

Theoretical and Experimental Relationships between Soil Adsorption, Octanol-Water Partition Coefficients, Water Solubilities, Bioconcentration Factors, and the Parachor

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It is shown how approximate values of the constants in the Collander equation, $\log K_1 = a \log K_2 + b$, where K_1 and K_2 are organic solvent-water partition coefficients, can be calculated knowing only the water concentration in the two organic solvents. When this is used, equations are derived relating adsorption on soil organic matter, octanol-water partition coefficients, water solubility, and bioconcentration factors. The derived equations are closely similar to regression equations from experimental results. Measurement or calculation of one property allows prediction of the other properties to within 1 order of magnitude. Water solubility of organic solids requires a correction for the melting point for good prediction of other properties. Relationships to the parachor are also demonstrated which allow a good preliminary assessment of the environmental partitioning properties of a compound from its chemical structure and melting point.

Recent legislation in many countries requires extensive testing of all manufactured chemicals for environmental evaluation and registration. Among the requirements are water solubility, solvent (usually octanol)-water partition coefficient, soil adsorption, and bioconcentration factors in aquatic organisms.

water solubility (WS) partition coefficient (K) bioconcentration factor (BCF) soil adsorption (K_d)	pure chemical \rightleftharpoons aqueous solution chemical in organic solvent \rightleftharpoons aqueous solution chemical in organism \rightleftharpoons aqueous solution chemical adsorbed on soil \rightleftharpoons aqueous solution
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Water solubility can be regarded as the partition of a chemical between itself and water and bioconcentration factors as a partition between water and the lipid and protein phases in an organism. Thus, three of the above properties are organic solvent-water partition coefficients, and any pair of these should be related by the log-log relationship between partition coefficients suggested by Collander (1950):

$$\log K_1 = a \log K_2 + b \quad (1)$$

Adsorption of nonionic chemicals by water from soil can also be regarded as an organic phase-water partition. Goring (1962) recognized that the close correlation between K_d , the soil-water distribution, and the organic matter content of the soil indicated that there was a soil organic matter-water distribution, K_{om} , for each chemical which was relatively constant in all soils.

$$K_{om} = 100K_d / (\% \text{ om}) \quad (2)$$

For nitrapyrin, Goring (1962) found K_{om} in the range 86-262 for 10 soils with a mean of 155. The results of Graham-Bryce (1967) and Graham-Bryce and Etheridge (1970) give similar ranges of values of K_{om} in different soils with mean values of 491 (range 329-758) for disulfoton and 5 (range 2-12) for dimethoate.

Such variation in K_{om} is no greater than the variation in partition coefficients in pure solvent-water systems reported by different investigators [see data in Leo et al. (1971)] so that, despite the complexity of soil organic

matter, K_{om} for a particular chemical is virtually a constant. Assuming that K_{om} is a constant, relationships with molecular properties have been sought. Lambert (1967) and Hance (1969) found relationships with the parachor and Briggs (1969) used free-energy substituent constants. Lambert (1968) drew attention to the relationship between K_{om} and R_m data from partition chromatography, and Briggs (1973) showed that data for 30 chemicals fitted the Collander relationship

$$\log K_{om} = 0.52 \log K_{ow} + 0.62 \quad (3)$$

where K_{ow} is the octanol-water partition coefficient.

Since all the environmentally important properties are partition coefficients, there should be a Collander equation relating any pair of them so that all the properties could be predicted from a measured or calculated value of any one of them. The aim of this paper is to derive these Collander equations theoretically and to show that they are consistent with a wide range of experimental results.

EXPERIMENTAL SECTION

Chemicals. The chemicals were analytical samples from chemical companies (Du Pont, Ciba, Sandoz, Shell, and Murphy), commercial chemicals (Koch-Light and Aldrich), or synthesized by standard methods. Purity was checked by TLC and NMR.

Soils. Details of the soils are given in Table I. The soils were air-dried and ground to pass a 2-mm sieve. Organic carbon was determined by the Walkley-Black method using a correction factor of 1.3 and converted to organic matter content by multiplying by 1.724.

Soil Adsorption. One gram of soil was shaken for 2 h with 10 mL of chemical solution in 0.01 M CaCl_2 in 40-mL glass centrifuge tubes with glass stoppers. After centrifugation for 10 min, the chemical remaining in solution was measured. The chemicals in Table II were determined at an appropriate wavelength by UV absorption against a soil blank. The solution concentrations of the chemicals in Table III were determined by GLC using appropriate conditions and detectors after solvent extraction, except for simazine and carbaryl which were measured by UV absorption. The first four compounds in Table IV were determined by UV absorption, oxamyl and aldicarb sulfone using ^{14}C -labeled compounds, and the remainder by GLC.

Adsorption of the chemicals in Table II was measured in soils 1-4 at four initial concentrations, 20, 15, 10, and 5 ppm, or the same dilutions of saturated solutions for less

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Table I. Soil Characteristics

no.	soil series	texture	history	organic matter, %	pH (CaCl ₂)
1	Batcombe	silt loam	100 years arable	1.09	7.5
2	Batcombe	silt loam	100 years arable	2.51	6.7
3	Batcombe	silt loam	old grass, then arable	3.53	6.1
4	Batcombe	silt loam	old grass, then arable	4.25	6.2
5	Cottenham	sandy loam	arable	1.35	7.2
6	Cottenham	sandy loam	arable plus peat	5.92	6.8
7	Batcombe	silt loam	arable	2.64	5.9

Table II. Organic Matter-Water, Octanol-Water Distributions, and Water Solubility for Substituted Benzenes

ring substituent	pesticide common name	log K _{om}	log K _{ow}	log WS _{molar}	ring substituent	pesticide common name	log K _{om}	log K _{ow}	log WS _{molar}
Anilines					3-Phenyl-1-methyl-1-methoxyureas				
		1.17	0.90	-0.41	4-Cl	monolinuron	1.60	2.30	-2.57
3-CH ₃		1.41	1.42		4-Br	metobromuron	1.78	2.38	-2.89
3-CF ₃		2.12	2.39		3,4-Cl ₂	linuron	2.19	2.76	-3.52
4-CH ₃		1.66	1.40	-1.22	3-Cl-4-Br	chlorbromuron	2.34	3.09	-3.92
4-Br		1.72	2.03		3-Phenyl-1-methylureas				
3,4-Cl ₂		2.05	2.78				1.05	1.17	
3-Cl-4-OCH ₃		1.69	1.85		3-Cl		1.69	2.18	
3-CH ₃ -4-Br		2.02	2.53		3,4-Cl ₂	DMU	2.22	2.94	
Anilides					3-Cl-4-OCH ₃		1.6	1.76	
		1.19	1.16	-1.40	3-Cl-4-CH ₃		1.86	2.61	
2-Cl		1.34	1.23	-1.74	3-Phenyl-1-cycloalkylureas				
3-F		1.33	1.46		cyclopropyl		1.48	1.65	
3-Cl		1.62	2.02		cyclopentyl		1.69	2.65	
3-Br		1.77	2.04		cyclohexyl		1.83	2.77	
3-CH ₃		1.21	1.52	-2.09	cycloheptyl		2.13	2.95	
3-CF ₃		1.51	2.20		Phenylureas				
3-NO ₂		1.70	1.52				1.11	0.80	
4-F		1.24	1.23		2-F		1.08	0.88	
4-Br		1.71	2.14		2-Cl		1.37	1.27	
4-OCH ₃		1.16	1.04		3-F		1.53	1.29	
3-Cl-4-OCH ₃		1.68	1.82		3-Cl		1.77	1.82	
3,4-Cl ₂		2.10	2.54		3-Br		1.82	2.08	
butyranilide		1.47	1.78		3-CH ₃		1.32	1.29	
Nitrobenzenes					3-CF ₃		1.72	2.31	
		1.70	1.85	-1.81	4-F		1.28	1.04	
3-NH ₂		1.49	1.39	-2.06	4-Br		1.88	1.98	
4-NH ₂		1.64	1.37	-2.24	4-OC ₆ H ₅		2.32	2.80	
4-Br		2.18	2.60		3,4-Cl ₂		2.25	2.64	
3,4-Cl ₂		2.29	2.99		3-Cl-4-OCH ₃		1.76	1.37	
3-Cl-4-Br		2.36	3.25		3-CH ₃ -4-F		1.54	1.59	
3-Phenyl-1,1-dimethylureas					3-CH ₃ -4-Br		2.13	2.49	
	fenuron	0.88	0.96	-1.63	Alkyl N-Phenylcarbamates				
3-Cl		1.55	2.01		methyl		1.49	1.76	
3-OCH ₃		1.48	1.73		ethyl		1.58	2.26	
3-F		1.49	1.37		n-propyl		1.82	2.80	
3-CF ₃	fluometuron	1.58	2.42	-3.34	isopropyl	propham	1.71	2.60	
4-F		1.19	1.13		n-butyl		2.02	3.30	
4-Cl	monuron	1.46	1.98	-2.93	n-pentyl		2.37	3.8	
4-CH ₃		1.27	1.33		methyl N-(3-chlorophenyl)		1.91	2.58	
4-OCH ₃		1.16	0.83		methyl N-(3,4-dichlorophenyl)		2.50	3.09	
3,4-Cl ₂	diuron	1.97	2.68	-3.74					
3-Cl-4-OCH ₃	metoxuron	1.50	1.64	-2.52					
3-Cl-4-CH ₃	chlortoluron	1.78	2.41	-3.48					
3,5-(CH ₃) ₂		1.49	1.90						
3,5-(CH ₃) ₂ -4-Br		2.29	2.92						

soluble compounds. The adsorption isotherms for all of the chemicals were linear. As Graham-Bryce (1967) found for the adsorption of disulfoton by two soils from the same series, there was no better fit to the Freundlich isotherm. When K_d was converted to K_{om} , the value for each chemical on each of the four soils was within 20% of the mean values quoted in Table II.

Because the linear isotherm gave a good fit to the data, adsorption of the remaining chemicals (Tables III and IV) was measured at one initial concentration only. This was 20 ppm or saturated solutions of less soluble chemicals except for oxamyl and aldicarb sulfone where the initial concentration was 1 ppm.

Octanol-Water Partition Coefficients. These were determined as described by Fujita et al. (1964) using 50 gentle inversions in glass centrifuge tubes followed by centrifuging and analysis of chemical in the aqueous phase by the method used for the chemical in the soil adsorption studies. Initial aqueous phase concentrations were 20 ppm or saturated solutions of less soluble compounds. The volumes of the two phases were chosen to leave at least 10% of the chemical in the aqueous phase after partition. This could not be achieved for aldrin and dieldrin, and octanol-water distributions for these chemicals were estimated from reverse-phase TLC with liquid paraffin as the stationary phase and acetone-water (3:1) as the mobile

Table III. Organic Matter-Water Distribution in Soil 3

chemical	log K_{om}	log K_{ow}	log WS_{molar}
dimethoate	0.72	0.79	-0.96
aldicarb	1.39	1.57	-1.50
simazine	1.44	1.51	-4.60
carbaryl	1.78	2.32	-3.70
captan	2.06	2.54	-5.78
diazinon	2.12	3.11	-3.88
Dowco 275	2.17	3.51	
chlorfenvinphos	2.23	3.10	-3.39
fenamiphos	2.28	3.18	-2.64
phorate	2.58	4.26	-3.72
parathion	2.78	3.93	-4.08
folpet	3.03	3.63	-5.47
captafol	3.08	3.83	-5.39
dieldrin	3.87	6.2	-6.31
aldrin	4.45	7.4	-7.13

Table IV. Organic Matter-Water Distributions for Chemicals in Various Soils

chemical	log K_{om}	log K_{ow}	log WS_{molar}	soil
diphenylamine	2.54	3.42	-2.74	1-4
azobenzene	2.89	3.82	-2.78	1-4
phenol	1.48	1.46	-0.06	2
4-bromophenol	2.17	2.59		2
oxamyl	0.47	-0.47	0.11	5, 6
aldicarb sulfone	0.26	-0.57		5, 6
nitrapyrin	2.00	3.02	-3.76	5, 6
tetrachlorobenzene	3.25	4.68		7
hexachlorobenzene	4.25	5.44	-6.90	7
pentafluorophenyl methyl sulfone	1.22	1.11		7
methiocarb	2.08	2.92		1, 2
naphthalene	2.38	3.36		1-5

phase. Compounds of known log K_{ow} were run on the same plate, and a linear relationship between R_m and log K_{ow} was established and extrapolated to estimate the values for aldrin and dieldrin.

All adsorption and distribution experiments were carried out at 20 ± 2 °C. The results are given in Tables II-IV.

Water solubilities quoted were taken from Martin and Worthing (1977) for commercial pesticides and Seidell (1920) for other chemicals.

RESULTS AND DISCUSSION

Theoretical Derivation of Collander Equations.

The "hole" theory of solubility considers that, in order to dissolve, a solute must make a hole in the solvent. The parachlor (P) is one measure of molar volume and thus of the size of the hole. The bigger the molecule, the larger the hole and the lower the solubility unless there are H-bonding or other solute-solvent interactions.

The driving force for partition between two immiscible solvents is the difference in the energy required to make a hole in the two phases. Lambert (1967) derived the following expression relating the parachlor to the partition coefficient, neglecting any interactions

$$\log K = aP\Delta U \quad (4)$$

where a is a constant and ΔU is the difference in internal pressure [or more strictly cohesive energy density (Dack, 1975)] between the two phases. Where water is one of the phases, the ΔU term is dominated by the internal pressure of water which is ~ 10 times that of immiscible organic solvents. Therefore, for solvent-water partitions, the ΔU term is similar for all solvents and, in the absence of solute-solvent interactions, all partitions should be similar. The data compiled by Leo et al. (1971) demonstrate this except where the organic phase itself contains much water

Table V. Calculated and Experimental Collander Equations

solvent	W, M	constants for $\log K_{solv} = a \log K_{ow} + b$			
		calcd		exptl	
		a	b	a	b
water	55.5				
octanol	2.3				
heptane	0.0033	1.04	-2.84	1.06	-2.85
CCl ₄	0.010	1.04	-2.36	1.17	-2.16
xylene	0.0188	1.04	-2.08	0.94	-1.69
toluene	0.0256	1.04	-1.95	1.13	-1.78
benzene	0.026	1.04	-1.94	1.02	-1.40
CHCl ₃	0.0684	1.04	-1.53	1.12	-1.34
oils	0.0725	1.04	-1.50	1.10	-1.31
nitrobenzene	0.18	1.04	-1.10	1.2	-1.07
ether	0.69	1.03	-0.52	1.13	-0.17
ethyl acetate	1.62	1.01	-0.15	0.93	0.05
primary pentanols	5.00	0.95	0.26	0.81	0.27
2-butanone	5.46	0.94	0.29	0.49	0.32
cyclohexanol	6.51	0.92	0.34	0.74	0.87
primary butanols	9.44	0.86	0.42	0.69	0.38

(>5 M water). If the presence of water in the organic phase increases the internal pressure in the organic phase, it will decrease the difference between the two phases and hence decrease the partition coefficient. If we assume that the difference in internal pressure ΔU is proportional to the difference in the water concentrations in the aqueous and organic phases, ΔW , eq 4 becomes

$$\log K = a'P\Delta W \quad (5)$$

Hydrogen bonding is generally the most important solute-solvent interaction, the effect on the partition coefficient depending on the difference in H bonding in the two phases. If we assume that H bonding in a phase is proportional to the water concentration, W , in that phase then the contribution of H bonding to the solvent-water partition coefficient will be W_1/W_{aq} for organic solvent 1. Neglecting other solute-solvent interactions, eq 5 then becomes

$$\log K_1 = a'P\Delta W_1 + \log (W_1/W_{aq}) \quad (6)$$

So that the Collander relationship between K_1 for solvent 1 and K_2 for solvent 2 can be obtained, $a'P$ can be eliminated to give

$$\log K_1 = [\log K_2 - \log (W_2/W_{aq})]\Delta W_1/\Delta W_2 + \log (W_1/W_{aq}) \quad (7)$$

The Collander relationship can therefore be obtained from eq 7 for any two organic solvent-water systems if the water concentrations of the two organic phases in equilibrium with water are known.

The utility of eq 7 is first tested for predicting the Collander equation for pairs of partition coefficients and between water solubility and K_{ow} before introducing K_{om} and BCF. These properties have a range of values of at least 7 orders of magnitude so that estimates to within 1 order of magnitude would give a useful indication of behavior.

Partition Coefficients. Leo et al. (1971) obtained regression equations between partition coefficients in many solvent-water systems and K_{ow} . These are compared in Table V with equations calculated from eq 7, using water concentrations in the organic phase taken from Leo et al. (1971). There is generally good agreement. Leo et al. distinguished between H-donor and H-acceptor solutes for ether, oils, and hydrocarbon solvents which contain relatively little water at saturation. The equations in Table V are those for H-donor solutes. The equations for H-

Table VI. Relationship between K_{om} and K_{ow} for Different Chemical Classes

chemical group	$\log K_{om} = a \log K_{ow} + b$		n	r	range of $\log K_{ow}$
	a	b			
anilines	0.48	0.80	8	0.94	0.90-2.78
anilides	0.52	0.62	14	0.86	1.16-2.54
nitrobenzenes	0.45	0.93	6	0.98	1.37-3.25
dimethylphenylureas	0.53	0.57	14	0.94	0.96-2.92
methylmethoxyphenylureas	0.92	-0.44	4	0.97	2.30-3.09
methylphenylureas	0.59	0.42	5	0.97	1.17-2.94
cycloalkylphenylureas	0.40	0.77	4	0.86	1.65-2.95
phenylureas	0.57	0.68	15	0.95	0.80-2.80
N-phenylcarbamates	0.48	0.59	8	0.84	1.76-3.80
N-alkylcarbamates	0.50	0.62	5	0.99	-0.57-2.92
organophosphates	0.58	0.32	7	0.97	0.79-4.26
halogenated compounds	0.54	0.76	10	0.96	1.11-7.4
remaining compounds	0.57	0.60	5	0.99	1.46-3.82
all compounds	0.53	0.64	105	0.95	-0.57-7.4

acceptor solutes have the same slope but differ by having an intercept ~ 1 greater than that of the H-donor solutes except in the ether-water system where it is 1 less. For the more polar solvents, there is no distinction between donor or acceptor solutes.

Clearly there are interactions in addition to H bonding of the solute to water which affect the partition coefficient and the Collander equations are only approximations. The present discussion does not attempt to take other interactions into account.

Water Solubility. For organic liquids, water solubility can be considered as a partition of the chemical between itself and water. The partition coefficient describing this is

$$\log K = \log (C_L/WS) = \log C_L - \log WS \quad (8)$$

where C_L is the concentration of the liquid in itself and WS is the molar water solubility. For most low molecular weight compounds C_L is in the range 5-10 so that $\log C_L$ is ~ 1 and eq 8 becomes

$$\log K = 1 - \log WS \quad (9)$$

The concentration of water in a pure liquid in the presence of a saturated aqueous solution differs for each liquid so there is no single value of W which can be used in eq 7 to derive a relationship between WS and K_{ow} . The slope of the line will be close to 1 because the concentration of water in the liquid will be small in comparison with that in the aqueous phase but the intercept term will differ for each compound and the intercept value found in regression of K_{ow} and WS will vary with the compounds used to derive it.

Making the simplifying assumption that the H-bonding interactions in the liquid and octanol are comparable gives from eq 7

$$\log WS = 1 - \log K_{ow} \quad (10)$$

Hansch et al. (1968) reported the water solubilities and K_{ow} values of 156 organic liquids. Many of the K_{ow} values were calculated ones for which experimental values are now available (Hansch and Leo, 1979). Regression of these values gives

$$\log WS = 0.84 - 1.18 \log K_{ow} \quad (11)$$

When the assumptions made in deriving eq 10 are considered, it predicts this experimental eq 11 quite well.

For solids the influence of water in the organic phase can be neglected, but an additional term is required for the energy needed to break up the crystal structure. This melting term was shown by Yalkowsky (1977) to be approximately $(0.01T_m - 0.25)$ where T_m is the melting point

Table VII. Predicted and Experimental K_d Values for Soil from Victoria, Australia

chemical	$\log K_{ow}$	K_d - (exptl)	K_d - (calcd)
acetophenone	1.58	0.42	0.32
benzophenone	3.18	2.71	2.24
diphenyl ether	4.2	12.4	7.7
veratrole	2.00	0.67	0.54
benzyl alcohol	1.10	0.17	0.18
diphenylmethanol	2.7	1.38	1.20
permethrin	6.6 (calcd)	400	150

in degrees Celsius. Therefore, for solids the predicted equation is

$$\log WS = -0.38 - \log K_{ow} - (0.01T_m - 0.25) \quad (12)$$

Yalkowsky (1977) found for crystalline drugs that

$$\log WS = 0.25 - \log K_{ow} - (0.01T_m - 0.25) \quad (13)$$

and the data for chemicals of known solubility in Tables II-IV gives

$$\log WS = 0.01 - \log K_{ow} - (0.01T_m - 0.25) \quad r = 0.91 \quad (14)$$

Organic Matter Adsorption and K_{ow} . Having established that eq 7 gives reasonably good predictions of the Collander relationships between partition coefficients and WS, it is now tested for predicting relationships with K_{om} . The only additional information needed is the water concentration in soil organic matter. Well-decomposed peats retain approximately their own weight of water at 15-bar suction (Boelter, 1964) equivalent to 28 M water. Substituting in eq 7 gives

$$\log K_{om} = 0.52 \log K_{ow} + 0.41 \quad (15)$$

The regression equations calculated from the experimental results in Tables II-IV for each chemical class are given in Table VI. Each group of compounds gave a similar slope and intercept except for the four methoxymethylphenylureas. Even for these four compounds the experimental values of K_{om} were given within a factor of 2 by the equation for all the chemicals which was

$$\log K_{om} = 0.52 \log K_{ow} + 0.64 \quad r = 0.95 \quad (16)$$

This is almost identical with the previously reported eq 3 and the predicted eq 15.

Equation 16 was derived by using results in soils from only two soil series (Table I), but similar results can be derived from results with widely differing soils. Table VII gives K_d values measured on a red earth soil from South Australia for a different set of chemicals (Briggs, 1981) and

Table VIII. R_f Values of Oxime *N*-Methylcarbamates on Soil TLC Plates

chemical	log K_{ow}	R_f (obsd)	R_f (calcd)
aldicarb sulfoxide	-0.57	0.97	0.95
oxamyl	-0.47	0.96	0.94
acetaldoxime	-0.13	0.93	0.92
<i>N</i> -methylcarbamate benzaldoxime	1.47	0.63	reference
<i>N</i> -methylcarbamate 4-chlorobenzaldoxime	2.27	0.37	0.39
<i>N</i> -methylcarbamate 3,4-dichlorobenzaldoxime	2.89	0.17	0.23
<i>N</i> -methylcarbamate 4-phenoxybenzaldoxime	3.20	0.11	0.14
<i>N</i> -methylcarbamate			

values calculated from eq 16 and the organic matter content, 1.09%. Agreement is close and the equation relating adsorption on 17 Australian soils (Briggs, 1981) was almost identical with eq 16.

$$\log K_{om} = 0.52 \log K_{ow} + 0.69 \quad (17)$$

The data of Felsot and Dahm (1979) for insecticide adsorption on Iowa soils gives

$$\log K_{om} = 0.52 \log K_{ow} + 0.78 \quad (18)$$

and the data of Lord et al. (1978) for Brazilian soils gives

$$\log K_{om} = 0.53 \log K_{ow} + 0.98 \quad (19)$$

Similar equations can be calculated from the data of Sharom et al. (1980) for adsorption of insecticides by soils and a stream sediment from Eastern Canada. The slope and intercept for the stream sediment, 0.63 and 0.72, respectively, are similar to those for soils and contrast with the results of Karickhoff et al. (1979), who found a slope of 1.0 and an intercept of -0.21 for adsorption, on an organic carbon rather than organic matter basis, of aromatic hydrocarbons on sediments.

Soil TLC. A further test of eq 16 uses soil TLC data. Assuming that all adsorption is on the organic matter, then, as shown by Briggs (1973)

$$\log (1/R_f - 1) = 0.52 \log K_{ow} + \text{constant} \quad (20)$$

The constant term depends on the organic matter content and physical characteristics of the soil. By use of the R_f of a reference compound to calculate this constant, R_f values of other compounds can be calculated from eq 20. Table VIII gives data for oximecarbamates on a Rothamsted soil, and Table IX compares calculated and measured R_f values on Hagerstown soil from Maryland (Helling, 1971a-c; Helling et al., 1971, 1974).

The excellent agreement between calculated and experimental values of R_f , K_d , and K_{om} and the similarity of eq 15-19 obtained for soils from widely different parent materials and climatic conditions confirm that organic matter in all soils has very similar adsorbing properties for organic chemicals.

The mobility classes described by Helling and Turner (1968) in terms of R_f on Hagerstown soil can be further defined in terms of K_{ow} as was done by Briggs (1973). Mobility in other soils will depend on organic matter content, R_f increasing as organic matter decreases. The variation of mobility with organic matter is summarized in Figure 1, R_f being calculated from the approximate relationship eq 21, derived as follows.

The constant term in eq 20 has two components (Hamer, 1975) due to the pore space and the organic matter content and is equivalent to $k + \log om$. From regression of Helling's data, Briggs (1973) obtained a value of -0.95

Table IX. R_f Values of Pesticides on Hagerstown Soil TLC Plates

chemical	R_f (obsd)	R_f (calcd)	log K_{ow}
cycloheximide	0.89	0.84	0.55
oxycarboxin	0.73	0.78	0.9
fenuron	0.69	0.76	0.96
monuron	0.48	reference	1.98
simazine	0.45	0.62	1.51
pyrazon	0.44	0.62	1.50
captan	0.39	0.37	2.35
carbaryl	0.38	0.37	2.36
picloram methyl ester	0.35	0.38	2.3
banol	0.34	0.38	2.3
metobromuron	0.31	0.36	2.38
2,4-dichlorophenol	0.30	0.25	2.80
diuron	0.26	0.28	2.68
amiben methyl ester	0.25	0.25	2.8
propanil	0.24	0.25	2.8
3,4-dichloroaniline	0.22	0.26	2.78
linuron	0.17	0.26	2.76
chlorbromuron	0.14	0.19	3.09
fenac methyl ester	0.09	0.09	3.8
chloroxuron	0.09	0.10	3.7
pentanochlor	0.08	0.10	3.7
fluorodifen	0.04	0.05	4.4
trifluralin	0.00	0.01	5.3
dieldrin	0.00	0.005	6.2
TCDD	0.00	0.002	6.9

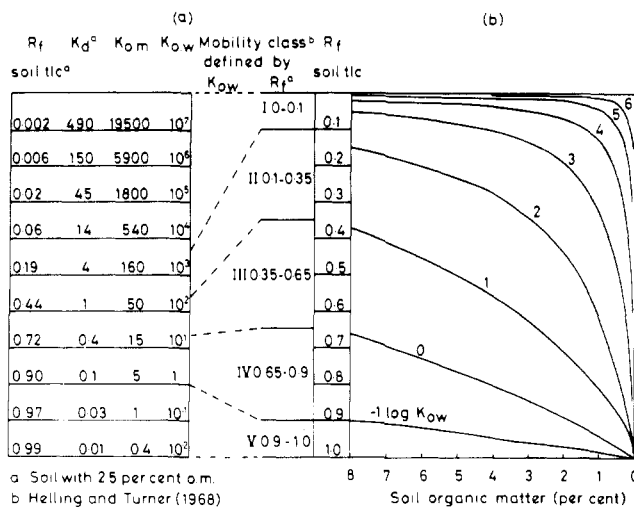


Figure 1. Variation of soil TLC R_f (a) with K_d , K_{om} , and K_{ow} at 2.5% organic matter and (b) with organic matter content for different values of K_{ow} .

for the constant in this soil with 2.5% om. Hence, assuming that the physical characteristics do not alter, R_f in soils with other organic matter contents is given by

$$\log (1/R_f - 1) = \log K_{ow} + \log om - 1.33 \quad (21)$$

Soil Adsorption and Water Solubility. The predicted relationships between K_{om} and water solubility obtained by substitution in eq 7, making similar assumptions to those made in deriving the K_{ow} -WS relationship, are

$$\log K_{om} = 0.9 - 0.52 \log WS \quad (22)$$

$$\log K_{om} = 0.3 - 0.52[\log WS + (0.01T_m - 0.25)] \quad (23)$$

for liquids and solids, respectively.

The data for compounds of known solubility in Tables II-IV give

$$\log K_{om} = 0.8 - 0.51[\log WS + (0.01T_m - 0.25)] \quad (24)$$

$r = -0.88$

and Chiou et al. (1979) found for a series of organic liquids

$$\log K_{om} = 0.74 - 0.55 \log WS \quad (25)$$

These experimental results are again much as predicted by eq 22 and 23.

Bioconcentration Factors. The distribution of a chemical between an organism and the aqueous phase around it can be regarded as a partition between the proteins and lipids in the organism and water. For substitution in eq 7, a bound water content of 0.4 g g^{-1} for proteins (Eagland, 1975) and 0.0725 M for triglycerides (Leo et al., 1971) was used.

For proteins, the calculated equation is

$$\log BCF_p = 0.62 \log K_{ow} + 0.46 \quad (26)$$

Data compiled by Leo et al. (1971) for the adsorption of small molecules by proteins has a mean slope of 0.55 for the regression of \log (binding) against $\log K_{ow}$. Lord et al. (1980) measured the adsorption of pesticides by earthworms from aqueous solutions. Earthworms contain at least 10 times as much protein as lipid (French et al., 1957), so that the adsorption measured would be dominated by the protein. The data gave, on a dry weight basis

$$\log BCF = 0.48 \log K_{ow} + 1.04 \quad (27)$$

Neely et al. (1974) measured the uptake of chemicals in fish muscle and found

$$\log BCF = 0.56 \log K_{ow} + 0.1 \quad (28)$$

The slopes of the experimental equations are close to those predicted by eq 26 although there is more variability in the intercepts.

For concentration in lipids, which contain very little water, separate consideration should be given to those chemicals which can H bond and those which do not. This latter group includes hydrocarbons and chlorinated hydrocarbons, the most significant environmental pollutants. For such compounds

$$\log BCF_l = \log K_{ow} \quad (29)$$

Bioconcentration factors on a lipid basis for DDT and PCB's are comparable to K_{ow} . For example, for pentachlorobiphenyl BCF lipid is 2×10^6 in zooplankton and fish and 10^7 in seals (Clayton et al., 1977), 5×10^6 in oysters (Vreeland, 1974), and 10^6 on a dry weight rather than a lipid basis in marine phytoplankton (Harding and Phillips, 1978). These values are all close to the experimental value of K_{ow} , 2×10^6 (Kenaga and Goring, 1979), or calculated values of K_{ow} (7×10^6 from the parachor, 3×10^7 from π constants, and 2×10^7 from f values).

For chemicals containing H-bonding groups, the appropriate equation is

$$\log BCF_l = \log K_{ow} - 1.5 \quad (30)$$

On consequence of the large intercept term in eq 30 is that chemicals with H-bonding groups would be expected to be bound more strongly to protein (eq 26) than to lipid unless $\log K_{ow}$ is greater than 5. For chemicals not containing H-bonding groups, the lipid phase will always contain more of the chemical if $\log K_{ow}$ is greater than 1.2.

For whole organisms the observed BCF of a compound will depend on the lipid and protein content. Rapid metabolism or limited penetration into the organism would result in less biological concentration than is predicted from the partition coefficients.

When the BCF for living organisms was calculated, 15% protein and 5% lipid content was assumed on a fresh weight basis. BCF for protein and lipid was calculated from K_{ow} from the appropriate equations for chemicals with and without H-bonding groups and the whole organism concentration calculated from the composition.

Calculated values of BCF for the whole organism were then regressed against $\log K_{ow}$. These calculated regressions are

$$\log BCF = 0.66 \log K_{ow} - 0.44 \quad (31)$$

for H-bonding compounds and

$$\log BCF = 0.87 \log K_{ow} - 0.62 \quad (32)$$

for hydrocarbons and chlorohydrocarbons.

Experimentally Veith et al. (1979) found that the uptake of chemicals, mostly organochlorine compounds, by fat-head minnows could be estimated within 60% by

$$\log BCF = 0.85 \log K_{ow} - 0.70 \quad (33)$$

which is remarkably, if fortuitously, similar to the theoretically derived eq 32.

Relationships between BCF and WS or K_{om} can be derived by substitution in eq 7 or more readily by substituting $\log K_{ow}$ by $\log BCF$ in the appropriate equations relating these other properties to K_{ow} . These will be discussed subsequently.

Relationships Including the Parachor. The parachor (P) was the first property correlated with K_{om} (Lambert, 1967), and it had previously been used to calculate water solubilities and partition coefficients (McGowan, 1954).

McGowan (1954) derived an empirical equation similar to Lambert's (eq 4) which he used to calculate partition coefficients for solutes not forming H bonds.

$$\log K = 0.012P \quad (34)$$

He later showed that the Hansch π constant for octanol-water partition is equivalent to $0.012(P_X - P_H)$ for a substituent X which does not form H bonds (McGowan, 1963). It should also be pointed out that the f value (Nys and Rekker, 1973) derived from $\log K_{ow}$ is equivalent to $0.012P_X$. For example, calculated f values for the hydrocarbon fragments H, C, and CH_3 are 0.18, 0.11, and 0.67 which are close to the values derived by Nys and Rekker, 0.19, 0.19, and 0.70, respectively.

For chemicals with H-bonding groups, McGowan proposed

$$\log K = 0.012P + E_a \quad (35)$$

where E_a is the hydrogen-bonding interaction. McGowan (1963) suggested values of E_a for various functional groups, and Moriguchi (1975) has suggested others. Like the π constants or f values, these E_a values differ with the molecular environment of the functional group and therefore offer no advantage for accurate calculations of partition coefficients.

However, the parachor does offer a very rapid way to calculate approximate values of K_{ow} and hence the other properties from the chemical structure alone if a value of -1.2 is taken for E_a for each H-bonding group in the molecule, as defined below, and -0.3 for each halogen atom attached to a saturated carbon atom. Then

$$\log K_{ow} = 0.012P - 1.2n \quad (36)$$

where n is taken as 1 for each O atom not bonded or conjugated to an aromatic ring (but including the ether O in aryl alkyl ethers), 1 for each singly bonded N atom, 1 for each heterocyclic aromatic ring however many heteroatoms it contains, and 0.25 for each halogen attached to a saturated carbon atom. Thus n is 2 for carbaryl and methiocarb, 3 for fenuron and simazine, 4 for dimethoate and metoxuron, and 5 for oxamyl and aldicarb sulfone. A simplified version of Quayle's (1953) parachor values was used for rapid calculation, the values used being the following: C, 9; O, 20; H, 15.5; N, 17.5; P, 40; S, 49; F, 26; Cl,

Table X. Calculated and Experimental Water Solubilities of Aromatic Hydrocarbons

hydrocarbon	parachor	mp, °C	water solubility, ppm		
			calcd		exptl ^a
			uncor	cor	
benzene	201		1509	1509	1791
naphthalene	304	80	100.7	28.4	31.7
fluorene	380	116	12.3	1.5	1.68
anthracene	407	216	5.7	0.07	0.045
phenanthrene	407	101	5.7	0.99	1.002
2-methylanthracene	447	207	1.8	0.027	0.021
1-methylphenanthrene	447	123	1.8	0.18	0.269
fluoranthene	443	111	2.1	0.29	0.206
pyrene	443	150	2.1	0.12	0.132
1,2-benzanthracene	510	162	0.29	0.013	0.009
chrysene	510	254	0.29	0.0015	0.0018

^a May et al. (1978).

Table XI. Predicted and Regression Equations between K_{oc} , K_{ow} , WS (ppm), and BCF_f^a

predicted	Kenaga and Goring (1979)
$\log K_{oc} = 0.52 \log K_{ow} + 0.65$	$\log K_{oc} = 0.544 \log K_{ow} + 1.377$
$\log K_{oc} = 3.1 - 0.52 \log WS$	$\log K_{oc} = 3.64 - 0.55 \log WS$
$\log BCF_f = 0.68 \log K_{ow} - 0.4$	$\log BCF_f = 0.935 \log K_{ow} - 1.495$
	$\log BCF_f = 0.767 \log K_{ow} - 0.973$
$\log BCF_f = 1.25 \log K_{oc} - 1.22$	$\log BCF_f = 1.119 \log K_{oc} - 1.579$
	$\log BCF_f = 1.225 \log K_{oc} - 2.024$
$\log BCF_f = 3.04 - 0.68 \log WS$	$\log BCF_f = 2.791 - 0.564 \log WS$
	$\log BCF_f = 2.183 - 0.629 \log WS$

^a BCF_f = flowing water systems; BCF_t = terrestrial-aquatic ecosystem.

55; Br, 68; double bond, 18; triple bond, 40. For the 26 chemicals in Tables III and IV

$$\log K_{ow} + 1.2n = 0.011P - 0.18 \quad r = 0.95 \quad (37)$$

so that eq 36 gives a good approximate value of $\log K_{ow}$.

McGowan (1954) also found an empirical relationship between WS and the parachor. When the E_a and melting point terms are included, this becomes

$$\log WS = 1 - 0.0135P + 1.2n - (0.01T_m - 0.25) \quad (38)$$

Table X gives water solubilities calculated from eq 38 for aromatic hydrocarbons. All of the solubilities are within a factor of less than 2 of the experimental values taken from May et al. (1978). The importance of the melting term for good prediction of solubility is illustrated by the difference in solubility of anthracene and phenanthrene, the 20-fold difference being largely accounted for by the 115 °C difference in T_m which produces a 14-fold difference (antilog 1.15).

Table XII. Experimental and Calculated Properties of Bench Mark Chemicals

		DDT	chlorpyrifos	trifluralin	simazine
WS, ppm	exptl	0.0017	0.3 (1.1) ^a	0.6	3.5
	calcd	0.0039	12.8	1.5	74
K_{ow}	exptl	960 000	97 700	220 000	155 (32) ^b
	calcd	7 830 000	18 700	143 000	56
K_{om}	exptl	138 000	7900 (2645) ^a	7950 (4270) ^c	78 (27) ^b
	calcd	17 200	800	2100	35
BCF	exptl	61 600	451	4750	1
	calcd	238 000	240	900	5

^a Felsot and Dahm (1979). ^b This paper. ^c Grover et al. (1979).

For the 38 chemicals of known solubility in Tables II-IV, the regression of solubility and parachor gave

$$\log WS - 1 - 1.2n + (0.01T_m - 0.25) = -0.0132P - 0.13 \quad r = 0.94 \quad (39)$$

Equation 38 gives an estimate of water solubility to within a factor of 4 for solids and liquids over a range of solubilities of 8 orders of magnitude from oxamyl to chrysene.

Because eq 36 gives a good estimate of K_{ow} the parachor can be used to substitute for K_{ow} in other equations. Substituting in eq 15 for $\log K_{ow}$ using the more convenient form of eq 36, $0.012(P - 100n)$, predicts

$$\log K_{om} = 0.0062(P - 100n) + 0.41 \quad (40)$$

The data for the 38 chemicals used to obtain the WS relationship to parachor give

$$\log K_{om} = 0.0062(P - 100n) + 0.58 \quad r = 0.92 \quad (41)$$

The slope of the line is the same as found in Lambert's (1967) plots of $\log K_{om}$ against the parachor which have slopes of 0.007 for phenylurea herbicides and 0.005 for homologues of the dinitroaniline herbicide nitratin. Lambert considered that H-bonding and other interactions would prevent use of the parachor except within related series of compounds where the interactions were constant. However, Hance (1969) successfully used the parachor with an estimate of H bonding similar to that suggested above by including a factor N which is the sum of the N and O atoms in the molecule. For urea, triazine, and other herbicides he found

$$\log K_{om} = 0.0067(P - 45N) - 0.65 \quad (42)$$

The slopes of all these regressions are close to those predicted by eq 40.

Appropriate substitution leads to relationships between the parachor and BCF. Tulp and Hutzinger (1978) pointed out that the data of Neely et al. (1974), eq 28, was correlated as well with the parachor as with K_{ow} . They regarded the parachor as a steric factor but it is clearly not so, it

being another way of deriving the partition coefficient.

Comparison of Derived Equations with Linear Regressions of Published Information. The theoretical equations derived above have been compared with individual worker's results. Kenaga and Goring (1979) collected results from many sources in the literature for the various properties and carried out regressions between pairs of them. The main regression equations are compared with the theoretical equations in Table XI. The theoretical equations were converted from molar solubility to ppm used by Kenaga and Goring assuming a molecular weight of 200 and from K_{om} to K_{oc} , soil adsorption on an organic carbon rather than an organic matter basis, by multiplying by 1.724.

The BCF data used values for whole organisms, individual tissues, or lipids, so that the values of slopes and intercepts of the regression lines could be influenced by the method of estimation as well as by the type of compound used.

However, there is substantial agreement between the theoretical and the regression equations, the slopes being close to those predicted and the intercepts within 1 order of magnitude and well within the 95% confidence limits given by Kenaga and Goring.

Water solubility was the property chosen by Kenaga and Goring (1979) as the most readily available parameter to use as a predictor of the other properties. It was not such a good predictor as K_{ow} , probably because the effect of melting point on solubility was not taken into account. They estimated the properties of four bench mark chemicals, DDT, chlorpyrifos, trifluralin, and simazine, from their water solubilities and concluded that this was a useful tool for potential hazard assessment. Table XII compares experimentally determined properties of these chemicals (Kenaga and Goring, 1979) with those calculated from their chemical structures and melting points alone by using eq 38 for water solubility, and eq 36 for K_{ow} and substitution of K_{ow} in eq 16 for K_{om} and using eq 31 (for DDT) and eq 32 to obtain BCF. Of the 16 values, 14 are predicted to within 1 order of magnitude and the other 2 to within 2 orders, giving a fairly accurate broad picture of behavior even with the simple calculations using the parachor.

Table XIII summarizes the relationships between the various properties for neutral molecules with compounds placed according to their K_{ow} values. It can be seen that pesticides with similar types of activity such as fumigants, preemergence herbicides acting on growing points of roots or shoots, or preemergence translocated herbicides fall within narrow ranges of properties. The limit for systemic activity in plants is taken from Briggs et al. (1977) and that for leaching of stable chemicals to ground water from Riley (1976).

For ionizable chemicals the situation is more complex than for neutral molecules, particularly for weak acids and bases where the extent of ionization depends on pH. Ionization of acids or bases decreases $\log K_{ow}$ by ~ 4 (Leo et al., 1971). Anions are therefore much less strongly adsorbed by soil organic matter than the free acids, and weak acids are more mobile in alkaline soils unless there is interaction with the inorganic fraction of soils. Weak bases are also more mobile in alkaline soils because cations are much more strongly adsorbed by ion exchange on organic and inorganic surfaces than the unionized bases are by organic matter. K_d is approximately 100 for monocations and 10 000 for dications such as paraquat (Austin and Briggs, 1976). The position of anions and cations in Table XIII is based on K_d for soil behavior and K_{ow} for water solubility and BCF.

CONCLUSION

The environmentally important partitioning properties of a chemical can be estimated by measuring or calculating the value of any one of them because these properties are all expressions of essentially the same process, partitioning between an aqueous and an organic phase. This process also determines R_f values in soil TLC or column leaching, R_m values in reversed-phase chromatography, or retention times in reversed-phase HPLC so that further relationships could be derived with these properties.

Any such relationships are unlikely to be perfect because the interactions in each solute-solvent-water system are different, but these differences are relatively small and likely to have little effect on the ranking of the chemicals in Table XIII.

Given the interrelationships between the various aspects of behavior and the generally good agreement between individual calculated and measured values, it is clear that chemicals having undesirable properties can be identified without extensive testing.

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Determination of Ivermectin in Cattle and Sheep Tissues Using High-Performance Liquid Chromatography with Fluorescence Detection

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An analytical procedure has been developed for the isolation and determination of the antiparasitic agent ivermectin in sheep and cattle tissues. The method is based upon the detection of a fluorescent derivative of this compound following high-performance liquid chromatography. The assay has a lowest limit of reliable measurement of 10 ppb and a limit of detection of 1-2 ppb. Recoveries of ivermectin spikes average 83% for liver, kidney, muscle, and fat. In residue studies liver appears to retain the residue the longest; a negligible residue of 11 ppb was found in cattle liver at the proposed withdrawal time of 28 days. In sheep liver no residue was detected at the proposed withdrawal time of 14 days.

The avermectins, which are isolated from the mycelia of *Streptomyces avermitilis*, are a new family of antiparasitic compounds which are potent broad-spectrum agents at very low dosage levels. For example, avermectin B_{1a} is effective against a wide range of helminths in sheep and cattle in single oral or parental doses of 0.1 mg/kg (Egerton et al., 1979). Ivermectin is a mixture of homologues, not less than 80% 22,23-dihydroavermectin B_{1a} and not more than 20% 22,23-dihydroavermectin B_{1b}. The structures of these compounds are shown in Figure 1.

So that the tissue distribution of ivermectin residues in cattle and sheep could be studied and the requirements of governmental regulatory agencies could be satisfied, a sensitive, specific, and reliable chemical assay for the parent drug and any major drug-related metabolites was needed. Radioactive metabolite studies have shown that dihydroavermectin B_{1a} is the major residue found in all tissues prior to the proposed withdrawal times of 28 days for cattle and 14 days for sheep. Dihydroavermectin B_{1b} is dosed at lower levels than dihydroavermectin B_{1a} and is generally metabolized more rapidly than the B_{1a} component (Jacob, 1979), so that the dihydroavermectin B_{1b} residues are always less than the B_{1a} residues. A tissue assay was, therefore, developed for dihydroavermectin B_{1a}.

The avermectins are not amenable to gas chromatography because of the complexity of the molecules. A reversed-phase high-performance liquid chromatographic (HPLC) assay with UV detection has been previously developed to determine the avermectins in fermentation

broth and formulations (Miller et al., 1979), but the assay did not have sufficient sensitivity for tissue residue analysis. Ivermectin is such a potent drug and is dosed at such low levels that the tissue assay needed a sensitivity of ~10 ppb (10⁻⁹ g/g) to ensure negligible residues. Tolan et al. (1980) developed an HPLC method using fluorescence detection for the avermectins in plasma. A fluorescent product was formed through a chemical reaction of the drug with acetic anhydride in pyridine which resulted in formation of a conjugated dehydration product. This method, however, was found to be too long (reaction time, 24 h), and the chemical yields through the reaction were too variable to meet the requirements for a tissue residue assay. Modification of these reaction conditions, however, has resulted in a new, shorter, more reproducible assay.

The present paper describes a procedure for the isolation, derivatization, and fluorescence HPLC determination of dihydroavermectin B_{1a} from cattle and sheep tissues. The same method has also been applied to swine and horse tissues. The drug is extracted into isooctane, carried through a series of liquid-liquid distributions, and then derivatized in a 1-h reaction to form the same fluorescent product as formed under the previously published reaction conditions (Tolan et al., 1980). The sample is cleaned up by column chromatography before quantitation by HPLC fluorescence detection. The fluorescent derivatives of dihydroavermectins B_{1b} and B_{1a} are resolved by the HPLC column. The assay has a lowest reliable measurement level (*Fed. Regist.*, 1979) of ~10 ppb and a limit of detection of 1-2 ppb. Recoveries of dihydroavermectin B_{1a} spiked into cattle and sheep liver, kidney, muscle, and fat averaged 79-84%.

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