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Estimation of Chemical Mobility in Soil from Liquid Chromatographic Retention Times

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A new method based on high performance liquid chromatography has been developed to assess the mobility potential of chemicals through soil. VEITH et al. (1979) have demonstrated the relationship between a chemical's retention time on a reverse phase HPLC column with its octanol/water partition coefficient (K_{ow}). BRIGGS (1973), and more recently KENAGA and GORING (1978), have shown the correlation which exists between K_{ow} and K_{oc}, the soil adsorption coefficient. SWANN et al. (1979) reported briefly on the correlation between measured K_{oc} values and HPLC retention times for several chemicals, while McCALL et al. (1979) outlined the relationship between K_{oc} and leaching distances on soil columns for those same materials.

In this paper data from the column leaching and HPLC experiments are combined to develop a mobility classification system based on HPLC retention times of chemicals. Such a technique can provide a rapid, reliable and inexpensive method to evaluate a chemical's transport potential through soil.

METHODOLOGY

The procedures and materials used to measure retention time, K_{oc} values and extent of column leaching are detailed by SWANN et al. (1979) and McCALL et al. (1979). In brief, these properties were measured for the following ^{14}C radiolabeled compounds: DDT, chlorpyrifos, trifluralin, diuron, nitrapyrin, lindane, carbaryl, carbofuran and 2,4-D. Measurements were made with soils whose properties are given below.

Soil	Location	% Organic Carbon	pH	Sand	Silt	Clay
Commerce	Miss.	0.68	6.7	38	48	14
Tracy	Ind.	1.12	6.2	56	30	14
Catlin	Ill.	2.01	6.2	12	56	32

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Adsorption measurements were made by equilibrating each chemical in a 1:4 soil:water slurry at solution concentration below the water solubility or at 1 ppm whichever was lower. Adsorption coefficients (K_d) were calculated from the ratio of the concentration of chemical/g soil to the concentration of chemical/g water. These values were then divided by the fraction of organic carbon present in each soil to obtain K_{oc} values.

Column leaching measurements were made with each chemical in each soil using 25 cm water saturated soil columns. After addition of chemical to the top of the column, the column was eluted with 20 acre inches of water as a 0.01 M $CaSO_4$ solution at a 1 cm/hr flow rate. After elution, the depth of penetration of the chemical was determined.

High performance liquid chromatography was performed to measure retention time of each chemical. The chemicals were chromatographed using a Waters Model 6000A pump in conjunction with an RCM 100 radial compression unit and a C_{18} reverse phase μBondapak column. Samples were injected with a Waters Intelligent Sample Processor and eluted at 1 ml/min with $MeOH:H_2O$ (85:15 v/v); peaks were detected with an Altex-Hitachi Model 100-40 u.v. detector. Retention times were recorded on a Hewlett-Packard Model 3380 integrator.

RESULTS AND DISCUSSION

Data from SWANN et al. (1979) and McCALL et al. (1979) are shown in Table 1 for three soils.

TABLE 1

Relationships between soil adsorption coefficients, soil, column leaching distance, and HPLC retention times for nine chemicals.

Chemical	HPLC Retention Time (min.)	K_{oc}[1]	Leaching Distance (cm)		
			Commerce	Tracy	Catlin
2,4-D	2.20	57	> 25	> 25	> 25
Carbofuran	3.88	105	> 25	> 25	> 25
Carbaryl	4.31	310	16	9	5.5
Diuron	5.08	387	17.5	7	3.5
Nitrapyrin	6.70	458	10	6	3.0
Lindane	7.00	735	6	4	1.5
Trifluralin	14.62	4,340	1	.5	.5
Chlorpyrifos	15.01	6,070	1	.5	.5
DDT	21.93	150,000	0	0	0

[1] Average of K_{oc} values from all three soils.

A clear correlation between retention time, K_{oc} and leaching distance is evident. Chemicals with higher K_{oc} values have longer retention times on reverse phase HPLC and and leach less. The plot of ln retention time vs ln K_{oc} presented in Figure 1 shows a linear relationship which can be used in the estimation of K_{oc} values for any chemical from its retention time. In doing so it is important to note that retention times are not absolute but values will vary among different manufacturer's instruments and columns. However, the relative relationship among chemicals holds and variation in absolute retention time can be overcome with calibration by a set of standard compounds.

HAMAKER (1975) has shown from chromatographic theory that the distance a chemical will leach can be related to its soil adsorption coefficient. The distance a chemical moves through a soil column is inversely proportional to its adsorption coefficient. Therefore, a plot of $1/(K_{oc} \times O.C.)$ or $1/K_d$ vs distance moved should be linear. Such a plot is shown in Figure 2 for Tracy soil; similar plots are obtained for the other two soils. Since 2,4-D and carbofuran

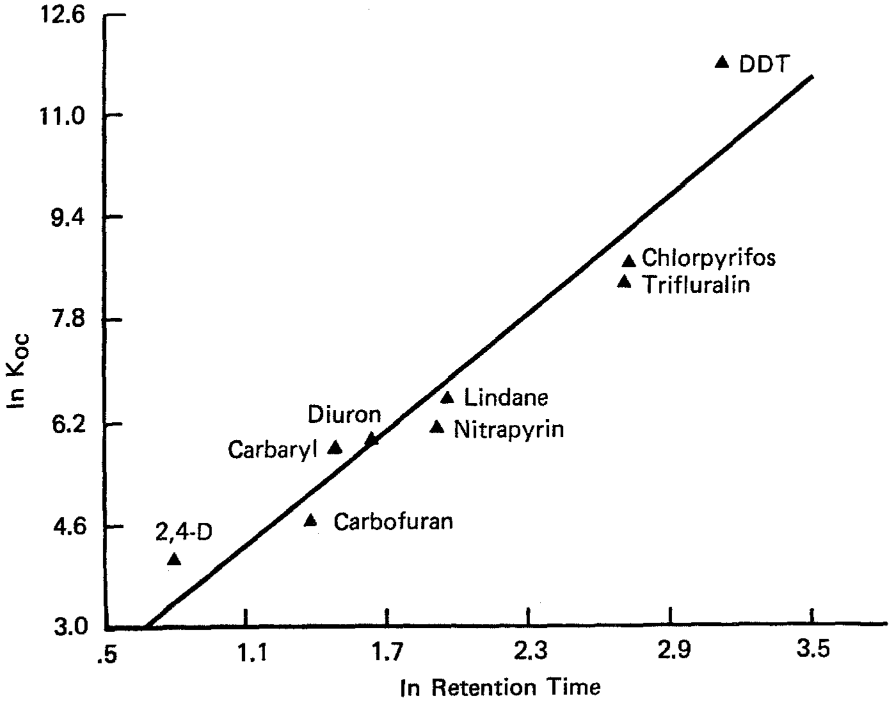

FIGURE 1. CORRELATION OF SOIL ADSORPTION COEFFICIENT WITH HPLC RETENTION TIME FOR NINE ORGANIC CHEMICALS.

leached completely through the columns they are not included in Figure 2.

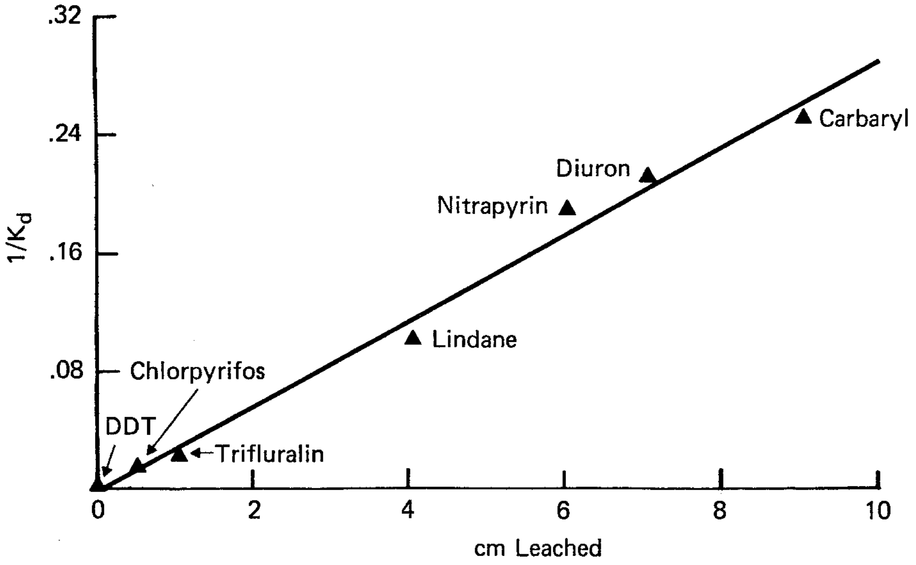

FIGURE 2. CORRELATION OF COLUMN LEACHING DISTRIBUTION WITH SOIL ADSORPTION COEFFICIENT.

The effect of organic carbon on leaching is also evident from the data in Table I. In the lower organic carbon soil (Commerce) where adsorption is the least, the chemicals are observed to move farther; distance moved decreases with increasing organic carbon in the other two soils.

These data establish a relationship between HPLC retention time and K_{oc} and between leaching distance and K_{oc}. Such correlations can be valuable in the prediction of chemical behavior in soil with respect to transport. Retention time of a chemical can be measured relative to several standard compounds to estimate its K_{oc} value, then a prediction of its mobility can be made. A classification system with general mobility classes is proposed in Table II where retention time is normalized such that 2,4-D has a value of 1.0.

TABLE II

Classification of soil mobility potential of chemicals from HPLC retention times.

Retention Time Relative to 2,4-D	K_{oc}	Mobility Class	Helling's Classification Scheme
0-1	0-50	Very High	5
1-1.8	50-150	High	4
1.8-3.1	150-500	Medium	3
3.1-4.5	500-2000	Low	2
4.5-7.0	2000-5000	Slight	1
>7.0	>5000	Immobile	1

This type of scheme provides the means to rank chemicals based on their physical properties (adsorption coefficients) as to their potential to move through soil. HELLING and TURNER (1968) have proposed a similar five point ranking system established from soil TLC studies, which is shown in Table II for comparison. In general the classification is similar with the exception that soil TLC cannot distinquish the relative degree of adsorption between chemicals that stay near the bottom of the plate. Although two chemicals with K_{oc}'s of 5000 and 50,000 are both essentially immobile by both ranking systems, the system based on K_{oc} values or relative HPLC retention times shows the inherent difference between the two chemicals.

Furthermore, this study indicates that K_{oc} values can provide a reliable estimate of a chemical's potential mobility without performing demonstrative tests such as column leaching on soil TLC studies. Results of such tests are highly dependant on the conditions under which they are conducted and the soils employed. Therefore it is difficult to compare results obtained in different studies. The use of K_{oc} values, however, can establish a common basis for comparison and eliminate the need for supportive type testing.

CONCLUSION

Mobility of a chemical through soil is a primary factor in assessment of its environmental fate. It is useful in the preliminary evaluation of new or existing chemicals to have a rapid and simple means to estimate mobility potential. HPLC can provide this type of tool for estimation of soil adsorption coefficient and therefore the tendency of a chemical to move through soil.

Movement of a chemical through soil can be difficult to predict under field conditions as a result of the complex interaction of variables that effect leaching. However, laboratory measurements can classify the tendency of a chemical to leach with respect to other chemicals so comparisons with known behavior of certain chemicals in the field can be made.

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