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## Influence of Organic Cosolvents on Leaching of Hydrophobic Organic Chemicals through Soils

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■ The sorption and leaching of two herbicides (diuron and atrazine) were measured in soil columns eluted with aqueous solutions and binary solvent mixtures of methanol and water. These data were used to evaluate the solvophobic theory recently outlined for describing sorption and transport of hydrophobic organic chemicals (HOC) from mixed solvents. The retardation factor ( $R^m$ ) for both herbicides decreased drastically as the volumetric fraction of organic cosolvent ( $f^c$ ) was increased in the binary solvent mixture. The log-linear decrease in  $(R^m - 1)$  observed with increasing  $f^c$  was well predicted by the solvophobic theory. All breakthrough curves (BTCs) were asymmetrical in shape, but the extent of asymmetry decreased with increasing  $f^c$  for  $0 \leq f^c \leq 0.5$ . At  $f^c = 0.5$ , the BTCs for both diuron and atrazine were similar in shape (symmetrical and sigmoidal) and location ( $R^m = 1$ ) to that of tritiated water, a nonadsorbed tracer.

### Introduction

Most of the research on leaching of organic chemicals through soils has been done with aqueous systems. It is, however, likely that a mixture of solvents (water plus organic cosolvents) may be present at land disposal sites where these chemicals are disposed. Only a few studies to date have addressed the leaching of organic chemicals through soils by mixed solvents. Hassett et al. (1) used a soil thin-layer chromatography (TLC) technique to measure  $R_f$  values for the elution of the herbicide dicamba, 2-naphthol, and 3-methylcholanthrene by various water-methanol mixtures. Griffin and Chiou (2) also used a soil TLC method to examine the influence of organic solvents on the mobility of polybrominated biphenyls (PBBs) and hexachlorobenzene (HCB). In neither study were attempts made to quantitatively describe the relationship between leaching and the amount and the nature of the cosolvent.

Rao et al. (3) presented a solvophobic approach to predict sorption and transport of hydrophobic organic

chemicals in soils in the presence of aqueous and aqueous-organic solvent mixtures. This theory was used (3) to explain the trends in the soil TLC leaching data reported by Hassett et al. (1). The same theory was also successfully used by Nkedi-Kizza et al. (4) to predict the sorption of two herbicides (diuron and atrazine) and anthracene by several soils from binary mixtures of methanol-water and acetone-water and by Woodburn et al. (5) for diuron sorption from ternary solvent systems.

The objective of this study was to test the validity of the solvophobic theory (3) by using data for leaching of diuron and atrazine herbicides in soil columns eluted with water and binary mixtures of methanol and water.

### Theory

The retardation factor ( $R$ ) is a measure of the mobility of solute being eluted through a soil column. For displacement with water,  $R$  is given by (6)

$$R^w = 1 + \frac{\rho(\text{OC})P^w}{\theta} \quad (1)$$

where the superscript w designates water and all the terms used in eq 1 and elsewhere in this paper are defined under Glossary. For a nonadsorbed solute,  $R^w = 1.0$  since  $P^w = 0.0$ . Thus, increase in sorption ( $P^w \gg 0$ ) leads to an enhanced retardation of solute leaching ( $R^w \gg 1$ ).

The retardation factor ( $R^m$ ) for leaching with binary solvent mixtures is given by (3)

$$R^m = 1 + \frac{\rho(\text{OC})P^m}{\theta} \quad (2)$$

where

$$P^m = P^w \exp(-\alpha\sigma^c f^c) \quad 0 \leq f^c \leq 1 \quad (3)$$

$$\sigma^c \simeq \Delta\gamma^c(\text{HSA})/kT \quad (4)$$

The superscripts m and c denote respectively mixed sol-

Table I. Soil Column Data for Various Displacements

expt no.	column no.	solute	methanol fraction ( $f^c$ )	bulk density $\rho$ , g/cm <sup>3</sup>	water content $\theta$ , cm <sup>3</sup> /cm <sup>3</sup>	pore-water velocity, cm/h
1	1	diuron <sup>a</sup>	0.0	1.64	0.38	5.58
2	2	<sup>3</sup> H <sub>2</sub> O	0.0	1.56	0.41	5.18
3	2	diuron	0.03	1.56	0.41	5.18
4	2	diuron	0.10	1.56	0.41	5.18
5	2	diuron	0.30	1.56	0.41	5.18
6	2	diuron	0.50	1.56	0.41	5.18
7	3	<sup>3</sup> H <sub>2</sub> O	0.0	1.77	0.33	6.44
8	3	atrazine <sup>b</sup>	0.0	1.77	0.33	6.44
9	3	atrazine	0.10	1.77	0.33	6.44
10	3	atrazine	0.30	1.77	0.33	6.44
11	3	atrazine	0.50	1.77	0.33	6.44

<sup>a</sup>  $C_0 = 30 \mu\text{g/mL}$  for diuron. <sup>b</sup>  $C_0 = 20 \mu\text{g/mL}$  for atrazine.

vent and cosolvent. It could be noted that in deriving eq 1 and 2 it has been assumed that solvent-solute-sorbent interactions are predominantly hydrophobic (3).

Rearranging eq 2 and using eq 3 we get

$$\ln(R^m - 1) = \ln \left[ \frac{\rho(\text{OC})P^w}{\theta} \right] - \alpha\sigma^c f^c \quad (5)$$

The two limiting values of  $\ln(R^m - 1)$  are given by

$$\ln(R^m - 1) = \begin{cases} \ln(R^w - 1) & f^c = 0 \\ \ln(R^w - 1) - \alpha\sigma^c & f^c = 1 \end{cases} \quad (6a)$$

$$f^c = 1 \quad (6b)$$

From the above equations, it is evident that the term  $(R^m - 1)$  decreases exponentially as  $f^c$  increases from 0 (i.e., water) to 1.0 (i.e., pure organic solvent).

### Experimental Section

Sorption and leaching experiments were conducted with two herbicides: diuron [3-(3,4-dichlorophenyl)-1,1-dimethylurea] and atrazine [2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine]. These two herbicides were chosen because a considerable amount of sorption data for these pesticides already exists (7-10). Eustis soil (Typic Quartzipsamments) was used in this study because it has a low organic carbon content ( $\text{OC} = 0.002$ ). This means that pesticide sorption on this soil will be low, such that the residence time during the leaching experiments will be short enough to avoid microbial degradation. Eustis soil used in this study had a pH of 5.7 (1:1 paste in 0.1 N  $\text{CaCl}_2$ ).

**Sorption Isotherms.** Sorption isotherms were measured with the batch equilibration method (4, 11). For each pesticide-soil combination, sorption isotherms were measured in aqueous solutions (with 0.01 N  $\text{CaCl}_2$  as the supporting electrolyte) as well as in various binary solvent mixtures of methanol and water. All pesticide solutions were spiked with the appropriate <sup>14</sup>C-labeled compound to give radioisotope activity of about 0.2  $\mu\text{Ci/mL}$ .

For measuring atrazine and diuron sorption isotherms in aqueous solutions, 5 mL of pesticide solution was added to 5 g of soil in Pyrex culture tubes fitted with Teflon-lined screw caps. The tubes were tumbled end-over-end on a shaker for 24 h at ambient temperature ( $298 \pm 1 \text{ K}$ ). At the end of the equilibrium period, the tubes were centrifuged at 3580g for 20 min, and <sup>14</sup>C activity in clear supernatant solutions was assayed by liquid scintillation techniques (4). The maximum initial solution concentrations used for isotherm experiments were 30  $\mu\text{g/mL}$  for diuron and 20  $\mu\text{g/mL}$  for atrazine.

Sorption of diuron and atrazine from binary solvent mixtures was measured as follows. The pesticide solutions were prepared in 0.01 N  $\text{CaCl}_2$ , and then an appropriate

volume of methanol was added to give the desired volumetric fraction cosolvent ( $f^c$ ). A larger soil:solution ratio was used at higher  $f^c$  in order to improve the precision with which sorption could be measured (12) as sorption was expected to decrease rapidly with increasing  $f^c$  (3, 4). All sorption data were fitted to the Freundlich equation ( $S = KC^N$ ), and the values of  $K$  and  $N$  were estimated by least-squares minimization procedures.

**Column Experiments.** Air-dry Eustis soil was packed into preparative high-performance liquid chromatography (HPLC) glass columns (ALTEX; catalogue no. 252-18), 2.5 cm in diameter and 30 cm in length. These columns are furnished with standard HPLC fittings so that they can be connected directly to HPLC pumps and detectors. Effluent breakthrough curves (BTCs) for diuron and atrazine were measured under steady saturated water flow conditions with a step-input boundary condition. BTCs were measured with aqueous solutions ( $f^c = 0.0$ ) and various methanol-water mixtures ( $0.0 \leq f^c \leq 0.5$ ). For each column, BTCs for tritiated water (<sup>3</sup>H<sub>2</sub>O) were also measured; these BTCs served as a reference for a nonadsorbed solute. Pesticide concentrations in the column effluent were measured either by use of a flow-through variable-wavelength UV detector (Waters Model 450) or by assaying radioactivity in effluent fractions with liquid scintillation techniques. Pertinent soil column data are summarized in Table I.

**Estimation of  $R^m$ .** An accurate determination of  $R^m$  in eq 2 is necessary in order to test the solvophobic theory during leaching of HOC through soil. There is no agreed on method in the literature for estimating  $R^m$  for HOC transport. Therefore, we decided to compare four methods of estimating  $R^m$  in order to select the best method to be used in verifying eq 2.

Four different methods were used to calculate the leaching retardation factors ( $R^m$ ). Two of these methods (methods 1 and 2) utilize sorption isotherm data, while the other two (methods 3 and 4) involve analyzing the column BTC data. This allowed for a comparison of sorption behavior measured under static conditions (batch isotherms) with that characterized under dynamic flowing conditions (BTC data).

In method 1,  $R^m$  values were calculated from

$$R^m = 1 + \frac{\rho K^m C_0^{N-1}}{\theta} \quad 0 \leq N \leq 1 \quad (7)$$

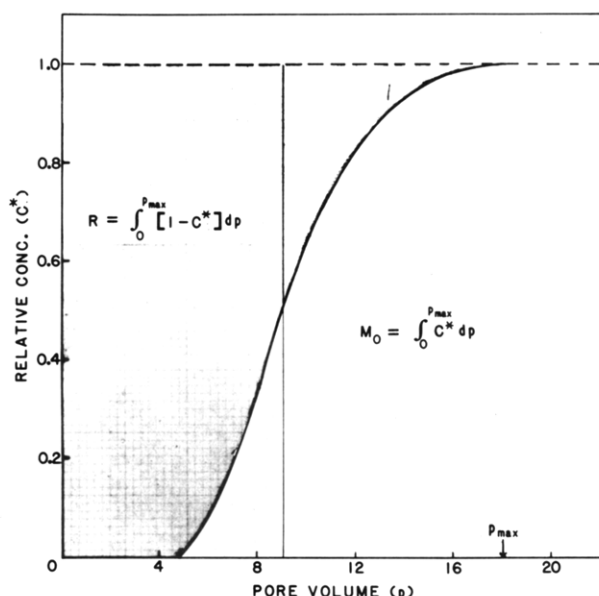
The  $R^m$  value computed by using eq 7 is appropriate for a BTC obtained by continually eluting the soil column with a pesticide solution of  $C_0$  concentration (13). Values of  $K^m$ ,  $\rho$ ,  $\theta$ ,  $C_0$ , and  $N$  were measured in this study.

Equations 2-4 were used in method 2 to calculate the  $R^m$  value with the values of  $P^w$ ,  $\text{OC}$ ,  $\sigma^c$ , and HSA reported

**Table II.** Values of  $\sigma^c$ ,  $P^w$ , and HSA Used To Calculate  $R^m$  in Method 2<sup>a</sup>

pesticide	$\sigma^c$	$P^w$ , mL/g	HSA, Å <sup>2</sup>
diuron	7.11	426	147
atrazine	6.99	96	144

<sup>a</sup> All values were taken from Nkedi-Kizza et al. (4).



**Figure 1.** Graphical representation of retardation factor ( $R^m$ ) calculation using method 4.

in the literature (see Table II). Also,  $\rho$  and  $\theta$  values for a specific column (Table I) and OC = 0.002, as well as  $\alpha$  = 0.83 on the basis of Karickhoff (8), were used to calculate  $R^m$ .

In method 3, the value of  $R^m$  was set equal to the number of pore volumes ( $p$ ) required for the effluent pesticide concentration ( $C_L$ ) to reach  $0.5C_0$ . This method is based on the assumption of symmetrical sigmoidal BTCs. The method involves the implicit assumption that equilibrium conditions prevail during HOC leaching through the soil columns. This method is the basis on which solute peak travel velocity (equivalent to retention time in chromatography) is used in estimating the retardation factor ( $R$ ) in the eluted pulse technique (5). This technique of estimating  $R$  has been used by earlier researchers (14–16).

Method 4 is based on the conservation of mass principle and involves computing the area above the pesticide BTC. As illustrated in Figure 1

$$R = \int_0^{p_{max}} 1 - C^* dp \quad (8)$$

Additional details for derivation of eq 8, which shows that the area above the BTC can be used to estimate the retardation factor, are presented in the Appendix. This approach of estimating  $R$  has been recognized by earlier workers (17, 18), but the method has not been tested with experimental data. The areas above the BTCs were determined by planimetry with a graphics tablet attached to an Apple II Plus microcomputer.

## Results and Discussion

**Sorption Isotherms.** Equilibrium isotherm data for sorption of diuron and atrazine on Eustis soil from aqueous and binary solvent mixtures are presented in Table III. For both herbicides the sorption coefficient  $K^m$  decreases rapidly as the fraction of the organic cosolvent ( $f^c$ ) in the

**Table III.** Freundlich Constants ( $K^m$  and  $N$ ) for Diuron and Atrazine Sorption on Eustis Soil<sup>a</sup>

methanol fraction ( $f^c$ )	chemical			
	diuron		atrazine	
	$K^m$	$N$	$K^m$	$N$
0.0	1.44 (1.16–1.80)	0.82 ( $\pm 0.14$ )	0.15 (0.05–0.28)	1.0
0.03	1.29 (2.07–2.84)	0.83 ( $\pm 0.11$ )	ND <sup>b</sup>	ND
0.10	0.84 (0.72–0.98)	0.91 ( $\pm 0.14$ )	0.07 (0.04–0.08)	1.0
0.30	0.26 (0.19–0.35)	0.87 ( $\pm 0.24$ )	0.03 (0.02–0.05)	1.0
0.50	0.05 (0.01–0.011)	1.04 ( $\pm 0.08$ )	0.02 (0.01–0.05)	1.0

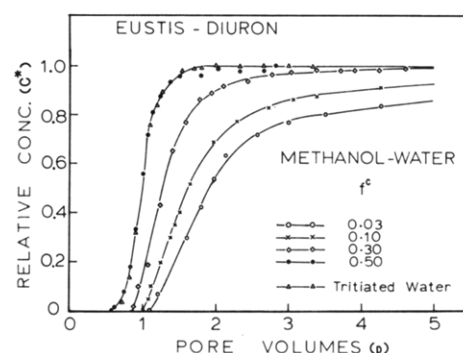
<sup>a</sup> Numbers in parentheses are for the 95% confidence interval. <sup>b</sup> ND = not determined.

**Table IV.** Effect of Organic Cosolvent (Methanol) on Diuron Mobility ( $R^m$ ) in Eustis Soil

expt no.	fraction of cosolvent ( $f^c$ )	method for calculating $R^m$			
		1	2	3	4
1	0.0	4.25	4.68	1.90	4.37
3	0.03	3.73	3.72	1.73	3.75
4	0.10	3.35	2.80	1.52	3.13
5	0.30	1.63	1.55	1.25	1.40
6	0.50	1.19	1.17	1.0	1.01

**Table V.** Effect of Organic Cosolvent (Methanol) on Atrazine Mobility ( $R^m$ ) in Eustis Soil

expt no.	fraction of cosolvent ( $f^c$ )	method for calculating $R^m$			
		1	2	3	4
8	0.0	1.80	2.03	1.39	1.80
9	0.10	1.38	1.58	1.14	1.28
10	0.30	1.16	1.18	1.03	1.13
11	0.50	1.10	1.06	1.0	1.003



**Figure 2.** Breakthrough curves for diuron and tritium displacement through Eustis soil column.

solvent mixture increases. The exponential decrease in  $K^m$  values as a function of  $f^c$  could be predicted by the solvophobic theory (3–5). The decrease in sorption coefficient ( $K^m$ ) can be attributed to an increase in pesticide solubility as the organic cosolvent fraction increases (3).

**Leaching Experiments.** The breakthrough curves (BTCs) for isocratic elution of diuron and atrazine through Eustis soil columns by methanol–water solvent mixtures are presented in Figures 2 and 3. As  $f^c$  was increased from 0 to 0.5, the pesticide BTCs shifted progressively to the left until at  $f^c$  = 0.5 the BTCs for both pesticides were essentially identical with those for tritiated water (nonadsorbed tracer). A leftward shift of BTCs, with a decrease in the area above the BTC, indicates a decrease in the retardation of pesticide leaching in the soil column as a result of a decrease in sorption. Both of these trends are consistent with eq 2.

$R^m$  values computed with the sorption and BTC data are summarized in Tables IV and V. Retardation factors

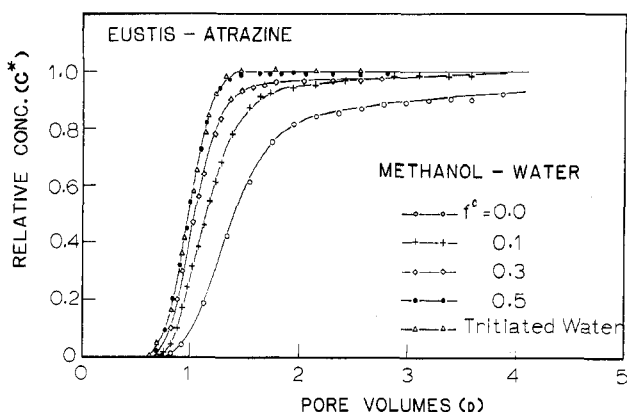


Figure 3. Breakthrough curves for atrazine and tritium displacement through Eustis soil column.

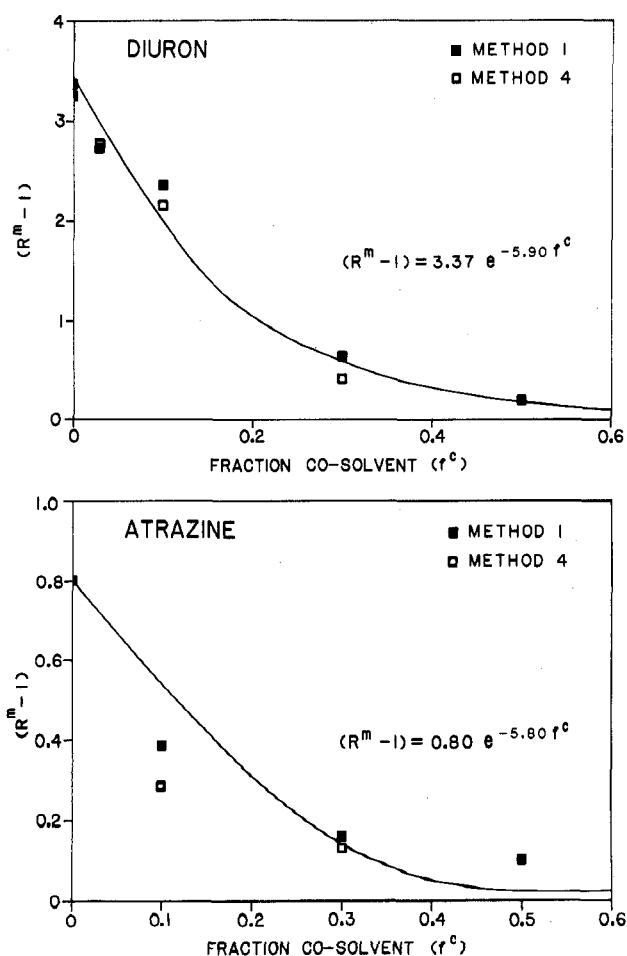


Figure 4. Log-linear decrease of  $R^m - 1$  values as a function of the organic cosolvent fraction ( $f^c$ ).

calculated on the basis of methods 1 and 4 are in close agreement at each  $f^c$ . The  $R^m$  values decrease rapidly with increasing  $f^c$ ; the log-linear decrease in  $R^m - 1$  values for diuron and atrazine with  $f^c$  is shown in Figure 4. The retardation factors calculated with eq 2 (method 2) are close to those calculated with batch sorption data (eq 7; method 1). It should be noted that an average  $P^w$  value based on literature data was used to calculate  $R^m - 1$  with method 2. The estimated value of  $P^w$  may vary within a factor of 2 as reported in the literature for a wide range of soils and sediments (8-10, 18). However, the maximum deviation between  $R^m$  values calculated with methods 1, 2, and 4 is only 20%. Another reason why  $R^m$  values calculated on the basis of method 2 are larger than those obtained with methods 1 and 4 is that in deriving eq 2 it

Table VI. Empirical Index of Sorption Nonequilibrium (ISNE) for Diuron and Atrazine Leaching through Eustis Soil

methanol fraction ( $f^c$ )	ISNE	
	diuron	atrazine
0.0	57	23
0.03	54	ND <sup>a</sup>
0.10	51	11
0.30	11	9
0.50	0	0

<sup>a</sup>ND = not determined.

was implicitly assumed that the isotherms are linear (3), whereas in methods 1 and 4 the nonlinear nature of the isotherms is accounted for. When the isotherms are linear, as for atrazine, there is a close agreement between  $R^m$  values calculated by methods 1, 2, and 4.

The BTCs for diuron and atrazine (Figures 2 and 3) are asymmetrical, while those for the tritiated water are sigmoidal and symmetrical in shape. The asymmetry in herbicide BTCs can be attributed to sorption nonequilibrium during leaching through the soil columns. Similar asymmetry in pesticide BTCs has been reported by a number of investigators (11, 20, 21). A relative measure of asymmetry in pesticide BTCs is given by the differences in the  $R^m$  values calculated by method 3 from those calculated by methods 1 and 4.  $R^m$  values estimated by methods 1 and 4 are in good agreement (Figure 4). The  $R^m$  values calculated by method 4 were therefore used to provide an empirical index for the degree of sorption nonequilibrium (ISNE) of HOC during leaching through soil:

$$\text{ISNE} = \frac{R_4^m - R_3^m}{R_4^m} \times 100 = \begin{cases} 0 & \text{if } R_4^m = R_3^m \\ 100 & \text{if } R_4^m \gg R_3^m \end{cases} \quad (9)$$

where  $R_3^m$  and  $R_4^m$  are retardation factors calculated by methods 3 and 4, respectively.

The calculated values of ISNE for diuron and atrazine as a function of the fraction of cosolvent are presented in Table VI. These data indicate that sorption nonequilibrium or BTC asymmetry (as defined in eq 9) decreases as  $f^c$  increases; for  $f^c > 0.5$ , both diuron and atrazine behave as a nonadsorbed tracer ( $R = 1$ ). Although diuron and atrazine have been shown to have similar TSA and HSA (about 66% of TSA) (4), diuron exhibits more nonequilibrium than atrazine (Table VI). The analysis presented in Table VI is intended to emphasize that the extent of asymmetry in BTCs decreases with increasing  $f^c$ . This could imply that the cosolvent (methanol) has an influence on the rate at which sorption equilibrium is attained during leaching. Freeman and Cheung (22) reported similar effects of organic cosolvents on desorption kinetics of HOC.

#### Summary and Conclusions

Data are presented for leaching of two pesticides in soil columns eluted with aqueous solutions and binary solvents. The trends in the data are consistent with the predictions based on the solvophobic theory (3). Increasing the fraction of organic cosolvent results in an exponential decrease in sorption, which, in turn, leads to an enhanced pesticide mobility through the soil. These data and the solvophobic approach may be used to quantitatively describe leaching of hydrophobic organic chemicals in the presence of mixed solvents.

It is also apparent from this study that batch isotherm data for hydrophobic organic chemicals can be used to predict HOC mobility in soils in aqueous solutions or in

mixed solvents. The retardation factor values ( $R^m$ ) calculated by method 1, which accounts for isotherm non-linearity, are in agreement with values calculated from the areas above the effluent BTCs (method 4). The observed decrease in asymmetry in the BTCs for hydrophobic organic chemicals with increasing  $f^c$  was attributed to the organic cosolvent effects on soil organic matter.

#### Glossary

$C$	equilibrium solution concentration ( $\mu\text{g/mL}$ )
$C_o$	influent solution concentration ( $\mu\text{g/mL}$ )
$C_L$	effluent solution concentration ( $\mu\text{g/mL}$ )
$C^*$	$C_L/C_o$ , relative effluent solution concentration
$f^c$	fraction of organic cosolvent, $0 \leq f^c \leq 1$
$g$	acceleration due to gravity ( $\text{cm/s}^2$ )
HSA	hydrocarbonaceous surface area ( $\text{\AA}^2$ )
$k$	Boltzmann constant ( $\text{erg/K}$ )
$K$	Freundlich sorption coefficient ( $\text{mL}^N \mu\text{g}^{1-N} \text{g}^{-1}$ )
$K_D$	sorption coefficient ( $\text{mL/g}$ )
$K^m$	sorption coefficient in mixed solvent systems ( $\text{mL}^N \mu\text{g}^{1-N} \text{g}^{-1}$ )
$K^w$	sorption coefficient in water ( $\text{mL}^N \mu\text{g}^{1-N} \text{g}^{-1}$ )
$L$	column length ( $\text{cm}$ )
$m$	total mass of soil in the column ( $\text{g}$ )
$M_c$	total mass of pesticide (solution phase + solid phase) retained in the column ( $\mu\text{g}$ )
$M_i$	total mass of pesticide applied to the soil column ( $\mu\text{g}$ )
$M_o$	total mass of pesticide leached out of the column ( $\mu\text{g}$ ) (i.e., area under the BTC)
$N$	Freundlich constant (dimensionless)
OC	organic carbon content ( $\text{g/g}$ )
$p$	$V/V_o$ , pore volumes
$p_{\max}$	$V_{\max}/V_o$ , total pore volumes displaced through the column
$P^m$	$K^m/(\text{OC})$ , sorption coefficient normalized with organic carbon content of the soil ( $\text{mL/g}$ of OC)
$P^w$	$K^w/(\text{OC})$ , sorption coefficient normalized with organic carbon content of the soil ( $\text{mL/g}$ of OC)
$R$	retardation factor (area above the BTC)
$R_f$	$1/R$ , retention factor on soil TLC plates
$R^m$	retardation factor in mixed solvent system
$R^w$	retardation factor in aqueous system
$S$	equilibrium sorbed concentration ( $\mu\text{g/g}$ )
$T$	ambient temperature ( $\text{K}$ )
$V$	effluent volume ( $\text{mL}$ )
$V_c$	total empty column volume ( $\text{cm}^3$ )
$V_o$	total solution volume in the column ( $\text{mL}$ )
$\alpha$	empirical constant (dimensionless)
$\gamma^w$ and $\gamma^c$	interfacial free energy at the aqueous interface and the organic cosolvent interface, respectively, with the hydrocarbonaceous surface area (HSA) of the sorbate ( $\text{erg/\AA}^2$ )
$\Delta\gamma^c$	$\gamma^w - \gamma^c$
$\theta$	$V_o/V_c$ , water content ( $\text{cm}^3/\text{cm}^3$ )
$\rho$	$m/V_o$ , bulk density ( $\text{g/cm}^3$ )

#### Appendix

The total solute mass introduced into the soil column ( $M_i$ ) and that exiting the soil column ( $M_o$ ) are given by

$$M_i = V_{\max} C_o \quad (\text{A-1})$$

$$M_o = \int_0^{V_{\max}} C_L dV \quad (\text{A-2})$$

The solute mass remaining in the column ( $M_c$ ), calculated as the difference ( $M_i - M_o$ ), is distributed between the solution and adsorbed phases. Therefore

$$V_{\max} C_o - \int_0^{V_{\max}} C_L dV = V_o C_o + m K_D C_o \quad (\text{A-3})$$

Dividing both sides of eq A-3 by  $V_o C_o$  and noting that

$$V/V_o = p, V_{\max}/V_o = p_{\max}, \text{ and } C^* = C_L/C_o$$

$$p_{\max} - \int_0^{p_{\max}} C^* dp = 1 + \frac{m K_D}{V_o} \quad (\text{A-4})$$

Recognizing that  $m/V_o = \rho$  and  $V_o/V_c = \theta$ , where  $V_c$  is the total column volume, eq A-5 can be restated as

$$p_{\max} - \int_0^{p_{\max}} C^* dp = 1 + \frac{\rho K_D}{\theta} = R \quad (\text{A-5})$$

Equation A-5 can be arranged to get

$$R = \int_0^{p_{\max}} 1 - C^* dp \quad (\text{A-6})$$

**Registry No.**  $\text{CH}_3\text{OH}$ , 67-56-1;  $\text{H}_2\text{O}$ , 7732-18-5; diuron, 330-54-1; atrazine, 1912-24-9.

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