Characteristics of Rhodamine WT and Fluorescein as Adsorbing Ground-Water Tracers

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Abstract

Fluorescent dyes are being used as adsorbing ground-water tracers for conducting solute transport studies for adsorbing organic chemicals (e.g., pesticides). In this research, the ability of two fluorescent dyes (rhodamine WT and fluorescein) to mimic the adsorptive behavior of two herbicides (atrazine and alachlor) with alluvial aquifer sands was evaluated. Laboratory studies (batch and column) indicated the following order of increasing adsorption: fluorescein, atrazine, alachlor, and rhodamine WT. Thus, the use of fluorescein and rhodamine WT as adsorbing ground-water tracers was observed to delimit the appearance of the atrazine and alachlor (fluorescein appeared before and rhodamine WT after the herbicides). Several adsorption characteristics of the fluorescent dyes differed from those commonly observed for pesticides. The levels of adsorption for the dyes were several orders of magnitude greater than predicted from empirical relationships based on K_{OW} and f_{OC}. The presence of divalent cations was observed to increase the level of rhodamine WT adsorption. The rhodamine WT breakthrough curves were not of the conventional sigmoidal shape but instead leveled off at a C/CO value of 0.5 for a number of pore volumes prior to increasing again towards a C/CO value of 1.0. These characteristics indicate that the adsorptive mechanisms for the fluorescent dyes differed from the adsorptive mechanisms for most pesticides. These variations in fundamental adsorptive mechanisms raise concerns as to the transferability of the results of this research (fluorescein and rhodamine WT delimiting the appearance of atrazine and alachlor) to other subsurface media.

Introduction

The presence of synthetic organic contaminants (e.g., pesticides) in ground water has become a major concern. The ability to understand and predict the transport and fate of synthetic organic contaminants in ground water is vital for responding to their detection in ground water. One mechanism affecting the transport and fate of many organics in ground water is adsorption. While the need exists to study the adsorption and transport of organic contaminants at the field scale, the health concerns and the expense of utilizing synthetic organic contaminants in field scale studies have caused researchers to utilize fluorescent dyes as adsorbing tracers (surrogates) to mimic the behavior of synthetic organic contaminants (e.g., pesticides in agricultural plots). However, little research has been conducted to evaluate the characteristics of fluorescent dyes as adsorbing tracers; most research with fluorescent dyes has been concerned with isolating conservative (nonadsorbing) tracers. The need thus exists for research to address the ability of these fluorescent dyes to be utilized as adsorbing ground-water tracers.

Background

Fluorescent dyes are those dyes which, when exposed to light, fluoresce (i.e., adsorb shorter wavelength light and emit a longer wavelength light). This property of the fluorescent dyes allows them to be detected at the $\mu g/l$ and ng/l range using a fluorometer.

Feuerstein and Selleck (1963) investigated the behavior of three fluorescent dyes, including fluorescein, for use in surface-water tracing (flow rate) studies. The following parameters were found to affect the analysis of the dyes: (1) temperature, (2) salinity, (3) pH, (4) background fluorescence of dye-free sample, and (5) turbidity and suspended solids. Fluorescein exhibited high photochemical decay, and high levels of background fluorescence were encountered when analyzing for fluorescein. The fluorescence of fluorescein was seen to decrease at pH values below 5. The fluorescein was the least adsorbed of the three dyes investigated on suspended solids and algae.

Smart and Laidlaw (1977) discussed the use of eight fluorescent dyes, including rhodamine WT (RWT) and fluorescein, in surface-water tracing (flow rate) studies. The fluorescence of both RWT and fluorescein was shown to be a function of temperature. The fluorescence of the dyes was seen to decrease at low pH and was observed to be a function of the ions causing the pH change and the buffering system. The presence of organic matter in the water samples produced greater background fluorescence for fluorescein than for RWT. Photochemical decay was observed to be significant for fluorescein (greater for sunlight than artificial light) but relatively insignificant for RWT. RWT was observed to be more strongly adsorbed to organic and inorganic solid

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Received June 1989, revised June 1990, accepted July 1990.
Discussion open until November 1, 1991.

phases than fluorescein. The organic phases (sawdust, humus, heather) were observed to result in more adsorption than inorganic phases (clays, limestone, orthoquartzite) for both RWT and fluorescein.

Equilibrium adsorption isotherm studies are typically utilized to assess the adsorptive capacity of a subsurface material for chemicals. Isotherm research conducted with synthetic organic contaminants and surface soils has found that equilibrium adsorption of the chemicals is linear or near linear, especially at low chemical concentrations (Rao and Davidson, 1980; Brown and Flagg, 1981). For relatively nonpolar chemicals, the linear partitioning coefficient (K_p) has been observed to be a function of the organic carbon content of the material (f_{oc}) and the octanol:water partition coefficient (K_{ow}) of the chemical. Empirical expressions for estimating K_{oc} (K_p/f_{oc}) based on K_{ow} have been developed. Equation (1) shows one such expression after Karickhoff et al. (1979) and equation (2) after Brown and Flagg (1981).

$$\log K_{oc} = \log K_{ow} - 0.21 \quad (1)$$

$$\log K_{oc} = 0.937 \log K_{ow} - 0.006 \quad (2)$$

It should be mentioned that predictive relationships based on K_{ow} and f_{oc} have been found inaccurate for polar (ionizable) pesticides (Bailey and White, 1970) and low f_{oc}:high clay content materials (Banerjee et al., 1985).

Several studies have been conducted to assess the adsorption of RWT and fluorescein with various sediments or soils. Omoti and Wild (1979) investigated the use of fluorescein as a ground-water tracer. In a column study utilizing a loamy sand soil (85% sand, 10% clay, and 2% organic matter—$f_{oc} = 0.012$) and a pore-water velocity of 2.44 cm/h, the K_p value was determined to be 1.3 cm^3/g. The corresponding value of K_{oc} is 108 cm^3/g. Bencala et al. (1983) studied the use of RWT as a water tracer in a mountain stream environment. Batch studies between the RWT and streambed sediments resulted in a K_p value of 5.6 cm^3/g. The f_{oc} for the sediment was not given. Trudgill (1987) investigated the use of fluorescent dyes for ground-water flow tracing. Batch experiments with RWT and a silty loam soil (f_{oc} of 0.034 to 0.053) resulted in a K_p value of 54 cm^3/g. This corresponds to a K_{oc} value of 1,000 to 1,600 cm^3/g for the RWT.

The primary objectives of this research were to utilize batch and column studies to (1) determine the adsorptive characteristics of RWT and fluorescein with a low organic content alluvial aquifer sand, and (2) to assess the applicability of utilizing fluorescent dyes (fluorescein and rhodamine WT) as adsorbing tracers for pesticides (atrazine and alachlor). A secondary objective of this research was to evaluate the ability of batch tests and estimation techniques to predict the column results.

Materials and Methods

Alluvium

The alluvial aquifer sand sample was obtained from a recent alluvium near the Skunk River south of Ames, Iowa. The alluvium was collected during the drilling of a water-supply well utilizing the rotary bucket technique. The sand layer was 30 feet below the ground surface with a clay layer directly above the sand layer. Table 1 lists pertinent parameters for the alluvial aquifer sand sample determined by conventional methods (ASTM, 1988; Nelson and Sommers, 1982; Rhoades, 1982). The clay fraction was qualitatively analyzed using x-ray diffraction and was observed to be comprised of approximately equal fractions of kaolinite, illite, and Na- and Ca-montmorillonite.

Table 1. Parameters for Alluvial Aquifer Sand

Parameter	
Median grain size diameter, d_{50} (mm)	0.58
Uniformity coefficient, d_{60}/d_{10}	3.5
Percent sand (%)	97.3
Percent silt (%)	2.2
Percent clay (%)	0.5
Fraction organic carbon content (f_{oc})	0.0027 ± 0.00029
Soil pH	7.9
Cation exchange capacity (meq/100 g)	13.3
Hydraulic conductivity (cm/s)	8.6×10^{-3}

Fluorescent Dyes

The fluorescent dyes investigated were rhodamine WT (RWT) and fluorescein. Smart and Laidlaw (1977) classified RWT as an orange fluorescent dye and fluorescein as a green fluorescent dye. Other available physical and chemical parameters for RWT and fluorescein which are pertinent to this study are given in Table 2. The RWT used in this study was obtained as a 20% solution from Pylam Products (Garden City, New York), and the fluorescein (color index #45350) was a purified grade powder obtained from Fisher Scientific (Houston, Texas) under the name Uranine. This fluorescein is equivalent in strength (77% active ingredient) to products commercially available (Chemcentral—Detroit, Michigan); however, some commercially available fluorescein has as little as 42% active ingredient (Quinlan, 1990). The dyes were analyzed using a Turner Model 110 fluorometer according to United States Geological Survey procedures (Wilson et al., 1986). The primary filters utilized for RWT were 1-60 and 58 and for fluorescein were 46B and 2A. The secondary filter utilized for RWT was 25 and for fluorescein was 58. The 1-60 filter was a Corning filter and the remaining filters were Wratten filters. While other filter combinations have been reported to provide greater sensitivity for the dyes, these combinations provided sufficient sensitivity for the concentration levels of concern in this study. Using these filters, the detection limit (taken as one dial reading on the most sensitive scale) for RWT was 1.0 μg/l and for fluorescein was 0.2 μg/l.

Pesticides

The pesticides investigated in this study were the herbicides atrazine and alachlor. Atrazine and alachlor are widely used and commonly detected in shallow ground waters in the Midwest. Atrazine is a triazine pesticide and alachlor is an amine pesticide. Other physical and chemical properties of atrazine and alachlor pertinent to this study are shown in Table 2. The atrazine and alachlor utilized for standards and stock solutions were analytical grade (99% pure, Chem

Table 2. Physical and Chemical Properties of Rhodamine WT, Fluorescein, Atrazine, and Alachlor

Parameter	*Rhodamine WT*	*Fluorescein*	*Atrazine*	*Alachlor*
Molecular formula	$C_{29}H_{29}N_2O_5Na_2Cl$	$C_{20}H_{10}Na_2O_5$	$C_8H_{14}ClN_5$	$C_{14}H_{20}ClNO_2$
Molecular weight	566	376	216	270
Log K_{ow}[a,b]	−1.33	−0.39	2.34	2.64

[a] Smart (1984).
[b] Rao and Davidson (1980).

Service, West Chester, Pennsylvania). Atrazine and alachlor were analyzed according to USEPA method 619 (USEPA, 1982) and 645 (USEPA, 1985), respectively. These methods consist of liquid-liquid extractions, concentration, and gas chromatography analysis. Recovery efficiencies for atrazine and alachlor were 87% and 84%, respectively. A Perkin Elmer Sigma 1 GC was used with a nitrogen/phosphorous (N/P) thermionic detector in the nitrogen mode. The glass column utilized was 1.8 m long × 2 mm (inside diameter) and was packed with 5% Carbowax 20M-TPA on Supelcoport (80/100 mesh). During GC operation, the injection temperature was 250° C, the oven temperature was 200° C, the carrier gas was helium, the carrier flowrate was 30 ml/min, and the sample injection was 5 μl. For these operating conditions, the peak detection time for alachlor was 8.4 min and for atrazine was 13.2 min. For a 40 ml original sample size, the detection limit (taken as twice the chromatograph noise level) for atrazine was 0.5 μg/l and for alachlor was 1.0 μg/l.

Batch Methods

Batch studies for the chemicals were conducted by placing a constant mass of aquifer material (50 g) and a constant volume of chemical solution (100 ml) at varying concentrations in a series of reactors (250 ml Erlenmeyer flasks) and shaking for two hours for the dyes and 24 hours for the pesticides (equilibrium). The initial and equilibrium concentrations for each reactor were determined and by mass balance the mass of chemical adsorbed was determined. Duplicates were evaluated for each set of conditions, and chemical and alluvium blanks were conducted for each isotherm study. Solid liquid separation was conducted utilizing gravity filtering with Whatman #2 or #5 filter paper (8 and 2.5 μm, respectively) and plastic funnels. No change in chemical concentration was observed using this solid liquid separation technique. Problems were encountered in eliminating the background fluorescence from the alluvium when analyzing for fluorescein. Use of 0.45 μm filter paper, 0.2 μm filter paper, and high speed centrifuging (17,000 rpm) did not decrease the background fluorescence observed, leading to the hypothesis that the background fluorescence was the result of colloidal or dissolved organics. The problem of background fluorescence for fluorescein has been reported by others (Feurestein and Selleck, 1963; Smart and Laidlaw, 1977). Alluvium blanks (with no fluorescein present) resulted in readings of 1 to 10 μg/l. This problem may be eliminated by use of a scanning spectrofluorometer. The batch tests were conducted at room temperature (25°C) utilizing Nanopure II water, and the pH was observed to be near neutral (7.5 to 8.0) for the batch reactors.

Column Methods

The laboratory column studies were conducted utilizing glass columns 5.0 cm in diameter (cross-sectional area of 19.6 cm^2) and 35.0 cm in length. A fine mesh stainless steel screen served as a media support near the bottom of the column. Masterflex peristaltic pumps were utilized to establish a constant flowrate through the column. Silicone tubing was utilized in the pump heads and Teflon tubing elsewhere in an effort to eliminate any adsorptive losses to the tubing. A time-controlled fraction collector was utilized to obtain discrete samples for fluorescent dye analysis. The breakthrough of a conservative tracer (chloride) was monitored utilizing an inline chloride electrode and a microcomputer-based continuous data acquisition system. The chloride was introduced as 0.01 N $CaCl_2$ and 0.01 N $CaSO_4$ was used in the absence of chloride. Figure 1 illustrates schematically the column apparatus utilized during this study. The column runs were conducted at room temperataure (25° C) with the flow maintaining a relatively neutral pH (7.5 to 8.0) for all column runs.

Results

Batch Studies

Batch studies were conducted to evaluate the equilibrium adsorption of the dyes and pesticides for the alluvium.

Adsorption of RWT and Fluorescein

Batch studies were conducted for rhodamine WT (RWT) and fluorescein using the aquifer material. The resulting isotherms (q versus C_e, where q is the mass of dye adsorbed per unit mass of alluvium, and C_e is the equilibrium concentration of the dye) for RWT and for fluorescein are shown in Figure 2 and Figure 3, respectively. Table 3 summarizes the results for the RWT (BRA) and fluorescein (BFA) batch tests.

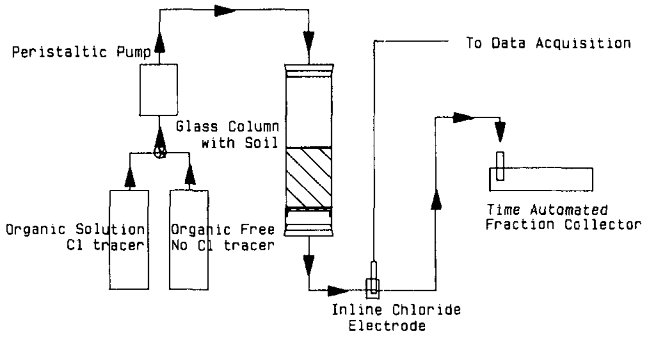

Fig. 1. Schematic of column apparatus.

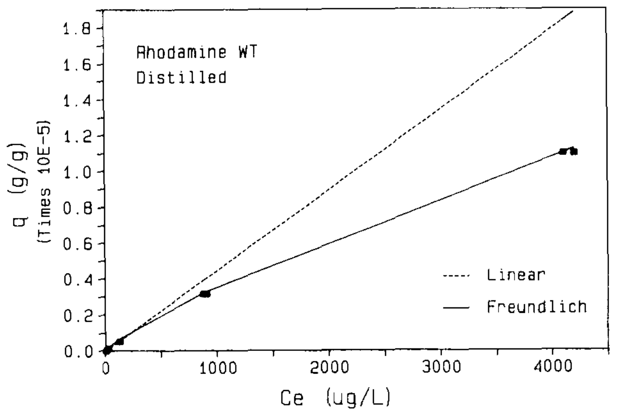

Fig. 2. Rhodamine WT adsorption isotherm.

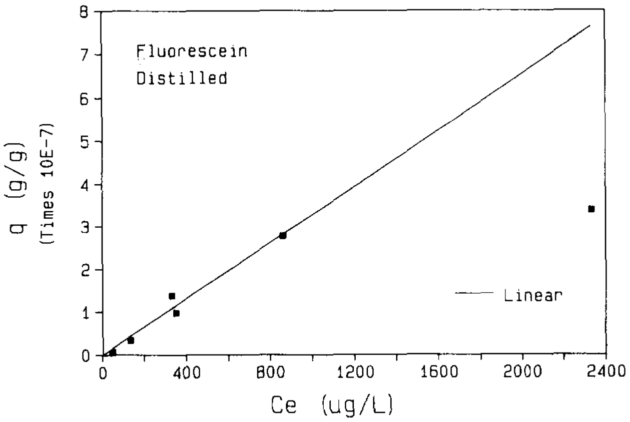

Fig. 3. Fluorescein adsorption isotherm.

As observed by the relative magnitude of the q values for RWT and fluorescein isotherms (Figures 2 and 3), the level of adsorption for the fluorescein was much less than that for the RWT. During the fluorescein batch studies, the reductions of the aqueous phase fluorescein concentrations were low (5 to 15%). As discussed previously, the alluvium blanks exhibited background fluorescence when analyzing for fluorescein which varied from blank to blank. These factors complicated the interpretation of the fluorescein batch results. Attempts to increase the level of fluorescein adsorption by increasing the alluvium to water ratio resulted in increases in the background fluorescence and unsatisfactory mixing of the alluvium and the solution.

Inspection of the adsorption isotherms for RWT and fluorescein indicates that both dyes demonstrated linearity at low concentrations with nonlinearity experienced at higher concentrations. The linear adsorption expression was used to describe the data at the lower concentrations. The K_{oc} values (Table 3) of 1,700 cm^3/g for RWT and 120 cm^3/g for fluorescein are similar to values reported by other researchers using other adsorbents (sediments and nonsoils). Using the data of Trudgill (1987), K_{oc} values for RWT in the range of 1,000 to 1,600 cm^3/g were determined. Using the data of Omoti and Wild (1979), a K_{oc} value for fluorescein of 108 cm^3/g was determined.

The Freundlich isotherm was able to predict the nonlinear nature of the RWT isotherm observed at higher equilibrium concentrations. However, the discontinuous nature of the fluorescein isotherm (caused by the highest equilibrium concentration data points) prevented the Freundlich expression from providing a good fit to the data. For this reason, only the linear expression is shown for the fluorescein isotherm. The adsorption parameters for the Freundlich isotherm (K_{fr} and N) are shown in Table 3. The Freundlich parameters were determined utilizing a nonlinear least error method in the Eureka microcomputer software package (Borland, Inc.). This method was observed to provide a better fit to the isotherm data than the conventional log transformation method. The failure of the log transformation method to provide as good of results as the nonlinear least error method could be due to the spacing of the data points utilized in the batch tests.

Table 3. Batch Adsorption Parameters for Rhodamine WT and Fluorescein

Parameter	*BRA*	*BFA*	*BRACA*
Dye	RWT	Fluorescein	RWT
Background solution	distilled	distilled	10^{-2} N $CaCl_2$
K_p (cm^3/g)	4.5	0.33	9.7
r^2	0.99	0.98	0.99
f_{oc}	0.0027	0.0027	0.0027
(K_{oc}) observed (cm^3/g)	1.7×10^3	1.2×10^2	3.7×10^3
N	0.80	—	0.73
K_{fr} $(g/g)/(g/l)^N$	8.8×10^{-4}	—	7.1×10^{-4}

Adsorption of Dyes Versus Pesticides

Batch studies were conducted to evaluate the adsorption of atrazine and alachlor on the alluvium. The K_p value for atrazine was 0.40 cm^3/g and for alachlor was 1.08 cm^3/g. The corresponding K_{oc} values for atrazine and alachlor are 148 and 400, respectively. Table 4 summarizes the observed K_{oc} values for the pesticides and the fluorescent dyes and indicates the following order of increasing adsorption: fluorescein, atrazine, alachlor, and RWT. Thus, the fluorescent dyes will bracket the appearance of the pesticides (the fluorescein will appear before the pesticides, and the RWT will appear after the pesticides). For more detailed information on the adsorption of the pesticides, the reader is referenced to Sabatini (1989) and Sabatini and Austin (1990).

Table 4. Measured and Predicted K_{oc} Values for Rhodamine WT, Fluorescein, Atrazine and Alachlor

Parameter	*RWT*	*Fluorescein*	*Atrazine*	*Alachlor*
log K_{ow}	−1.33	−0.39	2.34	2.64
(K_{oc}) estimated[a] (cm^3/g)	0.03	0.25	135	270
(K_{oc}) estimated[b] (cm^3/g)	0.06	0.43	153	293
(K_{oc}) observed (cm^3/g)	1700-3700[c]	120	148	400

[a] Estimated after Karickhoff et al. (1979).
[b] Estimated after Brown and Flagg (1981).
[c] Range is due to variation in valence of background ions.

Estimated Linear Adsorption Parameter

The estimation expressions for K_{oc} after Karickhoff et al. (1979) and Brown and Flagg (1981) were utilized to predict K_{oc} values for the pesticides and the dyes. Table 4 shows the K_{oc} parameters predicted by these expressions and measured in this study. It is observed that the levels of adsorption observed for both dyes in this study were several orders of magnitude greater than that predicted by either estimation technique. For the pesticides, the estimated values were within a factor of two or less of the experimental levels of adsorption. The estimation techniques of Karickhoff et al. (1979) and Brown and Flagg (1981) are empirical and were derived utilizing relatively nonpolar chemicals. RWT and fluorescein are polar and ionizable and thus violate the conditions necessary for these empirical relationships to be valid. This illustrates the danger of utilizing empirical relationships (which are widely used for nonpolar organics) for chemicals without verifying their applicability. It is also interesting to note that while inspection of the K_{ow} values for the dyes would have suggested that fluorescein would be more strongly adsorbed than RWT, in actuality the RWT was more strongly adsorbed than the fluorescein.

Effect of Background Ions

The batch studies discussed above were conducted with the dyes in distilled water (no background ions added). Given the polar nature of the dyes, the effects of varying the background ionic solution needed to be investigated. An isotherm study was conducted with 0.01 N $CaCl_2$ as the background solution for RWT with the resulting K_p and Freundlich parameters shown in Table 3 (BRACA). The value of K_p increased with the presence of the background ions indicating that increased adsorption occurred in the presence of the $CaCl_2$. Other tests (see Sabatini, 1989) indicated that the level of adsorption increased with increasing valence and increasing concentration of background cations but was relatively independent of the anion constituency. This suggests that the increased adsorption is the result of suppression of the diffused double layers about particles which allowed more of the polar RWT to be adsorbed. This demonstrates the polar nature of the fluorescent dyes and may account for the variations noticed between batch results and estimation techniques, as discussed above.

Column Studies

Although the predominantly one-dimensional flow experienced in relatively homogeneous packed laboratory columns does not exactly mimic actual ground-water flow, the continuous flow column studies can provide additional information as compared to equilibrium batch studies.

The breakthrough of a conservative tracer (chloride) was evaluated in each column run. The chloride breakthrough curve was complete within two pore volumes for all runs, and this information was utilized to obtain the hydrodynamic dispersion coefficient (D_x) for each column run. The chloride breakthrough curves indicated that saturated conditions existed during the column runs, that the flow through the porous media occurred without significant preferential flow, and that the P_e number (relative magnitude of advective and dispersive transport) was relatively independent of pore-water velocity (see Table 5).

Transport of RWT and Fluorescein

Breakthrough and elution curves for RWT and fluorescein were conducted using the alluvial aquifer sand. The conditions for the column studies are summarized in Table 5 (CRA for RWT and CFA for fluorescein). Figure 4 shows the breakthrough and elution curves for RWT (with NaCl versus with $CaCl_2$) and Figure 5 for fluorescein (where C/CO is relative concentration and V/VO is relative pore volumes). Based on results of the batch tests, the concentrations selected for the column runs were in the linear adsorption range. Mass balances of breakthrough and elution curves for the fluorescent dyes indicated virtually complete recovery of the dyes (85 to 110%) for all column runs. This indicates that the adsorption of the fluorescent dyes is reversible (physical adsorption) and that degradation (photo and microbial) of the fluorescent dyes was not evident in the column studies.

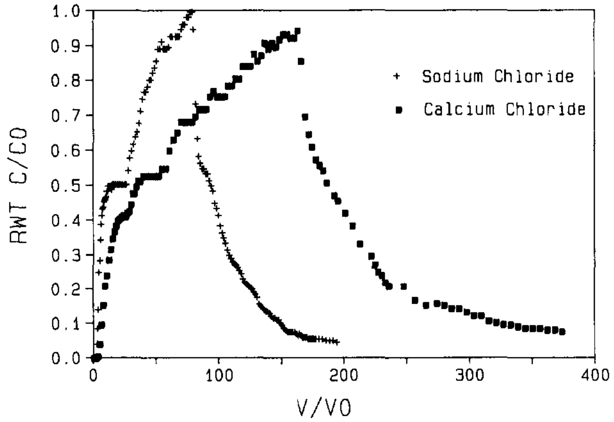

Fig. 4. Rhodamine WT breakthrough curves—$CaCl_2$ versus NaCl.

Table 5. Column Parameters for Rhodamine WT and Fluorescein Column Runs

Run	*Dye*	*CO (μg/l)*	*PWV (cm/h)*	*Length (cm)*	*Weight (g)*	*Porosity*	*Conservative tracer*	D_x (cm^2/h)	P_e
CRA	RWT	201	11.7	13.0	388.0	0.42	NaCl	7.6	20.0
CFA	Fluorescein	225	13.2	9.0	300.0	0.36	$CaCl_2$	5.9	19.8
CRACA	RWT	195	11.3	12.0	360.0	0.42	$CaCl_2$	7.9	17.2
CRAHP	RWT	198	34.1	11.0	352.0	0.38	NaCl	15.0	25.0
CRAHC	RWT	1950	11.9	11.5	352.0	0.40	NaCl	6.8	20.1

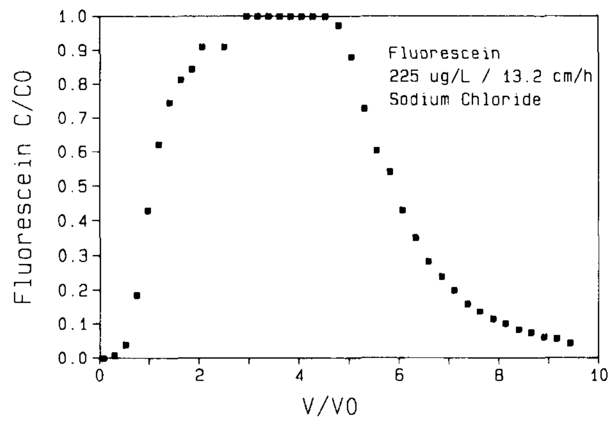

Fig. 5. Fluorescein breakthrough curve.

The breakthrough curve for RWT (Figure 4) is not the conventional sigmoidal form but instead has a plateau at a value of C/CO of 0.5. This plateau was evidenced for approximately 20 pore volumes prior to C/CO values increasing again. The second leg of the breakthrough curve was a smaller slope than the first leg. This two-leg breakthrough curve was verified for a second alluvial aquifer sand sample (Sabatini, 1989) and was also observed by Everts (1989) for a surface soil. The elution curve did not demonstrate a plateau but did demonstrate hysteresis of desorption (the elution curve had not reached a value of C/CO of 0.0 in the same number of pore volumes required for the breakthrough curve to reach a C/CO value of 1.0). The breakthrough curve for fluorescein (Figure 5) occurred in much fewer pore volumes than for RWT and did not demonstrate the plateau observed for RWT. Hysteresis of desorption was evidenced for fluorescein.

For purposes of comparison to batch results, the column data were converted into a single point isotherm (mass adsorbed at complete breakthrough was determined and combined with the equilibrium concentration responsible for this level of adsorption). These values are summarized in Table 6. The K_p value determined for RWT from the column run (CRA) is seen to be greater than that measured in the batch test with the ratio of column to batch K_p being 1.5. Typically, K_p values determined in columns are seen to be less than those determined in batch tests due to the kinetic limitations (physical or chemical) of adsorption during porous media flow. Bouchard et al. (1988) reported data that gave ratios of column to batch K_p values in the range of 0.43 to 0.74. It is observed that the column K_p values for RWT were greater than the batch K_p values. Either the nature of the batch system decreased the level of adsorption, or the nature of the column system increased the level of adsorption for RWT. The ratio of column to batch K_p values for fluorescein was 0.15. The fluorescein breakthrough curve was not significantly retarded from the chloride breakthrough curve (C/CO = 1.0 in three pore volumes for fluorescein versus two pore volumes for chloride). However, for higher organic carbon content surface soils, the fluorescein would be more significantly retarded from the conservative tracer (as observed by Omoti and Wild, 1979).

The previous column runs were conducted with NaCl as the conservative tracer. The presence of sodium in batch studies was not observed to significantly affect the adsorption of RWT. However, the presence of 0.01 N $CaCl_2$ was seen to affect the batch isotherms for RWT. For this reason, a column run was conducted with 0.01 N $CaCl_2$ as the background solution. This breakthrough curve is shown in Figure 4 and summarized in Table 6 as CRACA. The value of K_p determined from the column data was observed to be greater when $CaCl_2$ was present than when NaCl was present.

Use of Dyes as Adsorbing Tracers

Column studies were conducted with atrazine and alachlor. The breakthrough of the atrazine occurred first followed by the alachlor. The resulting K_p value for atrazine was 0.30 and for alachlor was 0.93 cm^3/g. Comparison of these values to the K_p values for the dyes shows the following order of increasing levels of chemical adsorption: fluorescein, atrazine, alachlor, and RWT. This is in agreement with results observed during the batch studies. If both fluorescein and RWT were used as adsorbing tracers, atrazine and alachlor would be expected to appear after the fluorescein and before the RWT. This is illustrated in Figure 6 which jointly shows the breakthrough curves for the pesticides and fluorescent dyes. Thus, the use of RWT and fluorescein as adsorbing tracers could be used to delimit the appearance of these two herbicides for media similar to those encountered in this study.

Effects of Size Fractions and Organic Content

In an attempt to evaluate the nature of the RWT two-leg column breakthrough curve, various steps were taken to reduce the organic content and/or percent fines (clays) in the alluvium columns. The alluvium treatments utilized included wet seiving, backwashing, and heating at 550 or 850°C.

Table 6. Column Adsorption Results for Rhodamine WT and Fluorescein Column Runs

Run	*Dye*	*Conservative tracer*	*Mass soil (g)*	*Mass dye adsorbed ($\times 10^{-4}$ g)*	*C_e ($\mu g/l$)*	*$(K_p)_{column}$ (cm^3/g)*	*$(K_p)_{batch}$ (cm^3/g)*
CRA	RWT	NaCl	388.0	5.2	201	6.9	4.5
CFA	Fluorescein	$CaCl_2$	300.0	0.03	225	0.05	0.33
CRACA	RWT	$CaCl_2$	360.0	11.0	195	15.7	9.7
CRAHP	RWT	NaCl	352.0	3.0	198	4.3	4.5
CRAHC	RWT	NaCl	352.0	17.0	1950	2.5	4.5

Figure 7 shows four column runs which utilized samples of the aquifer sand subjected to four different treatments. Calcium chloride was utilized as the conservative tracer in all of these column runs. The plot labeled CRACA corresponds to an unaltered sample, as shown previously in Figure 4. The plot labeled BW corresponds to a sample which was retained during wet sieving on a number 200 sieve (75 μm) and then backwashed in a column overnight to assure the removal of the clays. It should be noted that in this process the f_{oc} of the alluvium was decreased from 0.0027 to 0.0010. The plot labeled HT/850 corresponds to an alluvium sample heated at 850°C. This temperature will not only affect the organic carbon content but will also affect some of the clays. Analysis of the unaltered clay fraction of the sand by x-ray diffraction indicated the presence of kaolinite, illite and sodium, and calcium montmorillonite with kaolinite and illite the most likely to be affected at the temperature considered here (Deer et al., 1966). The plot labeled BW-HT/850 corresponds to the backwashed sample from above being heated at 850°C. This corresponds to the alluvial material minus the fines and the organic content.

The shift from the whole alluvium curve (CRACA) to the backwashed curve may be attributed to the loss of the clays and/or the loss of the organic content. Comparison of the breakthrough curves for alluvial materials heated at 850°C with and without backwashing (BW-HT/850 and HT/850, respectively) indicates that the clays provide adsorption sites for the RWT even upon heating at 850°C. Analysis of the breakthrough curves shows that the major shift occurred between BW and BW-HT/850, suggesting that the destruction of the organic content upon heating at 850°C caused the greatest reduction in adsorption (assuming the clays were washed out in the backwashing process). While no distinct plateau is observed for the heat-treated alluvial materials, the change in slope observed for the HT/850 plot could represent the same phenomenon. It was not possible, based on these studies, to derive decisive conclusions as to the mechanism(s) causing the two-leg breakthrough curve; however, adsorption is shown to be most sensitive to the level of organic content present.

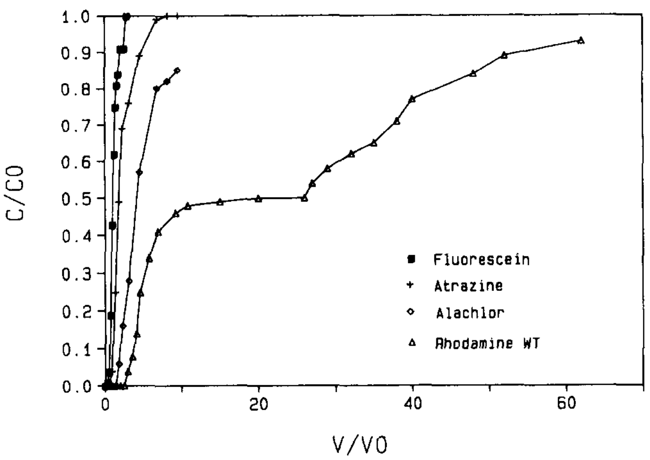

Fig. 6. Breakthrough curves for fluorescein, atrazine, alachlor, and rhodamine WT.

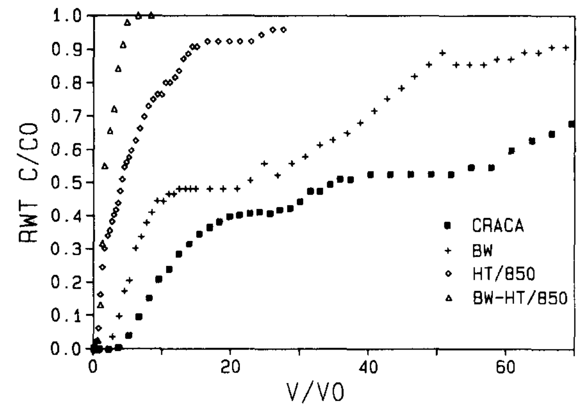

Fig. 7. Rhodamine WT breakthrough curves for treated alluviums.

Effect of Pore-Water Velocity/Concentration

To evaluate the kinetics of adsorption in the alluvium column, a column run was conducted with a pore-water velocity of 34.1 cm/h (CRAHP in Tables 5 and 6). These results are compared with a similar column run conducted at a pore-water velocity of 11.7 cm/h (CRA in Tables 5 and 6) with other parameters being the same. These runs were both conducted with sodium chloride as the conservative tracer. The column results for these two runs are shown jointly in Figure 8. It is seen that the two curves (with pore-water velocity as the variable) are virtually the same for the first leg of the breakthrough and that the plateau occurs at about 0.5 for both cases and at about the same relative pore volume. However, in the case of the higher pore-water velocity, the second leg of the breakthrough occurs sooner and has a steeper slope. It thus appears that the first adsorption mechanism (first leg) is not significantly affected by the reduced reaction time (is not kinetically limited) while the second adsorption mechanism (second leg) is kinetically limited).

To evaluate the impacts of the nonlinear adsorption of RWT (as observed in the batch studies) on the column data, a column run was conducted with an order of magnitude higher RWT concentration (1950 μg/l versus 201 μg/l) using the same alluvium and pore-water velocity (CRAHC and CRA, respectively, in Tables 5 and 6). This comparison is illustrated in Figure 8. It is observed that the higher concentration resulted in breakthrough at fewer pore volumes. While the amount of adsorption had increased with the higher concentration (q is larger), the ratio of the increase in adsorption to the increase of the concentration is less than one (which is indicated by the deviation from linearity in the isotherm test at C_e values for RWT greater than approximately 250 μg/l). The nonlinear ($N < 1.0$) adsorption causes breakthrough to occur with fewer pore volumes passed at increasing concentrations, as observed in this run. These results point out the danger of conducting isotherm tests at lower concentrations (which will typically result in a linear isotherm) and extrapolating the data to higher concentrations (where linearity may be violated). The time of first appearance for the RWT and the time till complete breakthrough will be overestimated if the nonlinear adsorption ($N < 1.0$) is not considered.

Summary and Conclusions

Adsorption isotherms and column runs for the fluorescent dyes showed that rhodamine WT (RWT) experienced significantly more adsorption by the alluvial sand than fluorescein. Batch values of K_p (with no background ions added) for fluorescein and RWT were 0.33 cm^3/g and 4.5 cm^3/g, respectively. Batch and column values for K_p were within a factor of 2 for RWT and within a factor of 6 for fluorescein. The isotherms for the dyes were observed to be linear at low concentrations ($\mu g/l$) with nonlinearity evidenced at higher concentrations (mg/l). Analysis of fluorescein batch tests was complicated by the presence of natural background fluorescence for the alluvial aquifer material. During column runs the problem of background fluorescence was not as significant.

Investigation of adsorption data obtained utilizing the same alluvium and two herbicides indicates the following order of increasing levels of adsorption: fluorescein, atrazine, alachlor, and RWT. Fluorescein would appear before and RWT after atrazine and alachlor if used as adsorbing tracers. Use of these two dyes as adsorbing tracers would thus be very effective in delimiting the appearance of these two herbicides in materials similar to that studied in this research. However, certain characteristics of the adsorption of the fluorescent dyes differed from those commonly observed for pesticides (as summarized in the following paragraphs). This suggests that different mechanisms were responsible for the adsorption and raises concern as to the transferability of these results to other subsurface medias. Future research should evaluate chemicals with fundamental properties closer to those of the pesticides being traced.

For both dyes, measured K_{oc} values (in batch and column studies) were several orders of magnitude greater than predicted using estimation techniques (based on K_{ow} and f_{oc}). The polar and ionizable nature of the dyes violates the premise of nonpolar chemicals which were utilized in developing the empirical estimation techniques. The estimation techniques predicted that fluorescein would be more highly adsorbed than RWT (fluorescein has a higher K_{ow} than RWT), while the batch and column studies showed RWT to be more highly adsorbed than fluorescein. These results point out the need to apply estimation techniques with care.

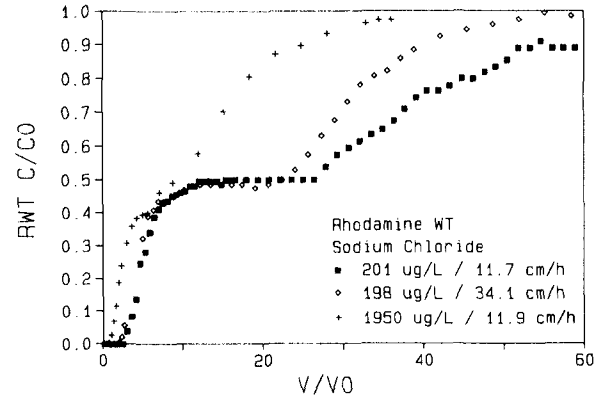

Fig. 8. Rhodamine WT breakthrough—effects of pore-water velocity and concentration.

Background ions were observed to affect the level of RWT adsorption. Increasing valence and increasing concentration of cations were observed to most significantly affect the level of RWT adsorption. Batch tests and column runs for RWT with 10^{-2} N $CaCl_2$ present resulted in K_{oc} values greater by more than a factor of 2 than without $CaCl_2$ added. It is hypothesized that increasing cation valence and concentration reduced the diffuse double layers about the alluvial aquifer particles and caused the increased adsorption observed.

The RWT breakthrough curves did not demonstrate the conventional sigmoidal shape but instead leveled off at a C/CO value of 0.5 for a number of pore volumes prior to increasing C/CO values again. Mass balances of breakthrough and elution data showed conservation of mass, indicating that degradation was not the mechanism responsible for this two-leg breakthrough curve. Treatment of the alluvial aquifer material to reduce the organic carbon content and/or the clay content resulted in decreases in RWT adsorption, but the two-leg breakthrough curve was still evident. This suggests that both organic carbon content and clays are involved in adsorbing RWT and responsible for the two-leg breakthrough curve. Additional study will be required to determine the mechanism(s) responsible for the two-leg breakthrough curve observed for RWT.

The batch K_p values for fluorescein were observed to be greater than K_p values determined from column runs, as observed in other research. For RWT, however, the batch K_p values were lower than those determined from column runs. It was beyond the scope of this research to determine the mechanism(s) responsible for greater RWT adsorption in the column runs than in the batch studies. The same mechanism(s) may be responsible for the two-leg breakthrough curves observed during column runs for RWT.

For RWT, increasing the pore-water velocity from 11.7 cm/h to 34.1 cm/h was not observed to affect the first leg of the breakthrough curve but resulted in earlier rise and steeper slope of the second leg of the breakthrough curve. This suggests that the mechanism responsible for the first leg of the RWT breakthrough curve was not rate limited but that the mechanism responsible for the second leg of the breakthrough curve was rate limited. Increasing the influent RWT concentration from 201 $\mu g/l$ to 1,950 $\mu g/l$ resulted in earlier breakthrough of the RWT. This is consistent with the nonlinear isotherm ($N < 1.0$) observed in the batch tests for RWT at the higher concentrations.

Nomenclature

C_e = liquid phase equilibrium concentration (M/L^3);

C/CO = relative concentration;

D_x = hydrodynamic dispersion coefficient (L^2/t);

f_{oc} = fraction organic carbon content (M/M);

K_{fr} = Freundlich partition coefficient $[(L^3/M)^N]$;

K_{oc} = linear partition coefficient normalized by fraction organic carbon content (L^3/M);

K_{ow} = octanol/water partition coefficient;

K_p = linear equilibrium partition coefficient (L^3/M);

N = Freundlich exponent;

P_e = Peclet number;

q = mass of solute adsorbed to solid phase per unit mass of soil (M/M);

RWT = rhodamine WT.

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