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Determination of bromacil transport as a function of water and carbon content in soils

SONG-BAE KIM[1], HAN-SANG ON[2], DONG-JU KIM[2], WILLIAM A. JURY[3] and ZHI WANG[4]

[1] *Environmental Biocolloid Engineering Laboratory, Seoul National University, Seoul, Korea*
[2] *Department of Earth and Environmental Sciences, Korea University, Seoul, Korea*
[3] *Department of Environmental Sciences, University of California, Riverside, CA*
[4] *Department of Earth and Environmental Sciences, California State University, Fresno, CA*

This study was conducted to determine the significance of bromacil transport as a function of water and carbon content in soils and to explore the implications of neglecting sorption when making assessments of travel time of bromacil through the vadose zone. Equilibrium batch sorption tests were performed for loamy sand and sandy soil added with four different levels of powdered activated carbon (PAC) content (0, 0.01, 0.05, and 0.1%). Column experiments were also conducted at various water and carbon contents under steady-state flow conditions. The first set of column experiments was conducted in loamy sand containing 1.5% organic carbon under three different water contents (0.23, 0.32, and 0.41) to measure breakthrough curves (BTCs) of bromide and bromacil injected as a square pulse. In the second set of column experiments, BTCs of bromide and bromacil injected as a front were measured in saturated sandy columns at the four different PAC levels given above. Column breakthrough data were analyzed with both equilibrium and nonequilibrium (two-site) convection-dispersion equation (CDE) models to determine transport and sorption parameters under various water and carbon contents. Analysis with batch data indicated that neglect of the partition-related term in the calculation of solute velocity may lead to erroneous estimation of travel time of bromacil, i.e. an overestimation of the solute velocity by a factor of R. The column experiments showed that arrival time of the bromacil peak was larger than that of the bromide peak in soils, indicating that transport of bromacil was retarded relative to bromide in the observed conditions. Extent of bromacil retardation (R) increased with decreasing water content and increasing PAC content, supporting the importance of retardation in the estimation of travel time of bromacil even at small amounts of organic carbon for soils with lower water content.

Keywords: Bromacil transport; sorption; carbon content; water content.

Introduction

Groundwater contamination by agrochemicals such as pesticides and herbicides has attracted considerable attention in recent years.[1−7] The principal processes affecting the transport of these chemicals from the surface to groundwater and the concentrations at which they arrive are advection, dispersion, degradation, and sorption. Retardation plays an important role in transport of a reactive chemical in soils and aquifers, by decreasing mobility and influencing the travel time from the surface to a point of interest. Thus, accurate characterization of the role that retardation plays in chemical transport through the subsurface is an essential part of any strategy for designing remediation

of contaminated groundwater or improved management of agrochemicals. Since sorption is essentially a partitioning of chemical mass between the dissolved phase and the surface sites, the magnitude of retardation is closely related to the degree of water saturation (or water content) in soils[8−11] and the sorption affinity of stationary organic and mineral surfaces for the chemical of interest.[12−16]

For reasons largely arising from expense and experimental difficulty, almost no direct observation has been made of chemical movement and fate in the lower vadose zone. For example, Loague et al.,[3] in their comprehensive investigation of regional-scale ground water contamination by Dibromochloropropane (DBCP), used soil survey information obtained in the near-surface regime to estimate water-holding capacity for the entire thickness of the vadose zone. These authors also assumed that soil organic carbon was insignificant below the surface meter of soil, and therefore that sorbing chemicals such as DBCP would move without interaction with the solid phase. This assumption was also

made by Spurlock et al.[5] in their use of the model leaching estimation and chemistry model LEACHM[17] to calculate travel times for simazine in alluvial coarse-textured soils in the Fresno, CA area.

Because of the importance of travel-time estimates in litigation and management, it is essential to examine in detail the appropriateness of assumptions such as those made by the above authors in neglecting sorption in soils low in organic matter. According to the partitioning assumption used in virtually all transport models a dissolved chemical that undergoes linear, equilibrium adsorption will be retarded with respect to the movement of the water by a factor:

$$R = 1 + \frac{\rho_b f_{oc} K_{oc}}{\theta} \qquad (1)$$

where R is the retardation factor, ρ_b is dry bulk density of soil, K_{oc} is organic carbon partition coefficient, and f_{oc} is soil organic carbon fraction.[18] The retardation factor R thus will increase significantly as water content decreases unless the ratio of organic carbon content to water and organic carbon content is negligible.

Since Spurlock et al.[5] and Loague et al.[3] essentially assumed that the solute velocity (v_s) was equal to the water velocity (v_w) in subsurface sandy soil, their assumption amounts to saying:

$$v_s = \frac{J_w}{R\theta} = \frac{J_w}{\theta + \rho_b f_{oc} K_{oc}} \approx \frac{J_w}{\theta} \quad \text{if } \theta \gg \rho_b f_{oc} K_{oc} \qquad (2)$$

Assessment of the validity of the assumption in the Equation 2 is complicated by the fact that K_{oc} for a given compound has commonly been observed to be higher than average K_{oc} in sandy soils,[19] which are generally at lower water content in the field. For example, Deeley et al.[1] measured an average K_{oc} for DBCP of 100 cm³/g in three non-sandy soils, but a much higher 330 cm³/g in two coarse-textured aquifer sediments.

This study was conducted to determine experimentally the significance of sorption of the nonionic herbicide bromacil as functions of water and carbon contents in soils using batch and column methods and to explore the implications of neglecting sorption when making assessments of travel time (solute velocity) through the vadose zone. Column data were analyzed with transport models to determine transport and sorption parameters under various water and carbon contents.

Materials and Methods

Equilibrium batch test

Equilibrium batch tests were performed to determine the equilibrium distribution coefficients (K_d) of bromacil for a loamy sand containing 1.5% organic carbon (OC), and a sandy soil mixed with various amounts of powdered ac-

tivated carbon (PAC) in order to investigate the accuracy of Equation 1 in describing sorption at various water contents and OC levels. The loamy sand, consisting of 93.0% sand, 2.0% silt, and 5.0% clay by weight, was collected from a Delhi sand field site adjacent to the Kearney Field Station in Fresno, California (USA), where substantial pesticide contamination has been observed.[3] The sandy soil was obtained from sediments near the Han river in Seoul, Korea after which it was treated to remove organic carbon. The average grain size of PAC was 27 μm, pH ranged from 6 to 8, and electrical conductivity (EC) was very low (100 μS/cm).

Batch samples were prepared by mixing 10 g of dry soil with 10 mL bromacil solutions containing a 5 mM CaCl$_2$ at six initial concentrations (10, 20, 50, 100, 200, 400 mg/L for loamy sand; 20, 50, 100, 200, 400, 500 mg l^{-1} for PAC-added sandy soil) and shaken at 110 rpm for 24 hr. Then, samples were withdrawn by syringe and centrifuged at 3000 rpm for 10 min, after which 10 μL supernatant was extracted and analyzed by high performance liquid chromatography (HPLC). The sandy soil was mixed with four different concentrations of PAC (0, 0.01, 0.05, and 0.1%) to produce material with different sorption potential.

Column experiments

Column experiments were conducted using bromide and bromacil as nonreactive and reactive tracers, respectively, under different water and carbon contents (Table 1). For the experiments with different water contents (case 1: Exp. 1-3), disturbed loamy sand was used. The soil was passed through a 2.0 mm sieve (US Standard Sieve No. 10), air-dried, mixed thoroughly, and then packed uniformly into a plexiglass column (5 cm diameter and 30 cm length) up to 25 cm, and the remaining 5 cm was filled with a solution-filling system.

Equipment used in the experiments of case 1 consisted of a column leaching system and a solution-feeding system. The leaching system (Soil Measurement Systems, Tucson, AZ, USA) had a chamber with a fraction collector inside connected to the bottom of the column to automatically collect effluent and also to a vacuum source to apply a suction pressure. The feeding system consisted of a variable speed pump (Fluid Metering, Syosset, NY, USA) to feed both leaching and tracer solutions to a solution-filling system. The solution-filling system consisted of a brass cylinder with a 1 mL reservoir and a ceramic porous disc (50 mm in diameter and 6 mm in thickness) with permeability of 800 cm/min. The filling system was placed on top of the soil column to achieve uniform flow across the cross-sectional area of the soil column even at low flow rates.

In the experiments of case 1, three different water contents were obtained by imposing different suction pressures of 0, 210 and 330 mbar on the chamber while the flow rates were applied at 5.3, 2.0 and 0.2 mL/min (Table 1). The imposition of a rather high suction pressure on the bottom of

Table 1. Experimental conditions of column tests with different water contents (Exp. 1-3) and powdered activated carbon (PAC) contents (Exp. 4-7)

Exp	Soil type	θ	ρ_b $(g\ cm^{-3})$	Carbon content (%)	Suction pressure (mbar)	Flow rate (mL min^{-1})
1	Loamy sand	23.0	1.58	1.5*	330	0.2
2	Loamy sand	32.0	1.58	1.5	210	2.0
3	Loamy sand	41.0	1.58	1.5	0	5.3
4	Sandy soil	36.0	1.49	0.0^	—	1.2
5	Sandy soil	36.0	1.49	0.01	—	1.2
6	Sandy soil	36.0	1.49	0.05	—	1.2
7	Sandy soil	36.0	1.49	0.1	—	1.2

*Organic carbon content in loamy sand (Exp 1-3); ^powdered activated carbon content in sandy soil (Exp 4-7).
–: No Data.

the soil column required low inflow rates to reduce the saturated water content to the specified unsaturated water content. As soon as a steady-state flow condition was achieved, a tracer solution (50 mL) containing bromide (5 g/L) and bromacil (200 mg/L) was injected as a square pulse. To ensure a steady-state flow condition, suction pressure in the chamber was checked by a tensiometer during the experiment. At the end of the experiment, water content of the soil column was measured by the gravimetric method.

In case 2 (Exp. 4-7) where experiments were carried out with various PAC contents under saturated flow conditions, sandy soil (grain size < 2 mm) was prepared by the same procedures as described in case 1 and uniformly packed into the column (2.5 cm diameter and 30 cm length) up to 30 cm. Four different organic carbon contents were obtained by adding different percent (weight basis) of PAC (0, 0.01, 0.05, and 0.1%) to sandy soil. As soon as a steady-state flow condition was achieved, a tracer solution (50 mL) containing bromide (5 g/L) and bromacil (200 mg/L) was injected as a step change in concentration.

Effluent samples collected using an automatic sample collector were analyzed to quantify tracer concentrations. Bromide concentration was determined using ion chromatography (4500i, Dionex, Sunnyvale, CA, USA), and Bromacil concentration was quantified using high performance liquid chromatography [(HPLC)(Hewlett Packard Agilent 1100, Agilent Technologies, Palo Alto, CA, USA)] with a C18 column (Hypersil ODS, 250 × 4.0 mm, Agilent Technologies, Palo Alto, CA, USA). Elution gradient was 70% acetonitrile/30% water with a flow rate of 1.0 mL/min. Bromacil concentration was determined at a wavelength of 225 nm.

Data analysis

Transport and sorption parameters of bromide and bromacil breakthrough curves (BTCs) were estimated using the CXTFIT program,[20] which includes analytical solutions of the one-dimensional equilibrium:[21]

$$R\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v_w\frac{\partial C}{\partial x}; \quad R = 1 + \frac{\rho_b K_d}{\theta} \quad (3)$$

where C is the dissolved solute concentration, D is the hydrodynamic dispersion coefficient (L^2/T), K_d is the equilibrium distribution coefficient (L^3/M), and non-equilibrium [(two-site) (Equations 4 and 5)] convection-dispersion equations[21] without decay or degradation:

$$\left(1 + \frac{f\rho_b K_d}{\theta}\right)\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v_w\frac{\partial C}{\partial x}$$
$$- \frac{\alpha\rho_b}{\theta}[(1-f)K_d C - S_k] \quad (4)$$

$$\frac{\partial S_k}{\partial t} = \alpha[(1-f)K_d C - S_k] \quad (5)$$

where f is the fraction of sorption sites at which equilibrium can be reached, α is the mass transfer coefficient (1/T), and S_k is the sorbed chemical concentration on the kinetic sorption sites (M/M).

Transport parameters v_w and D were determined by least squares optimization from the bromide BTCs while the remaining sorption-related parameters were determined from the bromacil BTCs assuming that the values of v_w and D determined from the bromide data were the same. In the column experiments (Exp. 1-3) where a square pulse was added, mass recoveries of bromide and bromacil in the effluent were quantified by the following expression:

$$\text{Mass recovery, } M_r\ (\%) = \left(\frac{\int_0^\infty C dt}{C_o t_o}\right) \times 100 \quad (6)$$

where t_o is the duration of tracer injection (injection time).

Results and Discussion

Adsorption isotherm

The adsorption isotherms of bromacil for sandy loam and PAC-added sandy soils are shown in Figure 1. The distribution coefficient (K_d) of loamy sand (Fig. 1a) was found to be 0.087 mL/g which corresponds to a $K_{oc} = 5.8$ ml g^{-1} for the $f_{oc} = 0.015$. This K_{oc} is very low compared to the previously studied values of $K_{oc} = 34$ mL/g,[12] $K_{oc} = 72$ ml g^{-1},[22] and $K_{oc} = 57$ mL/g.[13] The K_d of PAC-added sandy soils (Fig. 1b) increased with increasing PAC content. It is noted
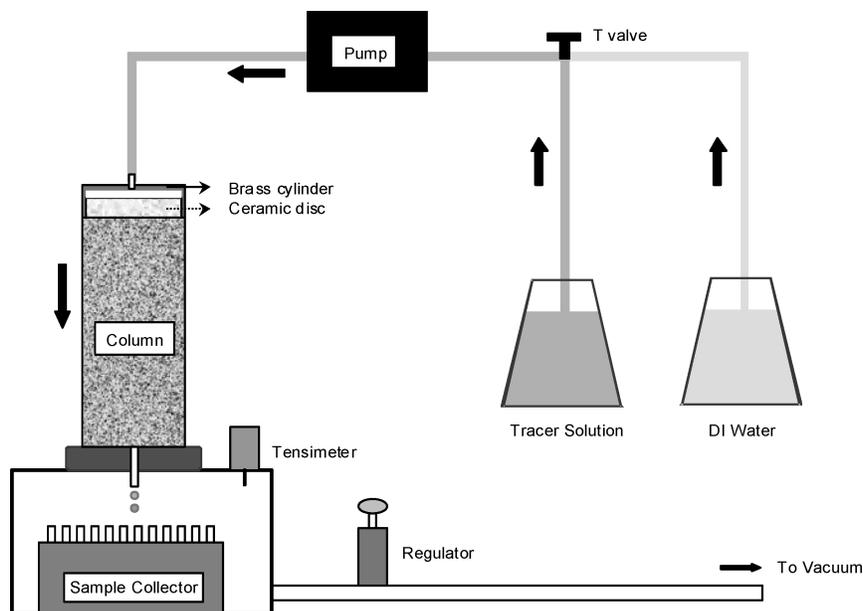
Fig. 1. Column experimental setup to obtain breakthrough data of bromide and bromacil for two sandy soils.

that the K_d of 0.081 mL/g for PAC = 0% is comparable to that obtained for loamy sand.

The partition coefficient of bromacil in PAC-added sandy soil (K_{pac}) was determined using the relationship ($K_d = f_{pac} K_{pac}$) between the distribution coefficient (K_d) measured in the batch test and the PAC fraction (f_{pac}). The value of K_{pac} was found to be 2450 mL/g based on the measurements of K_d at various PAC contents. This K_{pac} value is much higher than the K_{oc} values, which is attributed to the strong sorption behavior of PAC.

With K_{oc} (or K_{pac}) obtained from the batch test, the partition-related term, $\rho_b f_{oc} K_{oc}$ (or $\rho_b f_{pac} K_{pac}$), in Equation 2 along with retardation factor (R) were calculated (Table 2). For loamy sand, a decrease in water content from 0.41 to 0.23 resulted in an increase in R from 1.33 to 1.59, thus causing a difference in solute velocity and travel time for bromacil compared to the values obtained by neglecting $\rho_b f_{oc} K_{oc}$. Even at small amounts of organic carbon for soils at lower water content, neglect of $\rho_b f_{oc} K_{oc}$ may lead to an overestimation of travel time of bromacil.

A value of $R = 1.59$ at $\theta = 0.23$ of loamy sand is comparable to that observed by Turin and Bowman[13], who calculated R values of 1.76 and 1.63 for bromacil in sandy loam containing 0.2% organic carbon. The slightly higher value of R compared to our value, even though their soil contained much less organic carbon, seems to be due to a higher amount of clay (14.2%).

For PAC-added sandy soils, increasing carbon content from 0.0 to 0.1% resulted in an increase of R from 1.0 to 11.14, indicating that the solute velocity of bromacil through saturated soils with a trace amount of a strong sorbent such as activated carbon would be severely overestimated by neglecting $\rho_b f_{oc} K_{oc}$.

Column breakthrough data

The breakthrough data for bromide and bromacil obtained from the laboratory column experiments with different water contents in loamy sand (Exp. 1-3) along with equilibrium and non-equilibrium model fittings are shown in Figure 2.

Table 2. Partition coefficients (K_{oc} and K_{pac}) and retardation factors (R) calculated using the data obtained from the batch test

Exp	θ	ρ_b	Carbon fraction	K_{oc} (mL g^{-1})	K_{pac} (mL g^{-1})	$\rho_b f_{oc} K_{oc}$	$\rho_b f_{pac} K_{pac}$	R
1	0.23	1.58	0.015*	5.8	—	0.137	—	1.59
2	0.32	1.58	0.015	5.8	—	0.137	—	1.43
3	0.41	1.58	0.015	5.8	—	0.137	—	1.33
4	0.36	1.49	0.0^	—	2,450	—	0.0	1.0
5	0.36	1.49	0.0001	—	2,450	—	0.365	2.01
6	0.36	1.49	0.0005	—	2,450	—	1.825	6.07
7	0.36	1.49	0.0010	—	2,450	—	3.651	11.14

*Organic carbon fraction of loamy sand (f_{oc}) (Exp 1-3); ^fraction of powdered activated carbon of sandy soil (f_{pac}) (Exp 4-7).
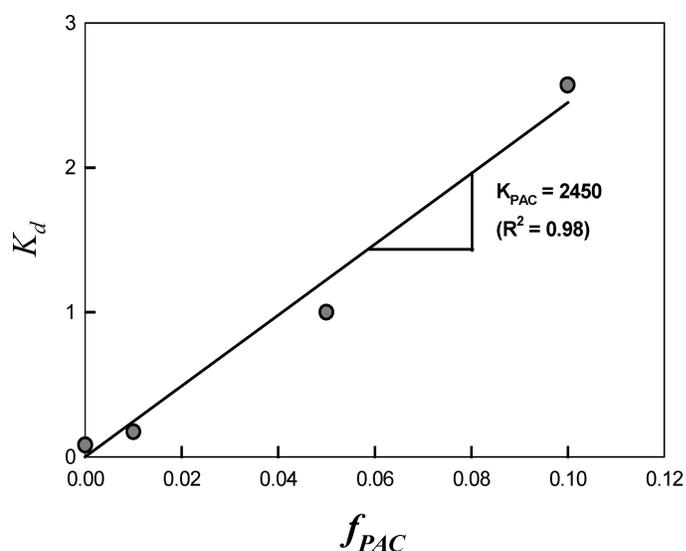–:No Data.
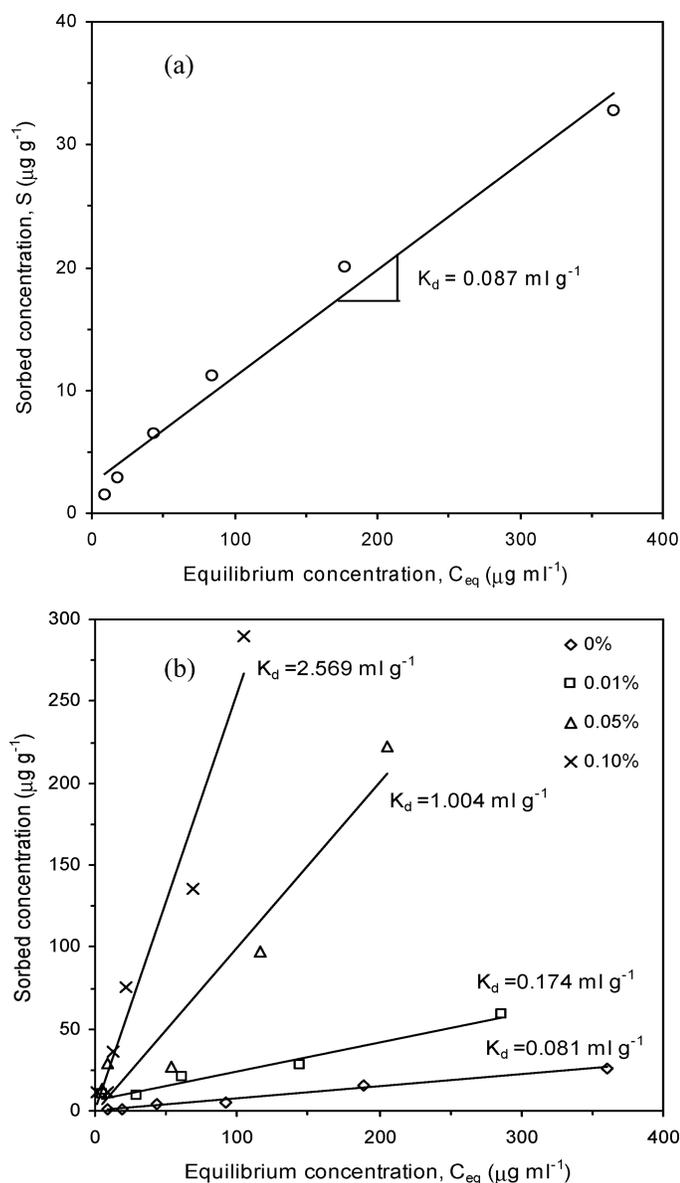
Fig. 2. Equilibrium sorption isotherms for bromacil: (a) loamy sand; (b) powdered activated carbon-added sandy soil.

Fig. 3. Determination of partition coefficient of bromacil in powdered activated carbon (PAC)-added sandy soil (K_{pac}) using distribution coefficient (K_d) from batch test and PAC fraction (f_{pac}).

model fittings were illustrated in Figure 3. The BTCs of bromide and bromacil were almost identical where no PAC was added (Fig. 3a). However, in the presence of PAC (Figs. 3b–3d), bromacil was retarded considerably compared to bromide with increasing PAC content. It also supported the importance of retardation in the estimation of travel time of bromacil in saturated flow conditions. These saturated column experiments also indicated that contribution of retardation to bromacil transport should not be neglected even when organic carbon content is low in natural soils. Neglecting organic carbon in soils and thus assuming "no retardation" would cause overestimation of solute velocity by a factor of R.

An illustration of the interacting role of water content and carbon content on retardation is shown in Figure 4 for the hypothetical case of a weakly sorbing solute (K_{oc} =10 cm^3/g) in a sandy soil (ρ_b =1.5 g/cm^3) at saturation ($\theta = 0.5$) and a low water content ($\theta = 0.05$) as a function of OC fraction. As seen in this figure, a solute with this K_{oc} moving through the same soil at a very low OC fraction 0.005 will experience virtually no sorption ($R = 1.15$) at high water content but significant sorption ($R = 2.5$) when water content drops to 0.05. Water contents at this level are not uncommon in sandy soils of the type reported by Spurlock et al.,[5] even when downward drainage is occurring. Thus, neglect of sorption (as did these authors as well as Loague et al.[3] merely because OC is low is not warranted and can cause significant travel time errors.

All BTCs showed well-defined single peaks, and mass recoveries ranged from 83 to 101% for bromide and 98 to 106% for bromacil, indicating that the column experiments were carried out successfully. Arrival time of the bromacil peak was later than that of bromide peak for all water contents, indicating that transport of reactive bromacil was retarded compared to non-reactive bromide. Retardation of bromacil in loamy sand increased with decreasing water content. Column experimental results supported the importance of retardation in the estimation of travel time of bromacil even at a small amount of organic carbon for soils with lower water content.

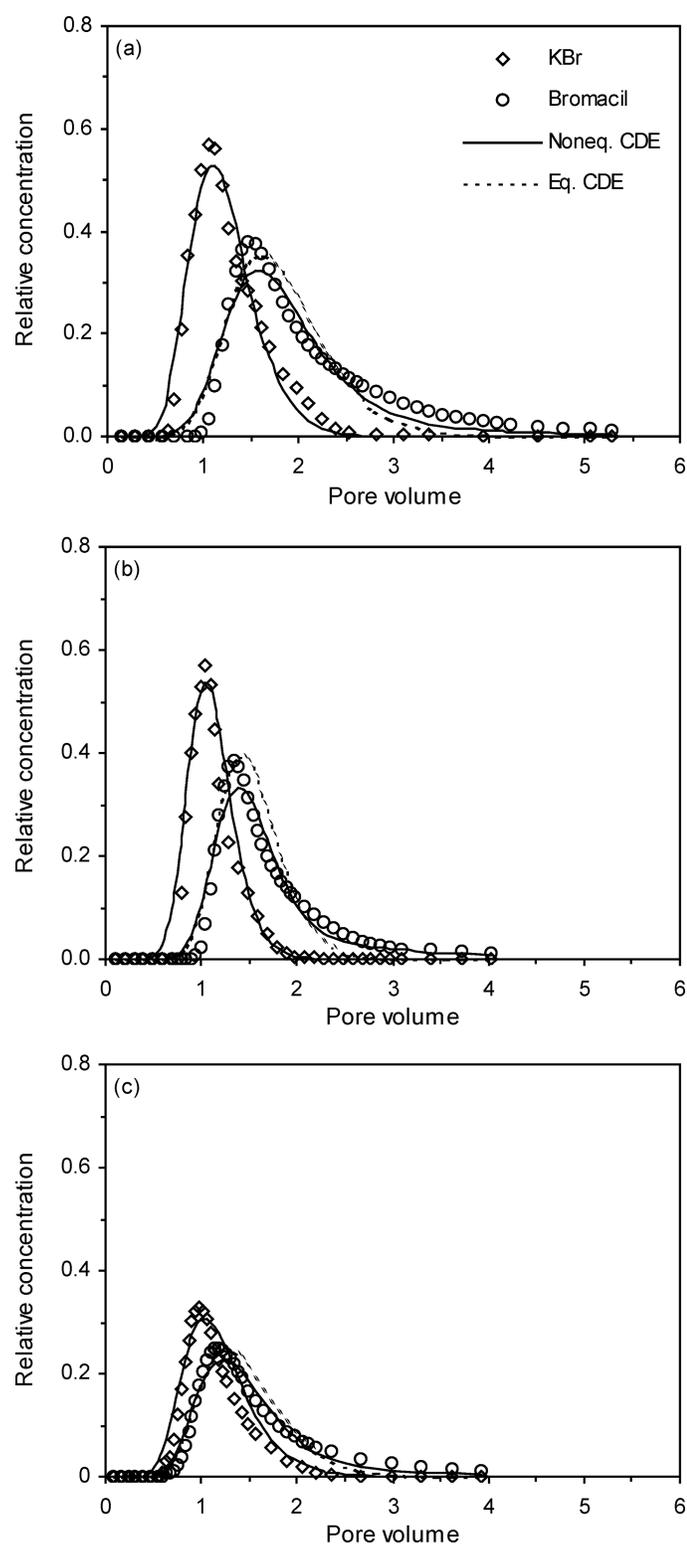Observed BTCs for PAC-added sandy soils (Exp. 4-7) for step injection along with equilibrium and non-equilibrium

Model fitting to column data

Fitted model parameters for the equilibrium and non-equilibrium (two-site) model were summarized in Table 3.
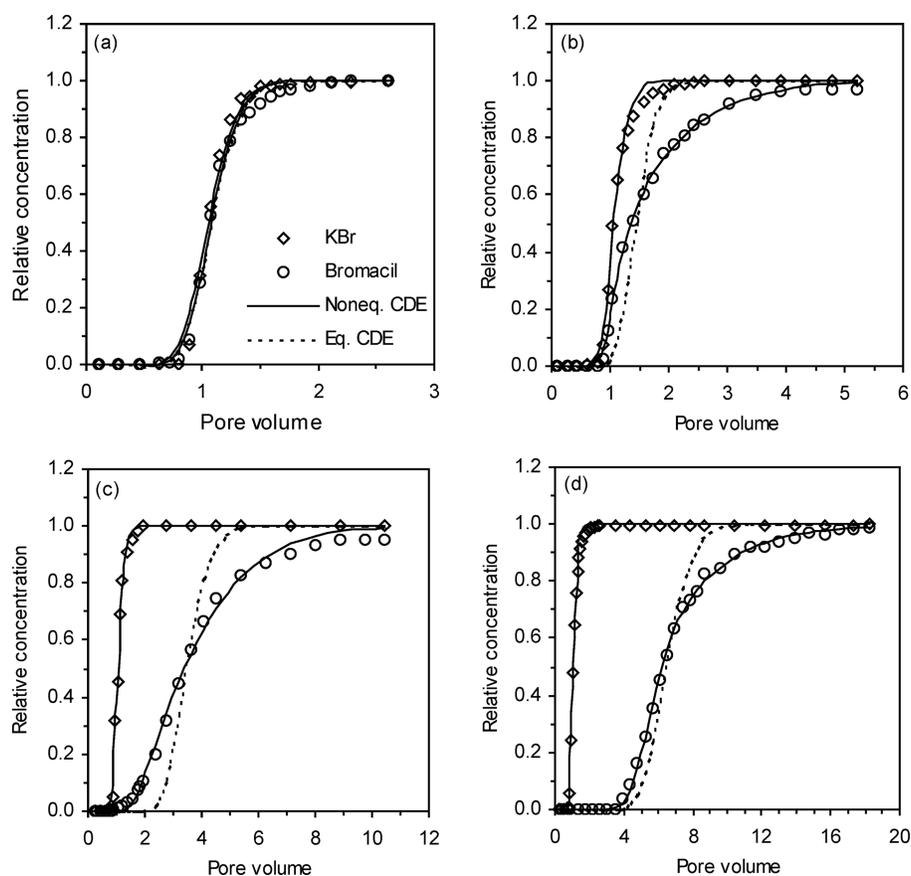
Fig. 4. Measured breakthrough curves and transport model fits for loamy sand at different water contents (Exp. 1-3): (a) 23.0%; (b) 32.0%; (c) 41.0%.

It should be noted that for loamy sand the estimated pore water velocity (v_w) decreased with decreasing water content due to a lower flux density imposed on the top of the column in order to obtain the lower water content. In the case of the non-equilibrium model, R values ranged from 1.47 to 1.73, which were slightly higher than the corresponding values from the equilibrium model. The increasing tendency of R with decreasing water content observed from the column test agrees well with the result of the batch test and also with the results of previous studies,[23] who found that retardation of bromacil was negatively correlated with pore water velocity. Similar results were also reported by several researchers,[24–26] who reported that retardation of sorbing chemicals increased with decreasing pore water velocities and/or lower water contents. The negative correlation was due to retention time of chemicals in soils[27] or a relative increase of the ratio of reactive surface sites to water volume.[28] In experimental cases where water content remained constant (Exp. 4-7), transport parameter (v_w and D) values were almost identical with estimated values of v_w ranging from 35.7 to 36.6 cm/hr and D values from 18.0 to 18.6 cm²/hr. Based on v_w and D from bromide data, R values of the equilibrium model increased from 1.02 to 5.96 with increasing PAC content. In case of the nonequilibrium model fitting, R values ranged from 1.00 to 6.49, which were slightly higher than those of the equilibrium model. Increase of R with organic carbon fraction (f_{oc}) in soil was also reported by Fesch et al. [28]

The fraction of equilibrium sites (f) increased while the mass transfer coefficient (α) decreased as both the water content and pore water velocity of loamy sand decreased. Increase of f and decrease of α for lower water content does not coincide with the result of Maraqa et al.,[9] who reported that f was independent of pore water velocity and further variations in the degree of water saturation had no impact on α for benzene transport. Independence of f from pore water velocity was also reported by Pang et al.[27] but f in their study was in fact inversely related to pore water velocity since the forward sorption rate constant (k_1) expressed as a function of (1-f) showed a proportional relation to pore water velocity. However, positive relation between v_w and α has been observed in several studies. For example, Brusseau,[29] reported that α decreased with decreasing pore water velocity because of a time-scale effect of diffusion. On the other hand, for PAC-added sandy soils f increased but α decreased as PAC content increased. The increase of f with increasing PAC content was also reported by Kim et al.,[30] indicating that bromacil sorption on PAC material is mainly controlled by rapid equilibrium sorption. The inverse relation between α and PAC content can be explained by the fact that due to the increased equilibrium sorption with increasing PAC the slow rate-limited sorption occurs at a relatively small mass of bromacil in the soil.

It should be noted that the equilibrium model fits deviated severely from the observed bromacil BTC for PAC-added sandy soils while the non-equilibrium model

Fig. 5. Measured breakthrough curves and transport model fits for powdered activated carbon (PAC)-added sandy soil at different PAC contents (Exp. 4-7): (a) 0%; (b) 0.01%; (c) 0.05%; (d) 0.1%.
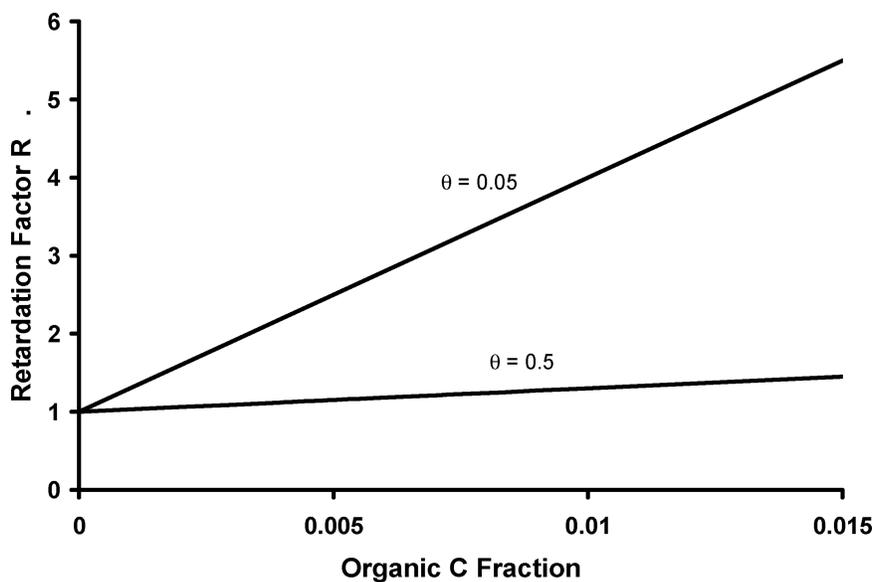
Fig. 6. Retardation factor R (equation 1) calculated as a function of organic C fraction in a hypothetical soil of bulk density $\rho_b = 1.5$ g/cm^3 at saturation $\theta = 0.5$ and a low-water content $\theta = 0.05$.

Table 3. Model parameters obtained from fitting equilibrium and nonequilibrium models to the column breakthrough data

				Equilibrium model		Nonequilibrium model			
Exp	θ	v_w (cm hr^{-1})	D (cm^{2}hr^{-1})	R	r^2	R	f	α (hr^{-1})	r^2
1	0.23	2.6	3.3	1.59	0.91	1.73	0.77	0.004	0.93
2	0.32	19.4	13.3	1.42	0.88	1.68	0.58	0.028	0.95
3	0.41	36.9	52.0	1.25	0.95	1.47	0.49	0.352	0.97
4	0.36	36.6	18.0	1.02	1.00	1.00	1.00	0.000	1.00
5	0.36	36.0	18.6	1.34	0.91	1.54	0.04	0.067	1.00
6	0.36	36.4	18.6	3.28	0.94	3.42	0.25	0.055	1.00
7	0.36	35.7	18.0	5.96	0.97	6.49	0.75	0.019	1.00

fitted perfectly to bromacil data. The deviation of the equilibrium model fit was much larger in PAC-added sandy soil than loamy sand soil as was reported by Liu et al.,[31] who found that the two-site model provided a better simulation of transport of more strongly sorbing material, and organic carbon, though small, was responsible for the sorption nonequilibrium during transport. In addition, r^2 values from the non-equilibrium model were higher than those from the equilibrium model (Table 3), indicating that the nonequilibrium model was more suitable at describing observed bromacil curves in two soils than the equilibrium one. Therefore, a proper transport model with relevant sorption parameters should be used for accurate estimation of travel time of pesticides in soils with various degrees of water saturation and organic carbon content.

Retardation factors (R) obtained from batch and column methods for various water contents and PAC contents are shown in Tables 2 and 3 respectively. For loamy sand, R values measured by the column method were higher than those from the batch method, and the deviation increased as water content decreased. For sandy soil where water content was constant but PAC content varied, the batch method yielded much higher values of R than the column methods especially for PAC = 0.05% or higher. Higher R values of reactive contaminants obtained from the batch method have been recently reported by some studies.[16,31,32] The discrepancy of R between two methods can be explained by i) chemical and physical non-equilibrium sorption in the column method due to relatively short residence time,[16] and

Table 4. Comparison of retardation factor (R) determined from batch and column tests.

		Column test	
Exp	Batch test	Nonequilibrium model	Time moment method
1	1.59	1.73	1.97
2	1.43	1.68	1.50
3	1.33	1.47	1.35
4	1.00	1.00	1.10
5	2.01	1.54	1.31
6	6.07	3.42	3.30
7	11.14	6.49	6.21

ii) low soil-to-solution ratio used in the batch test compared to the column condition.[33]

Conclusions

The significance of bromacil transport as a function of water and carbon content in soils was investigated in this study. Analysis with batch data indicated that neglect of the partition-related term in the calculation of solute velocity may lead to erroneous estimation of travel time of bromacil, i.e. an overestimation of the solute velocity by a factor of R. The column experiments showed that arrival time of the bromacil peak was larger than that of the bromide peak in soils, indicating that transport of bromacil was retarded relative to bromide in the observed conditions. Extent of bromacil retardation (R) increased with decreasing water content and increasing PAC content in two soils, respectively. Column experimental results also supported the importance of retardation in the estimation of travel time of bromacil even at small amounts of organic carbon for soils with lower water content. Model fittings indicated that the non-equilibrium model was more suitable for describing bromacil BTCs in soils than the equilibrium one. Comparison of bromacil retardation between batch and column methods revealed that the column method with the non-equilibrium model gave a slightly higher value of R for loamy sand but a much lower value of R for PAC-added sandy soil than the batch method. The magnitude of R difference between the two methods was more pronounced with increasing PAC content in sandy soil. Therefore, a proper transport model with relevant sorption parameters should be used for accurate estimation of travel time of pesticides in soils with various degrees of water saturation and organic carbon content.

Acknowledgment

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