \qquad (6)$$

where DOC is in units of g/ml. Using Equation 6 to calculate the slope in Equation 2, the retardation factor for DOC-facilitated transport becomes:

$$R = 1 + (\rho_b/n)(N)K_{soil} C^{(N-1)}/(1 + K_{DOC}\text{DOC})^N. \qquad (7a)$$

Note that when N in Equation 7a is equal to one, the retardation factor is simplified considerably:

$$R = 1 + (\rho_b/n)K_{soil}/(1 + K_{DOC}DOC). \qquad (7b)$$

In previous transport experiments [28], the sorption between naphthalene and the soil used in this study was determined to be best fitted by a Freundlich isotherm where the Freundlich isotherm constant $K_{soil} = 2.71$ and the exponent $N = 0.81$. The naphthalene/soil isotherm also includes an empirical linear proportionality factor to account for the effect of pH [28]:

$$K_{soil} = K_{soil,pH}(1 - 0.1\Delta pH), \qquad (8)$$

where $\Delta pH = pH - 7$. For natural ground water aquifers, the pH correction in Equation 8 is rarely greater than 20%. When $N = 1$, the partition coefficient K_{soil} in Equation 4 is generally found to be proportional to the soil organic carbon fraction, OC (wt/wt). A soil-independent partition coefficient, K_{oc}, is obtained by dividing K_{soil} by OC, the wt/wt fraction organic carbon in the soil [24].

$$K_{oc} = K_{soil}/OC. \qquad (9)$$

The driving force for partitioning to soil OC is assumed to be related to the hydrophobic effect and therefore proportional to the octanol/water partition coefficient of a compound. Karickhoff et al. [29] demonstrated that the K_{oc} in Equation 9 could be calculated from the octanol/water partition coefficient, K_{ow}:

$$K_{oc} = 0.63\ K_{ow}, \qquad r = 0.98 \qquad (10)$$

If the same proportionality holds for the partitioning of compounds to dissolved organic carbon, the K_{DOC} in Equation 5 becomes:

$$K_{DOC} = 0.63\ K_{ow}. \qquad (11)$$

The approximate validity of Equation 11 for naphthalene, phenanthrene and DDT will be demonstrated below.

MATERIALS AND METHODS

Chemicals and soil

Chemicals used in this research were reagent grade or better. Unlabeled naphthalene (98+% purity) and phenanthrene (98+%) were purchased from Aldrich Chemical Co. (Milwaukee, WI). Radiolabeled [^{14}C]naphthalene, -phenanthrene, and -DDT were purchased from Sigma Chemical Co. (St. Louis, MO) with specific activities of 4.7, 14 and 13.4 mCi/mmol, respectively. Radiolabeled compounds were >98% purity (Sigma Chemical Co., St. Louis, MO). Tritiated water was purchased from Amersham Co. (Arlington Hts., IL). A pseudocumene-based scintillation cocktail (Readysolv MP) was purchased from Beckman Instrument Co. (Fullerton, CA).

Bovine serum albumin (essentially globulin free; No. A7638) was purchased from Sigma Chemical Co. Triton X-100 (No. 23,472-9) was purchased from Aldrich Chemical Co. Triton X-100 is the trade name for octyl-phenyl polyoxyethylene ethers, $C_{14}H_{21}(OCH_2CH_2)_nOH$, where $n = 5$–15. Triton X-100 is a polydisperse nonionic surfactant with properties close to the homogeneous compound with $n = 10$. The critical micellar concentration of Triton X-100 is 207 mg/L [30]. The micelle typically has a molecular weight of 90,000 and an aggregate size of 139 monomers [31]. BSA is a small protein, M.W. = 69,000, and has water solubility of 5% (wt/wt) [32]. BSA contains 50% carbon and Triton X-100 contains 63% carbon.

Water used in this research was prepared by passing deionized water (Continental Water Co., Bedford, MA) through a Barnstead Ultrapure Mixed Bed Cartridge (Barnstead Co., Boston, MA; Part No. D8911) to remove silica and CO_2. The water was further purified with an Amberlite XAD-2 resin (Rohm & Haas Co., Philadelphia, PA) column to remove trace organic materials. The Amberlite XAD-2 resin was first purified according to the procedure of Thurman and Malcolm [3] and packed into a glass column (5.1 cm i.d. by 60 cm long, ACE Glass Inc., Vineland, NJ) to a depth of 38 cm. Water quality was monitored by UV spectrophotometry between 200 and 300 nm wavelength.

Unlabeled naphthalene stock solution (1,000 mg/L) was prepared in methanol. Upon receipt of the radiolabeled naphthalene, a stock solution of 0.1 mCi per 10 ml methanol was prepared. Appropriate amounts of unlabeled and labeled naphthalene stock solutions were mixed to yield a specific activity of 0.5 mCi/mmol naphthalene. Labeled and unlabeled phenanthrene stock solutions were prepared similarly with a specific activity of 1 mCi/mmol. Radiolabeled DDT stock solution in methanol was used without dilution with unlabeled DDT. The purity of naphthalene stock solution was monitored by gas chromatography with Flame Ionization Detector (FID) to assure that no autoradiolysis had occurred.

Surface soil (Lincoln fine sand) was obtained from R.S. Kerr Environmental Research Laboratory, Ada, Oklahoma. The soil contained 92% sand, 6% silt and 2% clay [33]. The soil was sieved through 10 mesh sieve and cheesecloth to remove vegetative matter and washed five times with an excess of 0.01 M $CaCl_2$ solution and air dried before determining the organic carbon content. Organic carbon content was found to be 0.26%, 0.26% and 0.28% in triplicate experiments using the LECO combustion method corrected for inorganic carbonates (Galbraith Laboratories, Inc., Knoxville, TN). Brunaeur, Emmett, Teller (BET) surface area was determined to be 1.24 m^2/g using nitrogen (Micromeritics Instrument Co., Norcross, GA).

Batch sorption isotherm

Sorption isotherms of naphthalene to BSA and Triton X-100 were evaluated using dialysis procedures similar to West, Carter and Suffet [1,2]. Triton X-100 at 2000 mg/L and BSA at 250 mg/L, 1,000 mg/L and 2,000 mg/L were pipetted into dialysis bags (Spectra/Por 6, 1,000 mol. wt. cutoff). The dialysis bags were sealed with cotton-coated polyester sewing thread and submerged in 125-ml Erlenmyer flasks, which contained naphthalene solutions with no headspace. The flasks were closed with ground-glass stoppers and sealed with Phynal grease (Reliance Glass Works Inc., Bensenville, IL), a hydrophilic grease that does not sorb hydrophobic compounds [1]. The solutions were constantly mixed with a glass-covered magnetic stirrer at 20°C for 4 d and concentrations inside and outside of the bag were quantitated via scintillation counting. UV absorbance at 280 and 275 nm were used to quantitate BSA and Triton X-100 concentrations, respectively. At 1 g/L the optical absorbance of BSA is 0.667 [34,35] and of Triton X-100, 2.221. The mass balance of naphthalene for the dialysis experiments was 99 ± 3%.

Soil column

Sieved soil was air dried and packed into a borosilicate precision glass column (0.9 cm i.d., Spectrum, Inc.) to a depth of about 15 cm. The soil column was wetted with 0.01 M $CaCl_2$ solution at 20 μl/min for 7 d. The column end fitting had a 10-μm membrane to retain soil particles. Each new soil column was flushed with 200 ml 0.01 M $CaCl_2$ solution to stabilize the column. Formaldehyde, CH_2O, was added to the solution at 0.01 M concentration to control microbial growth. Formaldehyde at this concentration (1.8×10^{-4} mole fraction) should not affect the solubility properties of water [36]. A Sage extended-range, multichannel infusion pump (Cole Parmer Instrument Co., Chicago, IL) was used to deliver the aqueous solution. Chemicals in the effluent were detected by scintillation counting of the [^{14}C] tracer (Beckman, LS3801 scintillation counter). Two columns were used in this research: Column A was used for Triton X-100 experiments and Column B was used for BSA experiments with pH adjusted to 9. The porosities are 0.400 and 0.418 for column A and B, respectively, determined by tritiated-water breakthrough method. These values are consistent with the porosity values of similar soil columns reported previously [28].

Soil column breakthrough experiments

For most transport studies, the feed solution contained 0.01 M $CaCl_2$ and 0.01 M CH_2O. For transport studies involving BSA, the above solution was adjusted to pH 9.0 with 0.02 M borax to increase the negative charge of BSA and reduce the interaction of BSA with soil (isoelectric point of BSA = 4.7 pH). Pore volume was determined from the retention volume of tritiated water. Organic contaminants were diluted in methanol and spiked into the feed solution at a ratio of less than 1:500. Methanol at this concentration ($<0.2\%$) would only increase the solubility of organic compounds in water by about 1% or less, which should be negligible for purposes of this study. For this study, initial total concentrations were 2 mg/L naphthalene, 0.5 mg/L phenanthrene and 0.05 mg/L DDT.

Most experiments were performed in a 20°C constant-temperature room. In a typical experiment, the feed solution was pumped into the soil column via a Sage syringe pump at a flow rate of 19 μl/min to yield a pore velocity of 4.3 cm/h. Back pressure of the column was typically 1 psig measured with a pressure transducer (Omega Engineering Co., Stamford, CT; Part No. PX236-0606V). Fractions of the column effluent were collected in vials containing 10 ml Beckman MP scintillation cocktail, which helped trap the volatile organic compounds.

A total of 11 breakthrough experiments were run with naphthalene, phenanthrene and DDT in the presence of BSA and Triton X-100. Naphthalene breakthroughs were run at both unbuffered solution pH (5 ± 0.2 pH) and pH 9. Two Triton X-100 (457 and 1,882 mg/L) and two BSA (250 and 2,000 mg/L) concentrations were used with naphthalene experiments to evaluate the transport of naphthalene in the presence of dissolved organic matter. Three phenanthrene breakthrough experiments were evaluated in the presence of 0 and 2,000 mg/L Triton X-100 and 2,000 mg/L BSA. DDT breakthroughs were measured in the presence of 1,000 and 2,000 mg/L of Triton X-100 and BSA, respectively.

Breakthrough data simulation

Concentration versus time breakthrough data were simulated using both analytical and numerical solutions via the ADE, Equation 1. All parameters were determined using nonlinear least-squares procedures and reported intervals were as 95% confidence intervals. A finite difference transport model was used [37]. The size of the time steps and nodes were first determined by testing a set of theoretical breakthrough curves created with the analytical solution to insure that the procedure converged accurately. A maximum of 3,000 to 4,000 time steps and 60 nodes was found to be more than adequate. For naphthalene experiments, average ΔT was $9 \times 10^{-3} \pm 1 \times 10^{-3}$ h.

To account for the sorption of Triton X-100 on soil, the time steps were adjusted explicitly for each data set to allow Triton X-100 to saturate one node within an integer number of time steps (generally within five time steps). It was shown that the input of Triton X-100 can be assumed to be a step function by ignoring the apparatus dispersion effect [28].

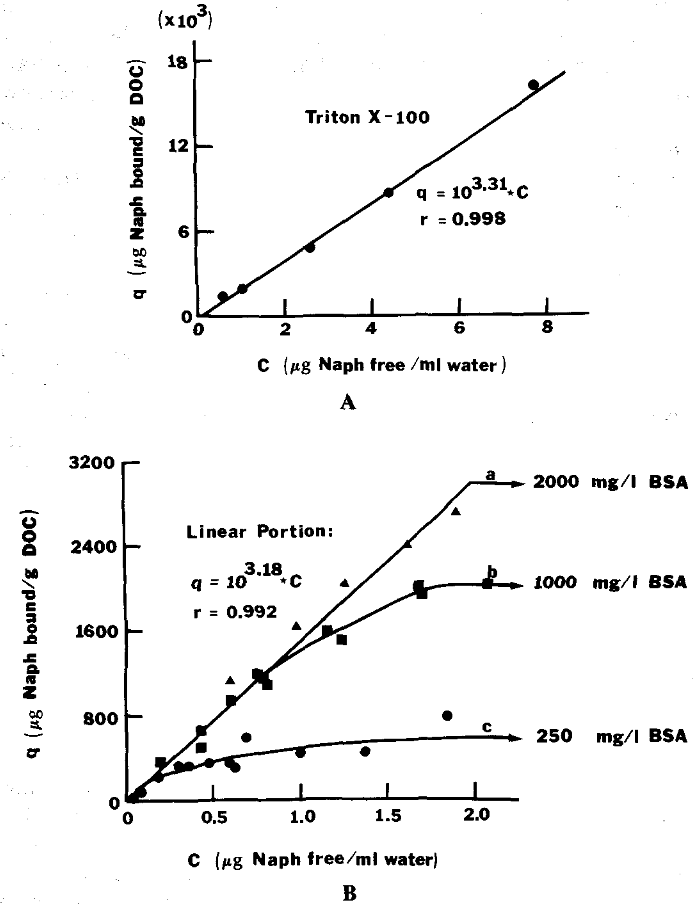

Fig. 1. Sorption isotherms of naphthalene with Triton X-100 (A) and BSA (B). BSA was evaluated at (a) 2,000, (b) 1,000 and (c) 250 mg/L. X axis is µg naphthalene-free/ml water and Y axis is µg naphthalene-bound/g dissolved organic carbon.

For naphthalene adsorption to the soil phase a Freundlich isotherm was assumed, Equation 4. Because of limited data, a linear isotherm was assumed for phenanthrene and DDT transport ($N = 1$ in Equation 4). Linear isotherms were assumed for naphthalene, phenanthrene and DDT with dissolved organic matter, Equation 5. The breakthrough curves were also simulated with the analytical solution of a one-dimensional convective dispersion equation assuming local equilibrium and linear isotherms [38].

RESULTS AND DISCUSSIONS

Batch sorption isotherms

Figure 1 presents the sorption isotherms of naphthalene to BSA and to Triton X-100 using the batch dialysis procedure. There was 53 ± 9 mg/L Triton X-100 outside the dialysis bag equilibrating with 1,230 mg/L Triton X-100 inside the bag. The Triton X-100 on the outside was assumed to be monomer Triton X-100 since the critical micelle concentration (CMC) is 207 mg/L. The Triton X-100 monomer does not enhance the solubility of contaminants [39]. Therefore, the isotherm was determined based on 1,177 (1,230 – 53) mg/L micellar Triton X-100. Using a linear isotherm, the sorption isotherm of naphthalene with Triton X-100 (Fig. 1A) was best fitted with $K_{DOC} = 10^{3.31}$ ($r = 0.998$, $n = 5$) where K_{DOC} is the dissolved organic carbon-based partition coefficient, Equation 5.

Figure 1B presents the sorption isotherms of naphthalene to BSA at three BSA concentrations (250, 1,000 and 2,000 mg/L). In the 2,000 mg/L BSA solution, the sorption is linear between 0 and 2 mg/L naphthalene (Fig. 1B, curve a). For the 1,000 mg/L BSA solution, the sorption is linear between 0 and 0.8 mg/L naphthalene (Fig. 1B, curve b). In 250 mg/L BSA solution, the sorption is linear between 0 and 0.20 mg/L naphthalene (Fig. 1B, curve c). The linear portions of the isotherms at the three BSA concentrations have the same slope. The lower two sets of data in Figure 1B, curves b and c, deviate from linearity at about the same ratio of naphthalene to BSA. This might suggest a saturation phenomenon, which has not been investigated further. When the linear portions of the three curves were fitted with a linear isotherm, Equation 5, the slope was $K_{DOC} = 10^{3.18}$($r = 0.992$).

Sorption of small organic chemicals by BSA has been reported by numerous authors where the BSA concentrations have typically been greater than 0.2% [40–42]. Helmer et al. [40] studied the sorption of naphthalene with BSA. When the data of Helmer et al. [40] is expressed in terms of DOC, a partition coefficient, $K_{DOC} = 10^{3.38}$, at pH 7 is obtained. Helmer's value is slightly higher than the experimental values of this study, $10^{3.18}$. The difference may be caused by the difference in sorption at pH 7 and 9 (see Equation 8).

Movement of BSA and Triton X-100 in soil columns

The mobilities of BSA and Triton X-100 in soil columns were studied. The soil column breakthroughs of Triton X-100 at 150 and 2,000 mg/L were measured. The differences between the breakthroughs of Triton X-100 and the water front correspond to the amount of Triton X-100 sorbed onto the soil. The amount of Triton X-100 needed to saturate the soil column was 0.26 and 0.28 mg/g soil at 150 and 2,000 mg/L Triton X-100, respectively. The hydrophobic partition coefficient of Triton X-100 is very low (octane-based $K = 0.257$ [16]), from which it can be shown that the sorption of Triton X-100 to soil is not caused by hydrophobic interaction.

Assuming that each Triton X-100 molecule occupies about 2 nm^2 of surface area, adsorption of 0.3 mg/g would correspond to a soil-specific surface area of 0.6 m^2/g. BET surface area of this soil was 1.24 m^2/g (Micromeritics Instrument Co.). The difference in the surface areas may be a consequence of the smaller N_2 molecule being able to penetrate into smaller pores. Triton X-100 probably coats the soil with a monomolecular coverage before it migrates at the water velocity. The amount of Triton X-100 sorbed to the soil only increases the soil organic carbon content by about 6%. The sorption capacity of the soil should not be affected significantly by this amount of added organic carbon.

It was shown that 0.018 mg BSA is adsorbed per gram soil at pH 9 by comparing the breakthrough of 250 mg/L BSA with that of tritiated water. This soil demand is considerably less than that for Triton X-100 and was ignored in the BSA breakthrough simulations. When 2,000 mg/L BSA was flowed through the column, the 0.018 mg/g adsorption was negligible, but the BSA moved through the column 1.16 times faster than water. This suggests that BSA is excluded from 16% of the pore volume. A similar size exclusion effect was observed by Enfield and Bengtsson [19] with blue dextran. This 16% pore volume exclusion was taken into account when the BSA-facilitated transport experiments were modeled in the next section.

Contaminant transport in the presence of dissolved organic matter

The typical breakthrough curves of naphthalene in the presence and absence of BSA and Triton X-100 are shown in Figure 2. The breakthrough of naphthalene is enhanced to almost 50% in the presence of 2,000 mg/L BSA or Triton X-100. Since the column breakthrough experiments are highly reproducible, the observed enhancement of naphthalene breakthrough cannot be the result of column channeling. Table 1 lists the simulation results of 11 column breakthrough data sets of contaminants in the presence and absence of BSA and Triton X-100. Retardation and dispersion values listed in Table 1 were obtained using the analytical solution of the one-dimensional advective dispersive equation assuming linear isotherm, Equation 7b. This analytical solution is commonly used in ground water modeling and is a good first approximation of the relative retardation factors. The simulated results are compared to the calculated retardation factors of naphthalene, phenanthrene and DDT. The retardation factor of naphthalene is calculated using the batch sorption data via Equation 7b. The retardation factors of phenanthrene and DDT are calculated from K_{ow} via Equations 7b, 10 and 11 since the corresponding batch sorption data for phenanthrene and DDT are not available. The sorption of phenanthrene and DDT on BSA or Triton X-100 probably follows similar proportionality as suggested by Equations 10 and 11 if the sorption is hydrophobic in nature. The overall good agreement of the experimental data with the predictions of Equation 7b is apparent for R_{exp} and R_{calc} in Table 1.

Examining the data in column 7 of Table 1, it is seen that the transport of naphthalene in the presence of 1,882 mg/L Triton X-100 or 2,000 mg/L BSA is over twice as fast as the transport in the absence of dissolved organic matter. The transport of phenanthrene in the presence of 2,000 mg/L Triton X-100 or BSA is more than 26 times faster than that in the absence of dissolved organic matter. The transport of DDT in the presence of 1,000 mg/L Triton X-100 or 2,000 mg/L BSA is

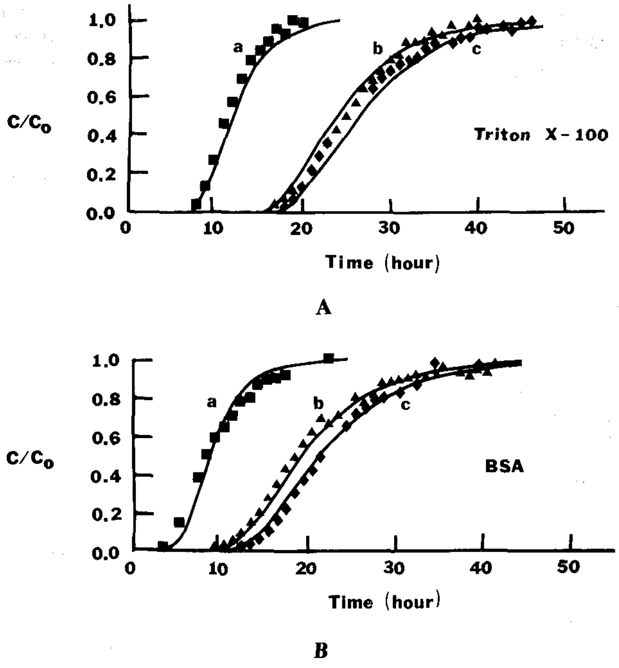

Fig. 2. Facilitated transport of naphthalene in the presences of Triton X-100 and BSA. Fig. **2A**: (a) 1,887, (b) 457 and (c) 0 mg/L Triton X-100. Fig. **2B**: (a) 2,000, (b) 250 and (c) 0 mg/L BSA. The points are experimentally observed concentration and the solid curves were drawn using the simulated breakthrough results via Equation 7a of the text. The constants of Equation 7a are listed in columns 2 and 3 of Table 2, with $N = 0.81$.

Table 1. Breakthrough of naphthalene (2 mg/L), phenanthrene (0.5 mg/L) and DDT (0.05 mg/L) in the presence of Triton X-100 and BSA

No.	Contaminants	Dissolved organic matter	DOM[a] conc (mg/L)	Velocity (cm/h)	pH	R_{exp}	R_{calc}[b]	D (cm^2/h)	r
1.	Naphthalene	None	0	4.339	(5)[c]	7.35 ± 0.08	8.5	2.4 ± 0.2	0.999
2.	Naphthalene	Triton X-100	457	4.292	(5)	6.95 ± 0.04	6.7	1.8 ± 0.1	0.999
3.	Naphthalene	Triton X-100	1,882	4.198	(5)	3.17 ± 0.03	3.4	2.0 ± 0.2	0.999
4.	Naphthalene	None	0	4.238	9	5.93 ± 0.13	8.5	2.9 ± 0.6	0.995
5.	Naphthalene	BSA	250	4.009	9	5.31 ± 0.12	7.3	5.1 ± 0.9	0.994
6.	Naphthalene	BSA	2,000	4.966	9	3.06 ± 0.04	4.0	9.4 ± 0.8	0.999
7.	Phenanthrene	None	0	4.386	(5)	234.23 ± 7.11	249.4	5.5 ± 1.3	0.999
8.	Phenanthrene	Triton X-100	2,000	4.480	(5)	7.88 ± 0.11	9.1	6.1 ± 0.7	0.998
9.	Phenanthrene	BSA	2,000	4.867	9	9.50 ± 0.30	10.5	9.3 ± 1.9	0.994
10.	DDT	None	–	–	–	–	15,315.0	–	–
11.	DDT	Triton X-100	1,000	4.433	(5)	9.56 ± 0.10	17.8	5.4 ± 0.5	0.998
12.	DDT	BSA	2,000	4.402	9	12.11 ± 0.27	10.8	10.0 ± 1.3	0.996

Data simulated with the analytical solution of 1-D advective dispersion equation assuming local equilibrium and linear isotherm.

[a] DOC in Equations 6 and 7 is DOM times 0.63 for Triton X-100 and 0.50 for BSA.

[b] R_{calc} for naphthalene was calculated from Equation 7b using K_{DOC} slopes in Fig. 1 and previously measured soil K_{oc} of 708 [28]. For phenanthrene and DDT, Equations 10 and 11 were used to calculate K_{oc} and K_{DOC}, respectively. The values of K_{ow} for DDT ($10^{6.36}$) and phenanthrene ($10^{4.57}$) were obtained from Carter and Suffet [2] and Karickhoff et al. [24], respectively.

[c] Numbers in parentheses are approximate pH in that no buffer was added.

over 1,000 times faster than would be estimated based upon the $K_{oc} = 0.63 * K_{ow}$ value (Eqn. 10) for DDT and neglecting facilitated transport ($R_{calc.} = 10^{4.19}$, calculated from Eqn. 7 with DOC = 0, N = 1, and $K_{ow} = 10^{6.36}$ for the same soil column).

Naphthalene breakthrough data at 0, 457 and 1,882 mg/L Triton X-100 were modeled simultaneously (Table 2). A Freundlich model was used for the sorption of naphthalene to the soil. Previous studies had shown that for a Freundlich model, $N = 0.81$ yielded the best fit to the sorption of several hydrophobic compounds to soil [27–28]. For naphthalene with the Freundlich model, only the values of K_{soil} and K_{DOC} in Equation 7a were allowed to vary in the least-squares procedures. The corresponding naphthalene breakthrough data with 0, 250 and 2,000 mg/L BSA is also presented in Table 2. The correlation coefficients of the two sets of data where three breakthrough curves were fitted simultaneously were only slightly less than that in Table 1, where the breakthrough curves were fitted individually. The least-squares-calculated K_{DOC} values for naphthalene sorption to Triton X-100 and BSA are $10^{3.53}$ and $10^{3.26}$, respectively, which compare reasonably well with the batch experiment data (Fig. 1, $10^{3.31}$ and $10^{3.18}$). The differences may be due to the differences in data interpretation between the batch and flow-through experiments.

Table 2. Breakthrough of naphthalene in the presence of Triton X-100 and BSA

Dissolved organic matter (DOM)	Triton X-100[a]	BSA[b]
Contaminant/soil sorption isotherm	Freundlich	Freundlich
Contaminant/DOM sorption isotherm	Linear	Linear
K_{soil}	2.14	2.72
K_{oc}[c]	$10^{2.90}$	$10^{3.00}$
K_{DOC}	$10^{3.53}$	$10^{3.26}$
K_{oc}^{cal}[d]	$10^{3.17}$	$10^{3.17}$
D (cm^2/h)	4.5	9.2
r	0.997	0.993

Data simulated by Equation 7a using a finite difference procedure and a Freundlich isotherm for the sorption of naphthalene to the soil, assuming $N = 0.81$. Only the values of K_{soil} and K_{DOC} in Equation 7a were allowed to vary in the least-squares procedures.

[a] Data of experiments 1–3 (Table 1) simulated via Equation 7a with $N = 0.81$.

[b] Data of experiments 4–6 (Table 1) simulated via Equation 7a with $N = 0.81$.

[c] Calculated from Equation 9 ($K_{oc} = K_{soil}$/OC). These values are included for comparison to the theoretical K_{oc} values.

[d] Theoretical K_{oc} and K_{DOC} values calculated from Equations 10 and 11: $K_{oc}^{cal} = K_{DOC}^{cal} = 0.63K_{ow}$ with naphthalene $K_{ow} = 10^{3.37}$ [16].

Using the relationship $K_{DOC} = 0.63 * K_{ow}$, the naphthalene K_{DOC} is calculated to be 10^3 [17]. The higher than expected least-squares-calculated K_{DOC} values may reflect a real affinity difference between DOC and soil OC, or it may be a numerical consequence of using a Freundlich isotherm for the soil.

The results in Table 2 indicate that the facilitated transport equation reported by West [1], Hutchins et al. [43], and Enfield [44] can model the transport of contaminants in the presence of dissolved organic matter. Ignoring the effect of pH and concentration generally yields an error in the calculated retardation factor of less than one order of magnitude [20,28], but ignoring the effect of dissolved organic matter may result in an error of several orders of magnitude for very insoluble contaminants. The sorption coefficients for both the soil and dissolved macromolecules can be predicted within a factor of 2.5 by K_{ow} values using the relationships developed by Karickhoff et al. [29].

A further consequence of facilitated transport can be developed using a linear isotherm, for simplicity, by substituting Equations 9, 10 and 11 into Equation 7b to calculate the retardation factor:

$$R = 1 + \frac{0.63\ K_{ow}\ \mathrm{OC}\ \rho_b/n}{1 + 0.63\ K_{ow}\ \mathrm{DOC}}. \tag{12}$$

For either highly hydrophobic compounds (i.e., large K_{ow}) or high DOC water, a relatively negligible fraction of the compound will be free in the water and the following inequality will hold:

$$0.63\ K_{ow}\ \mathrm{DOC} \gg 1 \tag{13}$$

or

$$R = 1 + (\rho_b/n)\ (\mathrm{OC/DOC}). \tag{14}$$

Equation 14 is independent of K_{ow} and suggests that for any given soil and DOC all compounds with K_{ow} values larger than some cutoff value will move in an aquifer with the same average velocity relative to water. This theory is supported by the experimental results of phenanthrene and DDT breakthroughs in the presence of 2,000 mg/L BSA (Table 2). In Figure 3, several constant DOC isopleths are plotted for log R vs. log K_{ow} using Equation 12 with OC = 0.27%. Figure 3 shows that facilitated transport has little effect with more soluble contaminants such as benzene, toluene and xylene ($K_{ow} < 10^3$), which concurs with the finding of two API reports [45–46], while it has significant consequences to the movement of PCBs ($K_{ow} > 10^5$) as reported by Ellis et al. [47].

In conclusion, this study demonstrates the enhanced or facilitated transport of organic com-

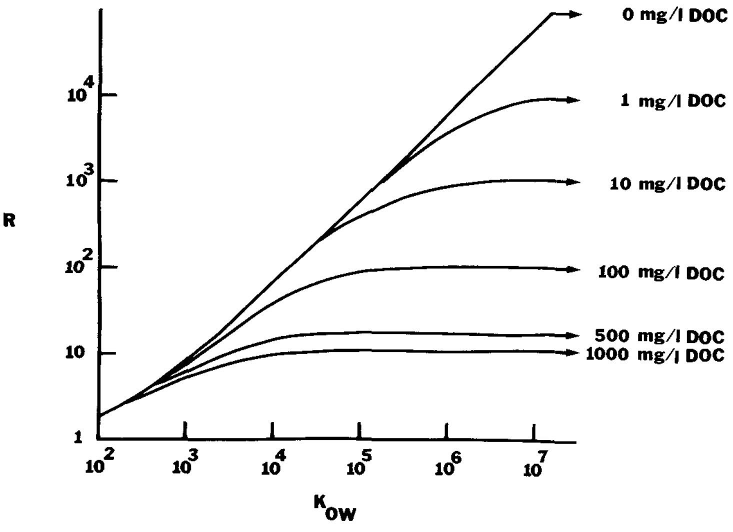

Fig. 3. Plot of the logarithm of relative retardation tactor (R) vs. the logarithm of the octanol/water partition coefficient (K_{ow}) at DOC concentrations from 0 to 1,000 mg/L. The curves were drawn using Equation 7b of the text, $R = 1 + \{0.63K_{ow}\mathrm{OC}\ \rho_b/n\}/\{1 + 0.63K_{ow}\mathrm{DOC}\}$ with OC = 0.0027, $\rho_b = 1.572$ and $n = 0.4$.

pounds under the influences of dissolved macro molecules and micelles Both BSA and Triton X-100 micelles enhance the transport of the less soluble organic contaminants (e.g , $K_{ow} > 10^{3.5}$ for this soil) All less soluble organic contaminants (e.g., $K_{ow} > 10^{4.5}$) are likely to travel at the same velocity in this soil when the dissolved organic carbon content is greater than 100 mg/L.

Acknowledgement—We thank Drs J C Parker and J B Kool for providing most of the numerical codes used for this report and for their valuable advice on numerical analyses of breakthrough data

REFERENCES

1 **West, C.C.** 1984 Dissolved organic carbon facilitated transport of neutral organic compounds in subsurface systems Ph D thesis Rice University, Houston, TX

2 **Carter, C.W.** and **I.H. Suffet.** 1982 Binding of DDT to dissolved humic materials *Environ Sci Technol* **16** 735–740

3 **Thurman, E.M.** and **R.L. Malcolm.** 1981 Preparative isolation of aquatic humic substances *Environ Sci Technol* **15** 463–466

4 **Baker, J.E., P.D. Capel** and **S.J. Eisenreich.** 1986 Influence of colloids on sediment-water partition coefficients of polychlorobiphenyl congeners in natural waters *Environ Sci Technol* **20** 1136–1143

5 **Wershaw, R.L.** 1986 A new model for humic materials and their interactions with hydrophobic organic chemicals in soil-water or sediment-water systems *J Contam Hydrol* **1** 29–45

6 **Wershaw, R.L., P.J. Burcar** and **M.C. Goldberg.** 1969 Interaction of pesticides with natural organic material *Environ Sci Technol* **3** 271–273

7 **Pirrier, M.A., B.R. Bordelon** and **J.L. Laseter.** 1972 Adsorption and concentration of dissolved carbon 14 DDT by coloring colloids in surface H_2O *Environ Sci Technol* **6** 1033–1035

8 **Tanford, C.** 1973 *The Hydrophobic Effect* Wiley-Interscience, New York, NY

9 **Cook-West, C.J.** and **M.B. Tomson.** 1981 Total organic carbon facilitated transport of trace organics in subsurface systems Annual Report National Center for Ground Water Research, Rice University, Houston, TX

10 **Cook-West, C.J., M.B. Tomson** and **G.G. Waggett.** 1982 Total organic carbon facilitated transport of trace organics in subsurface systems Annual Report National Center for Ground Water Research, Rice University, Houston, TX

11 **Landrum, P.F., S.R. Nihart, B.J. Eadle** and **W.S. Gardner.** 1984 Reverse phase separation method for determining pollutant binding to Aldrich humic acid and dissolved organic carbon of natural waters *Environ Sci Technol* **18** 187–192

12 **McCarthy, J.F.** and **B.D. Jimenez.** 1985 Interaction between polycyclic aromatic hydrocarbons and dissolved humic material Binding and dissociation *Environ Sci Technol* **19** 1072–1076

13 **Hassett, J.P.** and **E. Milicic.** 1985 Determination of equilibrium and rate constants for binding of a polychlorinated biphenyl congener by dissolved humic substances *Environ Sci Technol* **19** 638–643

14 **Chiou, C.T., R.L. Malcolm, T.I. Brinton** and **D.E. Kile.** 1986 Water solubility enhancement of some organic pollutants and pesticides by dissolved humic and fulvic acids *Environ Sci Technol* **20** 502–508

15 **Gauthier, T.D., W.R. Seitz** and **C.L. Grant.** 1987 Effects of structural and compositional variations of dissolved humic materials on pyrene K_{OC} values *Environ Sci Technol* **21** 243–252

16 **Leo, A., C. Hansch** and **D. Elkins.** 1971 Partition coefficients and their uses *Chem Rev* **71** 525–616

17 **Thurman, E.M., L.B. Barber Jr.** and **D. LeBlanc.** 1986 Movement and fate of detergents in groundwater A field study *J Contam Hydrol* **1** 143–161

18 **Gschwend, P.M.** and **M.D. Reynolds.** 1987 Monodisperse ferrous phosphate colloids in an anoxic groundwater plume *J Contam Hydrol* **1** 309–327

19 **Enfield, C.G.** and **G. Bengtsson.** 1988 Macromolecular transport of hydrophobic contaminants in aqueous environments *Ground Water* **26** 64–70

20 **Said, A.S.** 1981 *Theory and Mathematics of Chromatography* A H Verlag, New York, NY

21 **Lyman, W.J., W.F. Reehl** and **D.H. Rosenblatt.** 1982 *Handbook of Chemical Property Estimation Methods* McGraw-Hill, New York, NY

22 **Malcolm, R.L.** and **P. MacCarthy.** 1986 Limitations in the use of commercial humic acids in water and soil research *Environ Sci Technol* **20** 904–911

23 **Bear, J.** 1979 *Hydraulics of Groundwater* McGraw-Hill, New York, NY

24 **Hamaker, J.W.** and **T.M. Thompson.** 1972 Adsorption In C A Goring and J W Hamaker, eds , *Organic Chemicals in the Soil Environment* Marcel Dekker, New York, NY, pp 49–143

25 **Rao, P.S.C.** and **J.M. Davidson.** 1983 Estimation of pesticide retention and transformation parameters required in nonpoint source pollution models In M R Overcash and J M Davidson, eds , *Environmental Impact of Nonpoint Source Pollution* Ann Arbor Scientific Publication, Ann Arbor, MI, pp 23–64

26 **Miller, C.T.** and **W.J. Weber Jr.** 1988 Modeling the sorption of hydrophobic contaminants by aquifer materials—II Column reactor systems *Water Res* **22** 465–474

27 **Weber, W.J. Jr.** and **C.T. Miller.** 1988 Modeling the sorption of hydrophobic contaminants by aquifer materials—I Rates and equilibria *Water Res* **22** 457–464

28 **Kan, A.T.** and **M.B. Tomson.** 1989 Effect of pH and concentration on transport of naphthalene in saturated aquifer media *J Contam Hydrol* **3** (in press)

29 **Karickhoff, S.W., D.S. Brown** and **T.A. Scott.** 1979 Sorption of hydrophobic pollutants on natural sediments *Water Res* **13** 241–248

30 **Mukerjee, P.** and **K.J. Mysels.** 1970 *Critical Micelle Concentrations of Aqueous Surfactant Solutions* National Bureau of Standards, Washington, DC

31 **Becher, P.** 1966 Micelle formation in aqueous and nonaqueous solutions In M J Schick, ed , *Nonionic Surfactants* Marcel Dekker, New York, NY, pp 478–513

32 **Haurowitz, F.** 1963 *The Chemistry and Function of Proteins* Academic Press, New York, NY

33 **Wilson, J.T., C.G. Enfield, W.J. Dunlap, R.L.**

Cosby, D.A. Foster and **L.B. Baskin.** 1981. Transport and fate of selected organic pollutants in a sandy soil. *J. Environ. Qual.* **10**:501–506.

34. **Cohn, E.J., W.L. Hughes Jr.** and **J.H. Weare.** 1947. Preparation and properties of serum and plasma proteins. XIII. Crystallization of serum albumins from ethanol-water mixtures. *J. Am. Chem. Soc.* **69**: 1753–1766.
35. **Janatova, J., J.K. Fuller** and **M.J. Hunter.** 1968. The heterogeneity of bovine albumin with respect to sulfhydryl and dimer content. *J. Biol. Chem.* **243**: 3612–3615.
36. **Nkedi-Kizza, P., P.S.C. Rao** and **A.G. Hornsby.** 1985. Influence of organic cosolvents on sorption of hydrophobic organic chemicals by soils. *Environ. Sci. Technol.* **19**:975–979.
37. **Kool, J.B., J.C. Parker** and **L.W. Zelazny.** 1989. Determination of cation exchange parameters from column displacement experiments. *Soil Sci. Soc. Am. J.* **53**:1347–1355.
38. **Parker, J.C.** and **M.Th. van Genuchten.** 1984. Determining transport parameters from laboratory and field tracer experiments. Bulletin 84-3. Virginia Agricultural Experiment Station, Virginia Polytechnic Institute and State University, Blacksburg, VA.
39. **Nakagawa, T.** 1966. Solubilization. In M.J. Schick, ed., *Nonionic Surfactants.* Marcel Dekker, New York, NY, pp. 558–603.
40. **Helmer, F., K. Kiehs** and **C. Hansch.** 1968. The linear free-energy relationship beteween partition coefficients and the binding and conformational perturbation of macromolecules by small organic compounds. *Biochemistry* **7**:2858–2863.
41. **Beyeler, M.** and **J. Solms.** 1974. Interaction of flavor model compounds with soy protein and bovine serum albumin. *Lebensmittel-Wissenschaft Technologie* **7**:217–219.
42. **Damodaran, S.** and **J.E. Kinsella.** 1980. Flavor protein interactions. Binding of carbonyls to bovine serum albumin: Thermodynamic and conformational effect. *J. Agric. Food Chem.* **28**:567–571.
43. **Hutchins, S.R., M.B. Tomson, P.B. Bedient** and **C.H. Ward.** 1985. Fate of trace organics during land application of municipal wastewater. *CRC Crit. Rev. Environ. Control* **15**:355–416.
44. **Enfield, C.G.** 1985. Chemical transport facilitated by multiphase flow systems. *Water Sci. Technol.* **17**: 1–12.
45. **American Petroleum Institute.** 1979. Underground movement of gasoline on groundwater and enhanced recovery by surfactants. Publication No. 4317. American Petroleum Institute, Washington, DC.
46. **American Petroleum Institute.** 1985. Test results of surfactant enhanced gasoline recovery in a large scale model aquifer. Publication No. 4390. American Petroleum Institute, Washington, DC.
47. **Ellis, W.D., J.R. Payne** and **G.D. McNabb.** 1985. Treatment of contaminanted soils with aqueous surfactants. EPA/600/2-85/129. U.S. Environmental Protection Agency, Cincinnati, OH.