Determination of Mobility and Adsorption of Agrichemicals on Soils

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Movement of certain agricultural chemicals in soil was studied in the laboratory by measurement of the R_f values of monuron, diuron, bromacil, terbacil, and chloroneb on thin layers (400 μ) of soil deposited on glass plates and developed in water, and by determination of the Freundlich isotherm constants (K) of these chemicals in soil-water systems. The relationship of the Freundlich constants (K) to the R_f values is discussed. An empirical equation relating these constants for the above agrichemicals on Keyport silt loam is shown to be $K = (1/R_f - 1) + 0.85$.

The fate of agricultural chemicals in soil is a problem of extreme importance and has been the object of a great deal of research in recent years. The rate of disappearance or inactivation of an agrichemical in soil is related to the following phenomena (Hill et al., 1955): leaching or adsorption, volatilization, chemical decomposition, and biological degradation.

The leaching and/or adsorption of agrichemicals in soil is of major importance in determining the fate of these compounds. In general, the literature has treated this problem in terms of sorption coefficients. This approach does not account for other variables which influence the leaching of chemicals from soils. This subject has been reviewed by Bailey and White (1964). Other workers have studied the movement of agrichemicals in soils by the use of soil columns. Helling and Turner (1968) reported on the use of soil thin-layer chromatography (tlc) as a rapid, reproducible, and inexpensive method to study the mobility of agrichemicals in soil.

The present paper describes the use of Freundlich constants (K) and soil tlc as two means of assessing leaching of agrichemicals in soil and discusses the possible information provided by soil tlc that is not obtained from K values. The relationship between K and soil tlc R_f values is also discussed.

EXPERIMENTAL

Materials. Four agricultural soils from various locations were selected to represent a variety of soil types. Analytical characterizations of these soils are given in Table I. The agrichemicals used were 2-C^{14}-bromacil (5-bromo-3-sec-butyl-6-methyluracil), 2-C^{14}-terbacil (3-tert-butyl-5-chloro-6-methyluracil), C^{14}-carbonyl labeled monuron [3-(p-chlorophenyl)-1,1-dimethylurea], C^{14}-carbonyl labeled diuron [3-(3,4-dichlorophenyl)-1,1-dimethylurea], and C^{14}-ring-labeled chloroneb (2,5-dichloro-1,4-dimethoxybenzene).

Apparatus. A Nuclear Chicago liquid scintillation spectrometer (Model 6801) was used for counting carbon-14 activity. The scintillation solution consisted of 100 g of naphthalene, 0.028 g of dimethyl POPOP [1,4-bis-2-(4-methyl-5-phenyloxazolyl)-benzene], 4.0 g of PPO (2,5-diphenyl-

Table I. Physical Properties of Soils Used

Soil	Location	pH	Organic[a] Matter, %	Av. Particle[b] size (μ)
Muck	Florida	6.7	83.5	8.7
Muscatine brown silt loam	Macomb, Ill.	6.4	6.0	8.6
Keyport silt loam	Newark, Del.	5.4	2.1	5.6
Cecil loamy sand	Raleigh, N.C.	5.8	0.7	10.5

[a] Determined by hot oxidative digestion with potassium dichromate and sulfuric acid followed by titration with ferrous ion ("Determination of Organic Matter," Circular 757, U.S. Department of Agriculture, 1947).
[b] Determined with a Fisher Subsieve Sizer after grinding and screening.

oxazole), 83 ml of anisole, 166 ml of anhydrous ethylene glycol diethylether, and 1 l. of dioxane.

PROCEDURE

Determination of Freundlich Isotherm Constants (K). Soils were oven-dried to constant weight at 105° C and ground to pass a 10 mesh (0.08-in.) screen. Twenty-five g samples of soil and 30 ml of an aqueous solution of radio-labeled agrichemical at concentrations ranging from 1 to 20 ppm were added to a 4-ounce wide-mouth, screw-cap bottle and equilibrated on a mechanical shaker for 72 hr. Agrichemicals with low water solubility (less than 20 ppm) were prepared in ethanol, and aliquots added to the 4-ounce bottles. The alcohol was evaporated before the soil and distilled water (30 ml) was added, and the system equilibrated. The shaking rate was adjusted to maintain the soil in complete suspension.

Following the equilibration period, the bottles containing the soil and agrichemical solution were allowed to stand to permit most of the soil solids to settle. The supernatant liquid was centrifuged at 5000 to 6500 rpm for 10 min in polypropylene tubes to effect good separation of the aqueous phase.

One milliliter of the supernatant was diluted to 100 ml with water. One milliliter of the diluted solution in 15 ml of scintillation solution was counted in the liquid scintillation spectrometer to determine the concentration of agrichemical in solution. The concentration of agrichemical adsorbed on the soil was determined by difference. The log of the concen-
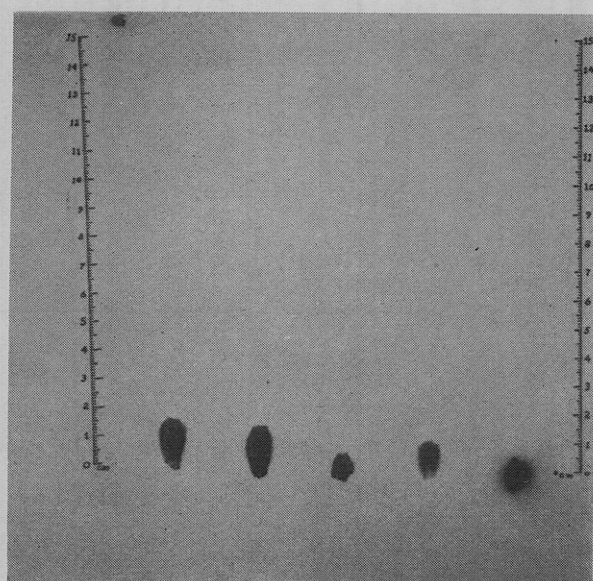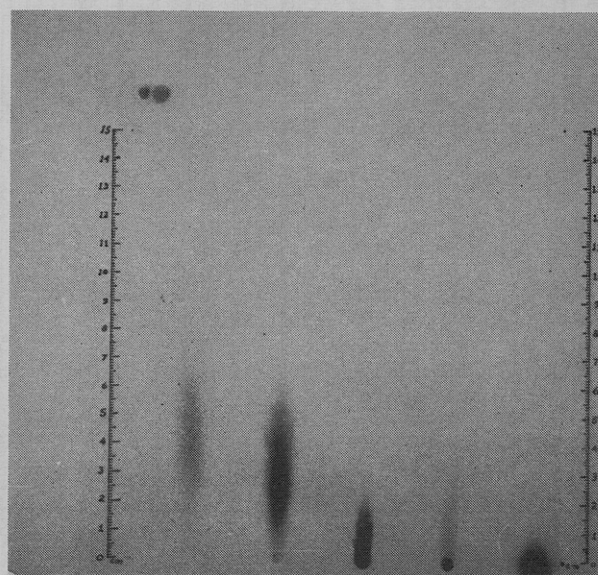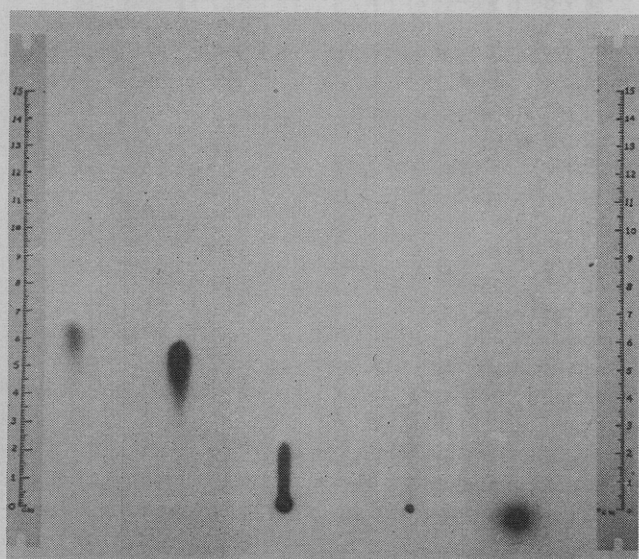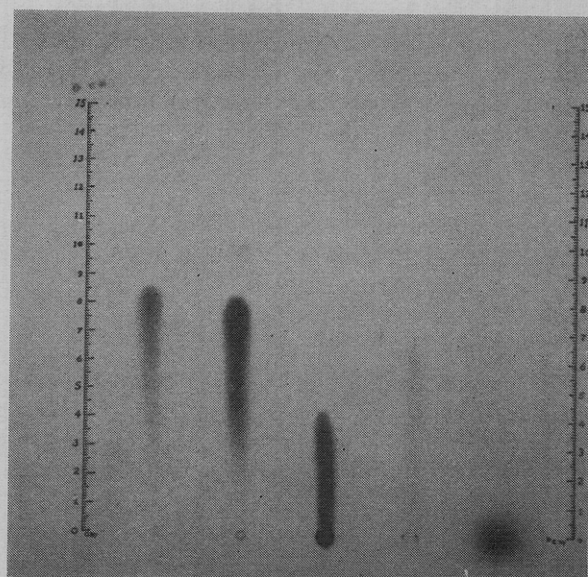
Figure 1. Radioautograms of soil tlc plates

A—Bromacil
B—Terbacil
C—Diuron
D—Monuron
E—Chloroneb
Upper left—Florida muck
Upper right—Muscatine brown silt loam
Lower left—Keyport silt loam
Lower right—Cecil loamy sand

tration of the agrichemical in solution *vs.* the log of the concentration on soil was plotted for each level of application. The Freundlich isotherm constant (K) was determined from the plot as the agrichemical concentration on soil when the concentration in solution is 1 ppm. Values were obtained on Keyport silt loam and Cecil loamy sand. The water solubilities for bromacil, terbacil, monuron, diuron, and chloroneb are 815, 710, 240, 42 and 8 ppm, respectively.

Determination of Mobility of Agrichemicals by Soil Thin-Layer Chromatography. Each soil was ground in a hammer mill fitted with an 0.020-in. screen to obtain samples with a small and nearly homogeneous particle size. The plates were coated with a water slurry of the soil at a thickness of 400 μ using a commercial tlc spreader and the plates were air dried. Each agrichemical (5 μg in 5 μl of methanol) was applied to the soil as a spot, 3 cm from the bottom of the
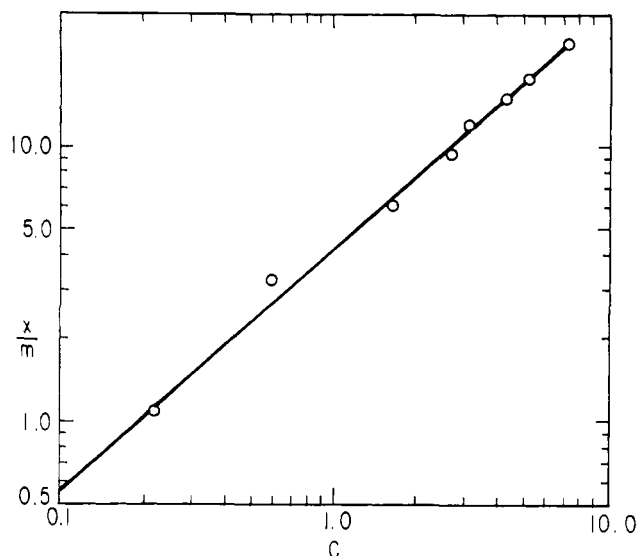
Figure 2. Freundlich plot for diuron on Keyport silt loam

plate, using a 10 μl syringe. A strip of paper towel, about 2 cm wide, was wet with distilled water and wrapped around the bottom of the plate so that the lower 1 to 2 cm of soil was covered. The plate was developed to 10 cm with water by ascending chromatography and was allowed to air dry. The developed plate was exposed to Ansco high-speed X-ray film for about 10 days. The R_f value for each compound was measured as the front of the corresponding spot or streak shown on the radioautogram (Figure 1).

RESULTS AND DISCUSSION

Adsorption-partition constants were determined for the agrichemicals in the study by use of the Freundlich isotherm

$$\frac{x}{m} = KC^{1/n} \tag{1}$$

where x is the weight of agrichemical adsorbed on soil (μg), m is the weight of soil (g), C is the equilibrium concentration of the agrichemical in solution, and K and $1/n$ are constants. In the log form, Equation 1 becomes:

$$\log \frac{x}{m} = \frac{1}{n} \log C + \log K \tag{2}$$

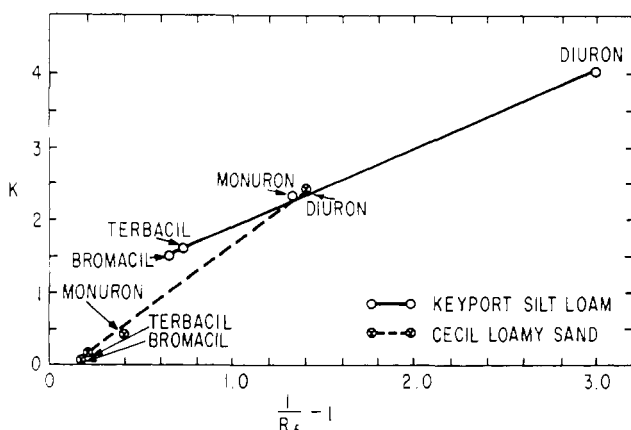Thus, the plotted isotherm becomes a straight line and can

Figure 3. Plot of K vs. $(1/R_f - 1)$ for agrichemicals on Keyport silt loam and Cecil loamy sand

Table II. Freundlich Constants of Agrichemicals on Soils

Compound	Keyport Silt Loam		Cecil Loamy Sand	
	K	$\frac{1}{n}$	K	$\frac{1}{n}$
Bromacil	1.5	0.85	0.08	0.58
Terbacil	1.7	0.50	0.15	0.96
Monuron	2.6	0.68	0.40	1.2
Diuron	4.0	1.25	2.4	0.95
Chloroneb	20	1.30	...	...

readily be solved graphically for the constants K and $1/n$. K is the intercept and $1/n$ the slope of the line. When the equilibrium concentration in solution is 1 ppm, the equation reduces to

$$\log \frac{x}{m} = \log K \tag{3}$$

where x/m is the concentration of agrichemical adsorbed on soil in ppm. A value of $1/n$ of less than unity indicates the relative adsorption decreases with increasing concentration.

The values for K and $1/n$ for the five agrichemicals on Keyport silt loam and Cecil loamy sand are listed in Table II. A representative plot is shown in Figure 2.

We found a correlation between K and R_f values of the compounds in this study similar to the relationship expressed in Equations 4 and 5. Martin and Synge (1941) and Stahl (1965) have shown the relationship of the partition coefficient Kp to R_f value in partition tlc to be

$$Kp = \frac{Am}{As} \left(\frac{1}{R_f} - 1 \right) \quad \text{or} \tag{4}$$

$$\log Kp = Rm + \log \frac{Am}{As} \tag{5}$$

in which Am and As are the cross sectional areas of the mobile and stationary phases and Rm is $\log (1/R_f - 1)$.

Straight lines were obtained when the K values of the agrichemicals on Keyport silt loam and Cecil loamy sand were plotted against $(1/R_f - 1)$ or $\log K$ against Rm, as illustrated in Figure 3. The equation for a straight line was applied to give the following empirical relationship for Keyport silt loam:

$$K = \left(\frac{1}{R_f} - 1 \right) + 0.85 \tag{6}$$

The relative order of mobility for the five compounds in each of the four different soils is bromacil $\geq$ terbacil $>$ monuron $>$ diuron $>$ chloroneb. The agrichemicals can be arranged into groups on the basis of their mobilities as suggested by Helling and Turner (1968). Helling and Turner have recommended the following classification based on R_f values obtained on Hagerstown silty clay loam (2.5% organic matter) and Chillum silt loam (3.1% organic matter).

Class	R_f	Agrichemical
1	0.00–0.09	Chloroneb
2	0.10–0.34	Diuron
3	0.35–0.64	Bromacil, Terbacil, Monuron
4	0.65–0.89	
5	0.90–1.00	

Class 1 represents the essentially immobile compounds on these soils and Class 5, the very mobile. R_f values on Hagerstown and Chillum soils are essentially identical to those obtained for the corresponding compounds on Keyport silt loam; consequently, the compounds may be classified on the basis of R_f values determined on either of these soils.

The soil-agrichemical adsorption characterization can be further systematized by classification of soils according to the method described by Lambert (1967, 1968). Several workers have reported that adsorption is highly correlated with organic matter content and cation exchange capacity (Bailey and White, 1964; Call, 1957; Lambert *et al.*, 1965; Lambert, 1968; Sheets *et al.*, 1962; Upchurch, 1958, and Upchurch and Mason, 1962), and that organic matter content offers the best single correlation. Lambert (1968) suggests classification of soils according to "corrected" or active organic matter content (Ω). Lambert designated Ripperdan sandy loam (1% organic matter) as a standard soil ($\Omega = 1.0$). The Ω value of a given soil can be determined by using the K value for an indicator compound determined on Ripperdan soil and the following relationship,

$$K = \frac{x/\Omega \text{ grams of soil}/100}{Ce} \qquad (7)$$

where K is the distribution coefficient of the chemical on Ripperdan soil, x is the amount of chemical sorbed on the soil, and Ce is the equilibrium concentration of the chemical in solution. Consequently, the soils can be arranged into groups according to active organic matter content, and the agrichemicals can be classified according to mobility on a given class of soil.

The profile of the agrichemical movement on soil, obtained from the radioautogram, provides information that cannot be obtained from Freundlich constants (K). X-ray images show whether the compound moves as a compact band or spreads out. R_f values are a measure of the maximum distance a chemical will move down into the soil when a given amount of water is applied. These values are listed in Table III.

R_B values are defined as follows:

$$R_B = \frac{\text{distance moved by bottom of spot (or streak)}}{\text{distance traveled by water}}$$

These values provide a measure of the relative depth through

Table III. Mobility $(R_f)^a$ and R_B Values of Agrichemicals on Soil

Soil	Agrichemical				
	Broma-cil	Terba-cil	Mon-uron	Diuron	Chloro-neb
	R_f				
Muck	0.15	0.15	0.13	0.00	0.00
Muscatine Brown silt loam	0.60	0.55	0.28	0.16	0.00
Keyport silt loam	0.61	0.58	0.43	0.24	0.00
Cecil loamy sand	0.89	0.85	0.68	0.42	0.00
	R_B				
Muck	0	0	0	0	0
Muscatine Brown silt loam	0.25	0.08	0	0	0
Keyport silt loam	0.40	0.24	0	0	0
Cecil loamy sand	0.42	0.34	0	0	0

a Precision about $\pm 5\%$ relative.

Table IV. Mobility (R_f) of Agrichemicals on Keyport Silt Loam *vs.* pH

Soil pH	Bromacil	Terbacil	Monuron	Diuron	Chloroneb
5.4	0.61	0.58	0.43	0.24	0.00
7.1	0.56	0.56	0.40	0.22	0.00
8.9	0.50	0.53	0.40	0.20	0.00

Table V. Effect of Time Before Development on R_f [a]

Time (days)[b]	Bromacil	Terbacil	Monuron	Diuron	Chloroneb
0	0.61	0.58	0.43	0.24	0.00
2	0.62	0.59	0.47	0.31	0.00
7	0.61	0.58	0.46	0.29	0.00
14	0.60	0.56	0.46	0.28	0.00
28	0.60	0.57	0.48	0.29	0.00

[a] On Keyport silt loam (pH 5.4).
[b] Days plate spotted before development.

which essentially all of the compound has leached. These values are listed in Table III.

R_B values, when used in conjunction with R_f values, provide a measure of the relative effectiveness of herbicides for control of deep rooted *vs.* shallow rooted weeds. For example, bromacil and terbacil have R_f values of 0.55 to 0.89 and R_B values of 0.24 to 0.42 in each of the soils studied (except Florida muck) and monuron and diuron have R_f and R_B values of 0.16 to 0.68 and 0.00, respectively, on the same soils. Consequently, it would be predicted that the uracil herbicides would be more effective against deep rooted perennial weeds.

The effect of soil pH on an agrichemical's mobility on Keyport silt loam was studied over a limited range. Keyport silt loam (pH 5.4) was adjusted to pH 7.1 and 8.9 with 5N ammonium hydroxide and plates prepared as previously described. The results, listed in Table IV, show a slight decrease in mobility of the uracil herbicides and very little or no change for the urea herbicides and chloroneb with an increase in soil pH. A more pronounced effect on R_f with changes in soil pH would be expected for more polar compounds.

The effect of the concentration of the agrichemical on mobility was examined. Terbacil was applied to Keyport silt loam in concentrations varying from 1 to 40 μg per spot. No change in mobility (R_f) was observed over this concentration range. An increase in the tailing and lateral movement of the spot was observed with increasing terbacil concentration. The concentration of compound per spot represents very high application rates; 1 μg per spot is equivalent to about 10 lb active per acre as a surface application.

Studies were carried out to determine if the tlc data could be used to predict accurately the depth that a compound will penetrate soil with a given amount of water, regardless of the time that elapses before the water is applied. Five tlc plates, coated with Keyport silt loam, were each spotted with the five test compounds. A plate was developed to 10 cm with water after 0, 2, 7, 14, and 28 days. The results are listed in Table V. No change in mobility was observed with time. These results indicate that a compound will penetrate to the same depth in Keyport silt loam with a given amount of water regardless of the time when the water is applied. Of course, this will be true only if the compound is not affected by such things as photodecomposition and volatility.

An estimate of the lateral diffusion of the chemicals was obtained by dividing the width of the appropriate spot at its

widest point by the width of the applied spot. Apparently the compounds (nonvolatile) with highest mobility show slightly greater lateral diffusion than those with lower mobility. An exception to this observation is chloroneb, which has the lowest mobility of the agrichemicals studied, but shows the greatest lateral diffusion. The large lateral diffusion, shown by chloroneb, is most likely due to soil-vapor equilibrium rather than soil-solution equilibrium. This effect is shown visually in Figure 1.

ACKNOWLEDGMENT

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