

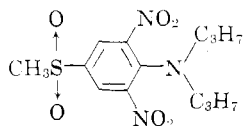
# Omega ( $\Omega$ ), a Useful Index of Soil Sorption Equilibria

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A characteristic index of soil sorption equilibria has been defined and designated as  $\Omega$ . This index is independent of chemical within the framework of the soil model and is intended for use in determining distribution ratios ( $K_p$ ) for chemicals between the "active fraction of soil-organic matter" and water. Its use provides a firmer basis for determining rates of leaching caused by rainwater percolation, and rates of pesticide application based upon sorption

phenomena. Soil sorption equilibria are discussed from the point of view of their relationship to distribution equilibria in other solvent systems. Previously derived expressions are developed further to show how data obtained in more readily accessible two-phase solvent systems and thin-layer chromatography systems may be utilized in place of soil sorption equilibria measurements.

In our model description of the interaction of chemicals with soil, the single, most characteristically important index for a given chemical is the distribution coefficient,  $K_p$ , between soil-organic matter and water. This constant, which was first defined by Lambert *et al.* (1965), has been used to describe, in quantitative terms, herbicide leaching through soil caused by rainwater percolation and the differences in observed biological activity of certain herbicides as a function of soil moisture (Lambert, 1965 and 1966). This definition represents a considerable departure from the distribution coefficient classically defined and used to describe soil sorption equilibria. It considers the sorbing medium to be the soil-organic matter, rather than the total mass of soil, and incorporates this aspect implicitly into the physical constant. The coefficient so defined becomes a constant which, for all practical purposes, is independent of soil type. Recently, a functional relationship between  $K_p$  and chemical structure was derived and established (Lambert, 1967) for two classes of herbicidal compounds—Planavin (Shell trademark) herbicide analogs, and Monuron analogs. This relationship, which was

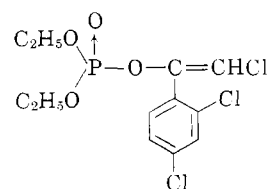


I. Planavin herbicide (SD 11831)

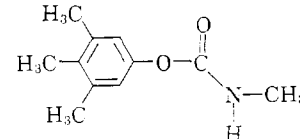
predicted as a natural consequence of our earlier work, provides some justification for our conceptual model.

This work has now been extended in two dimensions—first, in regard to two new classes of compounds, an organophosphorus insecticide and a carbamate insecticide, and second, to cover comprehensively a greater number and greater variety of soils originating from various locations across the United States.

This same conceptual model which holds for analogs of both Planavin herbicide and Monuron also serves to describe the sorption characteristics of SD 7859, Supona Insecticide, and SD 8530, principal ingredient of Landrin (Shell trademark) insecticide.



II. Supona insecticide



III. SD 8530

## EXPERIMENTAL

Soil sorption isotherms were determined using  $C^{14}$ -labeled SD 7859 and  $C^{14}$ -labeled SD 8530. The data for SD 7859 obtained on two standard soils, Ripperdan (1% O.M.) and Yolo (5% O.M.) are plotted in Figure 1 and show the expected linearity over the entire range. The  $K_p$

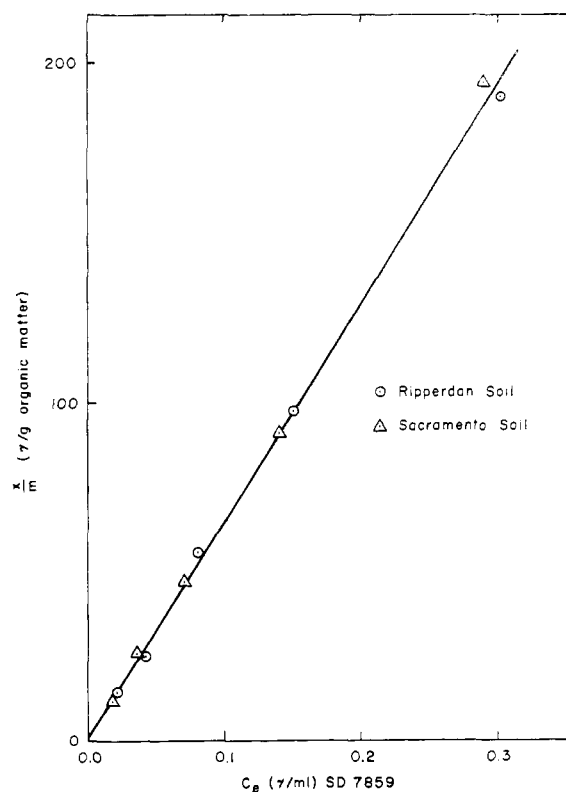


Figure 1. Soil sorption isotherms for SD 7859

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values obtained are 610 for Ripperdan soil and 617 for Yolo soil. These may be compared with the values of 500 and 520 determined from soil sorption isotherms using SD 11831 on the respective soils. Using SD 8530, the soil sorption isotherms were also linear with both Ripperdan and Yolo soils.

In addition to the sorption isotherms, single equilibrium point measurements were made in the more dilute concentration range on 23 different soils. These soils were gathered from various economically important locations around the United States including Oregon, California, Nebraska, Minnesota, and North Carolina. They range from clay to peat type soils containing from about 0.5 to 40% organic matter.

#### $\theta$ AND $\Omega$ VALUES

Designating the equilibrium concentration ratios on the basis of total mass of soil as  $\theta$ , one may write

$$\theta = \frac{\mu\text{g. chemical}}{\text{g. soil}} \bigg/ \frac{\mu\text{g. chemical}}{\text{ml. solution}} \quad (1)$$

These  $\theta$  values may be plotted against the percentage organic matter (as determined by classical organic carbon analysis) for the respective soils. Figure 2 depicts the results for SD 7859 and Figure 3 for SD 11831. Even with the expected minor deviations, the strong correlation between the two parameters is apparent. There are three principal causes for these minor individual deviations from linearity, one being, of course, associated with experimental methods and the precision of the result. Neglecting this aspect, deviations would be expected to occur if all of the organic matter (as determined by carbon chemical analysis) does not participate in the sorption equilibria. This consideration was discussed in some detail by Lambert *et al.* in a previous publication (1965). To circumvent difficulties that arise due to this factor, it was suggested that the term "active fraction" of organic matter be designated for that fraction which is found to actively participate in the sorption processes. Methods for determining this fraction based on equilibria measurements were suggested. The value so obtained would be an intrinsic index of the sorption characteristics of the respective soil.

The third reason for deviations from the linear correspondence between  $\theta$  values and per cent organic matter is that the soil used may exhibit anomalous characteristics; e.g., Palouse silt loam, or certain features about the chemical such as pH dependence of ionic chemicals may not have been taken into account. Essentially, this amounts to the soil or the chemical having properties which have not been adequately accounted for in the simple model.

The concept of active fraction of organic matter might best be illustrated by referring to Figure 4 where (for the 23 soils) the  $\theta$  values for SD 7859 are plotted against the  $\theta$  values for SD 11831. Except for one point, any given soil behaves characteristically the same, as regards sorption equilibria, even towards these two dissimilar chemicals. In effect, any deviations found in the linear correspondence when plotting per cent organic matter *vs.*  $\theta$ , are in approximately the same direction and of approximately the same magnitude for these two chemicals on a given soil.

This information suggests that a "corrected" organic matter content for a given soil might be obtained which would be useful for indexing that soil in regards to its sorption characteristics. This corrected value would result in a new soil constant, a measure of the active fraction of organic matter; it would be applicable to most soils, and

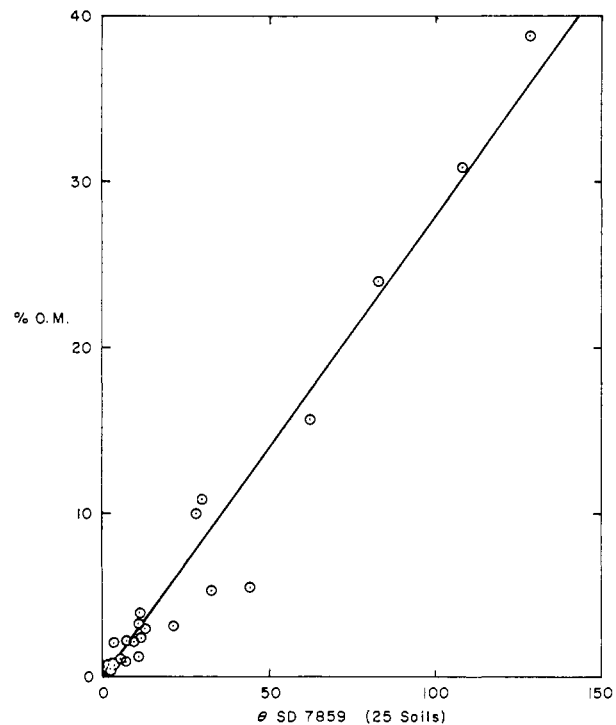


Figure 2. Relationship between soil sorption and per cent soil organic matter for SD 7859

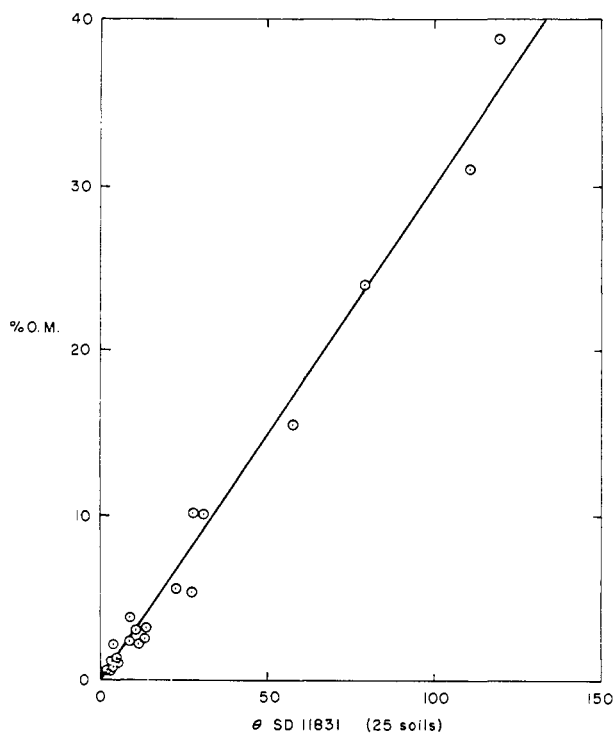


Figure 3. Relationship between soil sorption and per cent soil organic matter for SD 11831

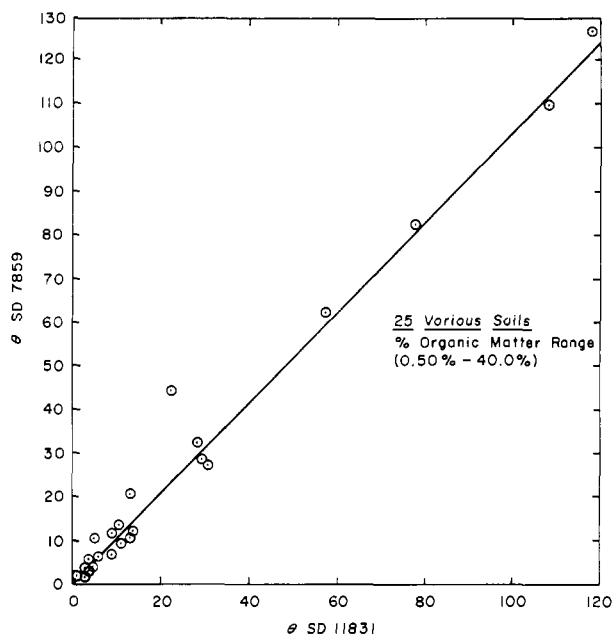


Figure 4. Relationship of  $\theta$  values for SD 7859 and SD 11831

of general validity for noncharged organic chemicals. We designate this active fraction of organic matter as  $\Omega$  (omega). A rather naive analogy for this term might be drawn from solution chemistry by use of the activity coefficient-activity relationship.

The determination of  $\Omega$  for a given soil is a relatively simple matter. One need only use a suitable indicator chemical to measure the soil sorption isotherms. For example, one obtains the  $\Omega$  value for a given soil from the sorption isotherm for that soil by utilizing the  $K_p$  for the indicator chemical determined on the standard soil (Ripperdan) and solving the following equation for  $\Omega$ :

$$K_p = \frac{X/\Omega \left( \frac{\text{grams of soil}}{100} \right)}{C_e} \quad (2)$$

$X$  represents the amount of indicator chemical sorbed on the soil under investigation, usually expressed in micrograms, and  $C_e$  is the equilibrium concentration of chemical in solution, usually expressed as micrograms per milliliter,  $K_p$  is the value of the equilibrium constant determined using the same indicator chemical on the standard soil. An extension to TLC techniques will be described later.

The use of a distribution coefficient,  $K_p$ , in which the active fraction of organic matter is considered as the sorbing medium circumvents the ambiguity inherent in the use of organic matter, as determined by organic carbon analysis, for soil sorption equilibria. Within the limitations imposed by the model then, this type of  $K_p$ , for a given chemical, is a true constant independent of soil origin or type; in addition, the percentage active organic matter is a truly characteristic sorption index for a given soil and is independent of the chemical.

Since there is no unequivocal method for fixing the numerical value of  $\Omega$  for any given soil, we, at Modesto, have arbitrarily set our standard Ripperdan soil (1% organic matter based on organic carbon analysis) to have

an  $\Omega$  value of unity. Hereafter, all  $\Omega$  values and all  $K_p$  values reported will be referred to this standard reference soil.

Evaluation of the characteristic soil sorption index,  $\Omega$ , has now been completed for 23 soils. Other soils are currently being collected and indexed; this is intended to be a continuing process eventually providing a picture of sorption characteristics on many U. S. soil types of major economic importance. The three compounds mentioned—SD 11831, SD 7859, and SD 8530—each from a different chemical class, were used to establish the  $\Omega$  values tabulated in Table I. While many of the  $\Omega$  values lie very close to the per cent soil organic matter value, a number of soils show considerable deviation. These deviations emphasize the importance of using the more representative  $\Omega$  value when considering soil sorption phenomena. The  $\Omega$  values are intended for use in determining where a chemical will reside in the soil under the influence of applied rainfall, the biological activity of a chemical resulting from its distribution between soil-organic matter and water, and rates of application of pesticides based upon the two preceding factors. It is suggested that this constant be evaluated routinely for soils as a measure of their sorption characteristics as regards noncharged organic chemicals. Such an index of soil sorption as the described  $\Omega$  value with its broad applicability to soil-chemical interactions should prove to be a valuable and useful soil constant.

#### DISTRIBUTION EQUILIBRIUM EXPRESSIONS

An expression relating the distribution coefficient of a solute between soil and water to the parachor value for that solute has been derived in an earlier publication (Lambert, 1967). This may be formulated generally as

$$\log K_e = aP\Delta U + b \quad (3)$$

Table I.  $\Omega$  Values for 23 United States Soils Based on Standard Ripperdan Soil

Soil	Organic Matter, %	$\Omega$
Ripperdan (standard) sandy loam	1.0	1.0
Aiken, clay—California	2.4	2.3
Ambrose, clay loam—California	3.1	2.6
Antioch, loam—California	10.8	5.4
Athena, slit loam—Oregon	0.69	0.73
Los Osos, clay loam—California	2.2	1.9
Minnesota, clay loam	3.8	2.5
Nebraska, clay loam	2.9	2.6
North Carolina		
No. 1	2.1	0.66
No. 2	0.69	0.31
No. 3	3.1	2.3
No. 4	5.5	5.7
No. 5	10.0	6.6
No. 6	38.8	29.8
No. 7	0.52	0.45
Panoke, clay loam—California	1.2	1.4
Rossi, clay loam—California	2.1	1.9
Yolo, loam—California	5.3	6.1
Armix A composite soil	15.5	12.9
Armix B composite soil	23.9	17.2
Armix C composite soil	30.8	23.3
Tujunga, loamy sand—California	0.52	0.51
Waha, silt loam—Washington	1.0	1.1

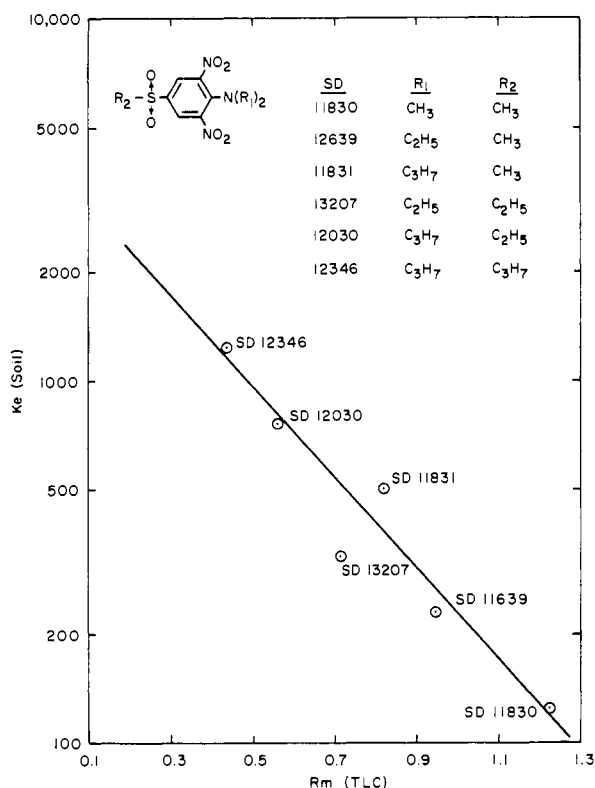


Figure 5. Comparison of  $K_p$  values from soil isotherms with  $R_m$  from TLC

where  $K_e$  is the distribution coefficient,  $P$ , the parachor value,  $\Delta U$ , the difference in internal pressures of the two solvent phases, and  $a$  and  $b$  are constants.

Equation 3 is useful in relating the  $K_e$  values for a solute between two different solvent systems. For a single compound distributed between two pairs of immiscible liquid phases,  $P$  remains constant while the values of  $\Delta U$ ,  $a$  and  $b$  are subject to change. In this case,  $\log K_e = aP\Delta U + b$  for the first solvent pair and  $\log K_e' = a'P\Delta U' + b'$  for the second pair. Combining these expressions leads to the following equation

$$\log K_e = \alpha \log K_e' + \beta \quad (4)$$

where  $\alpha$  and  $\beta$  are constants. This equation describes a linear relationship between the log of the distribution coefficients for a single compound in two different solvent systems.

The significance of Equation 4 is that if the soil equilibria for a chemical are described adequately by Equation 3, then the same information could be acquired by measurement of distribution ratios for that chemical in some appropriately chosen immiscible solvent system. This relationship has been established at Modesto for Planavin herbicide analogs using hexane/water as the selected solvent system.

In 1950, Collander compared the distribution coefficients of between 100 to 200 organic compounds which he determined in ether/H<sub>2</sub>O and isobutanol/H<sub>2</sub>O systems. The graphical correlation he obtained between the  $K_e$  values in the two solvent systems led him to postulate the following empirical relationship:

$$\log k_{\text{butanol}} = a \cdot \log k_{\text{ether}} + b \quad (5)$$

This relationship is, in turn, identical to the expression given by Equation 4, providing a rationale and some theoretical basis for the empirical expression of Equation 5.

This concept may be extended even further by considering the relationship between the distribution coefficient,  $K_p$ , as obtained through batch contacting techniques and the  $R_m$  value obtained using partition thin-layer chromatographic, PTLC, techniques. The relationship of the partition coefficient,  $K_p$ , to the chromatographic  $R_f$  has been shown by Martin and Synge (1941) to be

$$K_p = \frac{A_m}{A_s} \left( \frac{1}{R_f} - 1 \right) \quad (6)$$

in which  $A_m/A_s$  is a constant for a given chromatogram and is the effective ratio of the cross-sectional areas of the mobile and stationary phases. Bate-Smith and Westfall (1950) have proposed that the function

$$\log \left( \frac{1}{R_f} - 1 \right) \quad (7)$$

be called the  $R_m$  value of a substance. Converting Equation 6 to logarithmic form and eliminating  $\log (1/R_f - 1)$  terms between 6 and 7, one obtains

$$\log K_p = \log \frac{A_m}{A_s} + R_m \quad (8)$$

Thus, by judicious choice of a PTLC system, and by utilizing the linear relationship between  $\log K_p$  and  $R_m$  expressed by Equation 8, desired information concerning soil sorption equilibria may be obtained readily using TLC techniques. The limitations imposed by Equations 3 and 6 require that, in general, the TLC system utilized be a partition and not an adsorption system. It is possible that certain adsorption systems will be applicable, but in general these will be fortuitous circumstances.

The relationships discussed above are illustrated in Figure 5 in which the  $R_m$  values obtained from PTLC for a series of Planavin herbicide analogs are plotted against their respective  $K_p$  (soil-organic matter/water) values, obtained from batch contacting experiments.

#### ACKNOWLEDGMENT

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#### LITERATURE CITED

- Collander, R., *Acta Chem. Scand.* **4**, 1085 (1950).  
 Martin, A. J. P., Synge, R. L. M., *Biochem. J.* **35**, 1358 (1941).  
 Lambert, S. M., *Weeds* **14**, 273 (1966).  
 Lambert, S. M., Porter, P. E., Schieferstein, R. H., *Weeds* **13**, 185 (1965).  
 Lambert, S. M., *J. Agr. Food Chem.* **15**, 572 (1967).  
 Bate-Smith, E. C., Westfall, R. G., *Biochim. Biophys. Acta* **4**, 427 (1950).

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