ANOMALIES IN THE LOG FREUNDLICH EQUATION RESULTING IN DEVIATIONS IN ADSORPTION K VALUES OF PESTICIDES AND OTHER ORGANIC COMPOUNDS WHEN THE SYSTEM OF UNITS IS CHANGED

KEY WORDS: Isotherm, distribution coefficient, adsorption coefficient

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ABSTRACT

Freundlich K values cannot be directly converted from one set of units to another unless the slope, N, is unity. Dimensional analysis of the Freundlich equation shows the units of K to be $moles^{(1-N)} L^N g^{-1}$, instead of the commonly used units, moles/g. A mathematical relationship exists between the ratio of K values in two different sets of units, and N. The magnitude of K does not change by the same factor as the adsorption data (x/m, C) from which it was calculated, when units are changed, unless N=1.0. To avoid problems associated with units of K, it is recommended that mole fraction (a unitless quantity) be used to express equilibrium concentration, and that K no longer be used as an indicator of relative adsorption. An alternate means of assessing relative adsorption among pesticides is proposed.

INTRODUCTION

Recently there has been an increasing demand by regulatory agencies to quantify pesticide adsorption in soil-water systems. Although octanol-water partition coefficients have

rapidly been gaining acceptance as a means of estimating pesticide adsorption by soil organic matter, the Freundlich K value is still the most commonly quoted adsorption parameter. This communication deals with some anomalies in adsorption values created by the mathematics of the Freundlich equation and sounds a cautionary note on the use of Freundlich K values to measure the relative adsorption of pesticidal compounds in soil-water environments.

THEORY AND DISCUSSION

The Freundlich equation can be expressed as

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

where x/m = weight of adsorbate/weight of adsorbent

C = equilibrium concentration of adsorbate

K, N are constants.

The slope of this isotherm is obtained by differentiating Eqn. 1 with respect to C.

$$\frac{d(x/m)}{dC} = K N C^{N-1} \tag{2}$$

The slope is a function not only of K and N, but also one of the variables, concentration, and therefore itself varies continuously over the concentration range. If N is unity, the Freundlich isotherm is linear and K becomes the slope of this special case. This K value has been referred to as a distribution coefficient, Kd, and has units of mL/g adsorbent[5].

When N $\neq$ 1.0, the dimensions of K become somewhat complex because of the exponent (N) and can be derived by rewriting Eqn.(1).

$$K = \frac{x/m}{C^N} \equiv \frac{moles/g}{moles^N/L^N} = moles^{(1-N)} L^N g^{-1} \tag{3}$$

The units of K appear to be a function of the slope value, which would make it difficult to compare K values of isotherms having different slopes. Since adsorption data often produce non-linear isotherms, the log transformation of Eqn. 1 is used to produce a more easily managed linear form of the equation. In the log form, N becomes the slope and log K

becomes the value of log x/m at log C = 0, C = 1.0. The units of K are commonly, and incorrectly, shown the same as that for x/m, moles/g, when in fact they are $moles^{(1-N)} L^N g^{-1}$. This anomaly will be resolved later in this presentation.

Traditionally the K value has been used as a means of comparing the relative adsorption of pesticides. To make valid comparisons of K values, two conditions must be satisfied: 1) Experimental conditions such as adsorbent/solution ratios, adsorbents and temperature must be comparable; 2) Adsorption data must be expressed in the same units, preferably molar units. There are numerous instances of adsorption data being reported in weight units such as µg/g. Authors do not always indicate the units of K in tables of adsorption parameters[3], and should the K values mistakenly be assumed to be in molar units such as nanomoles/g, errors could be introduced.

Because of the great variation in solubility of pesticides, adsorption data (x/m, C values) may range from picomoles (p mole) (e.g. DDT, dieldrin) to nanomoles (n mole) or even micromoles (µ mole) for the more soluble compounds (e.g. fensulfothion, phorate sulfoxide). To compare adsorption tendencies of these diverse compounds, K values must be converted to common units. Because of an anomaly in the log Freundlich equation, K values expressed in one set of units (i.e. µg/g, n moles/g, p moles/g) cannot be converted directly to another set of units by a simple conversion factor unless N is unity. The magnitude of the error in converting K to another set of units is related to the size of the deviation of N from unity as well as to the magnitude of K itself.

The reason for this anomaly can be seen by re-arranging the log Freundlich equation to give:

$$\log K = \log x/m - N \log C \tag{4}$$

If we change the units of the adsorption data (e.g. n moles to p moles), a change in log units of + 3.0, then we could represent the resultant change in numerical magnitude of log K as

$$\Delta \log K = 4 \log x/m - N \Delta \log C \tag{5}$$

Thus

$$\Delta \log K = 3.0 - N (3.0) \tag{6}$$

If $N = 1$, $\Delta \log K = 0$ and the numerical magnitude of $\log K$ remains the same when the units change. If N is >1.0, the magnitude of $\log K$ decreases and if N is <1.0, the magnitude of $\log K$ increases.

There is a fundamental relationship between N and the ratio of the K values in the two unit systems involved. It is derived as follows:

let $(x/m)_1$, C_1 represent magnitude of x/m and C in one set of units

         $(x/m)_2$, C_2 represent magnitude of x/m and C in a second set of units

Then $\log (x/m)_1 \;=\; \log K_1 + N \log C_1$ (7)

         $\log (x/m)_2 \;=\; \log K_2 + N \log C_2$ (8)

If A represents the conversion factor between the two systems of units

then $(x/m)_2 \,/\, (x/m)_1 \;=\; A, \quad C_2/C_1 = A$ (9)

and $\log (x/m)_2 \;=\; \log (x/m)_1 + \log A$ (10)

         $\log C_2 \;\;\;\;=\; \log C_1 + \log A$ (11)

Substituting Eqns. 10 and 11 into Eqn. 8

         $\log (x/m)_1 + \log A \;=\; \log K_2 + N [\log C_1 + \log A]$ (12)

Adding $\log A$ to each side of Eqn. 7

         $\log (x/m)_1 + \log A \;=\; \log K_1 + \log A + N \log C_1$ (13)

Subtracting Eqn. 13 from Eqn. 12

         $0 \;=\; \log K_2 - \log K_1 - \log A + N \log A$ (14)

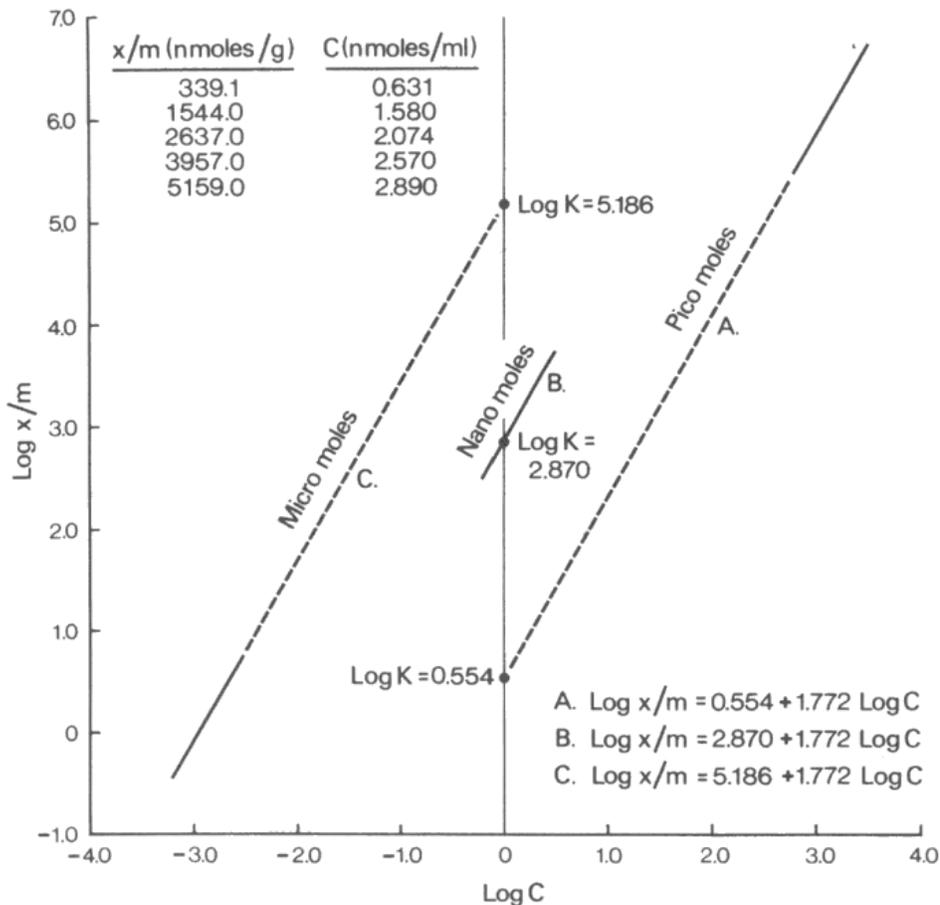 $\log K_1 - \log K_2 \;=\; N \log A - \log A$

or

         $\log (K_1/K_2) \;=\; \log A \;(N-1)$ (15)

Thus if the slope and K value are known, the new K values in another set of units can be calculated using either form of Eqn. 15.

Some experimental data from an earlier report[ ] were plotted in three molar units (p moles, n moles, μmoles) (Fig. 1) to demonstrate the dependency of K upon N. In this instance, units of n moles are the only appropriate way to show these data since $\log C = 0$ (where K is evaluated) is included within the data range.

x/m (nmoles/g)	C(nmoles/ml)
339.1	0.631
1544.0	1.580
2637.0	2.074
3957.0	2.570
5159.0	2.890

A. $Log \, x/m = 0.554 + 1.772 \, Log \, C$

B. $Log \, x/m = 2.870 + 1.772 \, Log \, C$

C. $Log \, x/m = 5.186 + 1.772 \, Log \, C$

FIGURE 1   Log-Log Freundlich Isotherm of the Fenitrothion-Fe^{3+}-Montmorillonite System Plotted in Three Different Systems of Units.

The K values obtained using the a mole or p mole data would not be valid since they fell considerably outside the data range. This particular example, with data points at log C=O, makes it easy to decide the appropriate system of units. However, it is common to find data ranges where 1.0 <log C <2.0 in which there are no data points near log C=0 in any of the data ranges, therefore requiring the questionable procedure of extrapolation to obtain the K value.

A series of adsorption parameters from the literature were re-calculated, using Eqn.15, to express K values in three commonly used sets of units (Table 1). The data range for each system is shown in the last column, indicating the most appropriate units for K. As noted

TABLE 1.   Effect of Slope Value on the Magnitude of Adsorption K Value when Changing Units.

| System | Slope | K | | | Molar Data Range |
		p moles /g	n moles /g	μ moles /g	
HBB[a]-Miami silt loam	0.50	137.4	4.37	0.138	Pico/Nano
Dieldrin-Plainfield sand[6]	0.88	106	46.8	20.4	Pico/Nano
Fonofos-Al^{3+}-Humic acid[4]	0.95	1550	1097	777	Pico/Nano
Parathion-Big Creek sediment[6]	0.99	22	20.5	19.1	Nano
Parathion-Beverly sandy loam[6]	1.00	20	20	20	Nano
Parathion-Na^+-Montmorillonite[1]	1.05	90	120	159	Nano
Dieldrin-Bradford muck[6]	1.08	4246	7413	1.29×10^4	Pico/Nano
Dieldrin-Beverly sandy loam[6]	1.12	112	257	588	Pico/Nano
Parathion-Fe^{3+}-Montmorillonite[1]	1.19	158	606	2319	Nano
Fenitrothion-Fe^{3+}-Montmorillonite[1]	1.77	3.6	741	1.53×10^5	Nano

[a.] HBB = 2,2',4,4',5,5',-hexabromobiphenyl.
 Superscript numbers refer to References.

above, there are several sets of data which fell between the ranges, and thus two units are shown. In accordance with Eqn.15, the effect of units on K increases with the deviation of N from unity, with one data set showing the constancy of K when N=1.0. With N<1.0, K values increase with smaller units, and conversely for N>1.0.

For deviations in slope value as small as 5% from unity (e.g. N=1.05 for parathion-Na^+-montmorillonite, Table 1) there was a 33% change in K value from the n mole to μmole or the p mole to n mole ranges. If the original data had been fitted to the Freundlich equation (Eqn. 1) assuming N=1.0 (instead of the actual 1.05 value), and forcing the

regression through the origin, the slope, or K_d value would have been 134.5 mL/g, 12.1% larger than the more precisely-fitted log transformed data in which K=120 nmoles/g. Since it will be a rare instance where the isotherm slope is exactly unity, it is recommended that all adsorption data be presented using the log-log plot, which is more universally applicable.

The data for hexabromobiphenyl[2] and fonofos[4] (Dyfonate[®]) were originally presented in ng and pg, respectively. The K values were converted to their respective molar values using the appropriate A factor (Eqn. 9) and substituting it into Eqn. 15. Unless N=1.0, K values cannot be directly converted from weight units (i.e. µg/g, ng/g to molar units (Table 2). The adsorption parameters were calculated from regression data in their respective units. Had the K value in µg/g (1995.4) been directly converted to nmoles/g using the molar conversion factor, K would have become 7198.4 nmoles/g (1995.4 µg/g x 3.61 nmoles/µg) instead of the correct value of 740.5 nmoles/g derived from actual data.

TABLE 2   Adsorption Data for the Fenitrothion-Fe^{3+}- Montmorillonite System and the Calculated Freundlich Adsorption Parameters.

x/m (pg/g)[1]	C (pg/mL)[1]	x/m (nmoles/g)	C (nmoles/mL)
94	0.175	339.1	0.631
428	0.438	1544	1.5801
731	0.575	2637	2.0743
1097	0.713	3957	2.570
1430	0.800	5159	2.890

1 µg = 3.6075 nmoles

Data Units	N	Log K	K	K (Direct Conversion)
µg/g	1.773	3.3000	1995.4	7198.4 nmoles/g
n moles/g	1.773	2.8685	740.5	

[1.] Bowman and Sans 1977.

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TABLE 3 **Adsorption Data for the Fenitrothion-Fe^{3+}- Montmorillonite System Using Mole Fraction to Express Equilibrium Concentration.**

x/m (n moles/g)[1]	x/m (p moles/g)	C (n moles/ml)[1]	Mole Fraction (Z)
339.1	339.1×10^3	0.631	$1.893 \times 10^{-8} / 1.6637 = 1.138 \times 10^{-8}$
1544	1544×10^3	1.580	$4.740 \times 10^{-8} / 1.6637 = 2.849 \times 10^{-8}$
2637	2637×10^3	2.074	$6.222 \times 10^{-8} / 1.6637 = 3.740 \times 10^{-8}$
3957	3957×10^3	2.570	$7.710 \times 10^{-8} / 1.6637 = 4.634 \times 10^{-8}$
5159	5159×10^3	2,890	$8.670 \times 10^{-8} / 1.6637 = 5.211 \times 10^{-8}$

Total Volume = 30 mL = 1.6637 moles (20^{0}C)

$\log K = 16.5937$ $\qquad\qquad$ $K = 3.924 \times 10^{16}$ n moles/g

$\log K = 19.5937$ $\qquad\qquad$ $K = 3.924 \times 10^{19}$ p moles/g

$\log K = \ \ 7.5937$ $\qquad\qquad$ $K = 3.924 \times 10^{7}$ moles/g

slope = 1.772

[1] Bowman and Sans 1977.

The problem of changing the units of K occurs because of the manner in which N acts on the log C value in Eqn. 4. There would be no anomaly if log C were unitless. This can be accomplished by reporting equilibrium concentration values in terms of mole fraction, Z. (Z was chosen rather than the customary X to avoid confusion with x/m). At equilibrium, the mole fraction in solution could be represented as

$$Z \quad = \quad \frac{\text{moles of solute}}{\text{moles of solute + moles of solvent}} \qquad (16)$$

Since moles solute « moles of solvent, Eqn. 16 becomes

$$Z \quad = \quad \text{moles of solute/moles of solvent} \qquad (17)$$

The log Freundlich equation can now be re-written as

$$\log x/m \ = \ \log K \ + \ N \log Z \qquad (18)$$

Using this relationship on the data of Fig. 1, K values calculated become consistent regardless of units selected (Table 3), and only reflect the 10^3 change in units. Similarly, units of K expressed in pg/g could be directly converted to molar units using the appropriate conversion factor, instead of converting the original data to the new units and re-calculating K. The replacement of concentration with mole fraction in Eqn. (18) eliminates the

discrepancy between the dimensional analysis of units of K which were complex (Eqn. 3), and the units of moles/g in which K is often expressed. The units of K, when mole fraction is used to express equilibrium concentration, will always be the same as the units for x/m, preferably moles/g.

The use of mole fraction, however, does require that the modified Freundlich equation be interpreted differently. K can no longer be used as a relative measure of adsorption because it is evaluated at log Z=0, Z=1. This would occur when there was only pure solute (insecticide) in equilibrium with adsorbent and no solvent (water) present. Instead, relative adsorption should be evaluated in the Z range where there is adsorption data - in the 10^{-7} to 10^{8} range for many pesticides. It is suggested that instead of K values, $(x/m)_Y$ values be used to compare adsorption among pesticides, where Y = log Z value would be used as a reference concentration. The log Z data range in Table 3 was -7.94 to -7.28 and in this situation $(x/m)_Y$ could be evaluated at log Z=-7.0 or -8.0. For log $(x/m)_{-7}$, Eqn. 18 becomes

$$\log (x/m)_{-7} = 7.5937 + 1.772 (-7.0) = -4.810 \text{ moles/g}$$
$$(x/m)_{-7} = 1.549 \times 10^{-5} \text{ moles/g}$$

It would be preferable to choose as a reference point, a log Z value which would translate into concentration values commonly found in nature. In the above example, a log Z value of -7.0 occurs at an equilibrium concentration of 1.54 µg/mL.

Although presentation of adsorption data using mole fraction to express equilibrium concentration solves the problem of expressing and converting units of K, it does not solve the problem of comparing relative adsorption of compounds which have greatly different adsorption tendencies and whose data ranges are quite separate from each other. Relative $(x/m)_Y$ (or K) values should not be regarded as being reliable if they are evaluated at log Z (or concentration) values much outside their data range. When constructing isotherms it would be desirable to collect data over the widest possible concentration range (up to solubility limit) in order to have a common log Z value at which relative adsorption can be assessed.

In summary:

1) To compare K values in the literature, the units of K must be consistent, and the point of evaluation (log C=0) must be included in, or close to the data range.

2) Freundlich K values expressed in one set of units cannot he directly converted to another set of units using a simple conversion factor unless the Freundlich slope, N=1.0.

3) The numerical magnitude of the Freundlich K values changes when reported in different units. A mathematical relationship was derived relating N to K values in different sets of units.

4) When equilibrium concentration is expressed in moles/L and the solute adsorption in moles/g, dimensional analysis shows the units of K to be $moles^{(1-N)} L^N g^{-1}$ instead of moles/g, the commonly used units.

5) To avoid problems of units with the use of K, equilibrium concentration data should be converted to mole fraction (Z).The log Freundlich equation then becomes

$$\log x/m = \log K + N \log Z.$$

K values lose their meaning in this context since they would be evaluated at Z=1 (pure solute, no solvent as equilibrium phase). It is suggested that relative adsorption, $(x/m)_y$, be evaluated at appropriate log Z values, where Y=log Z, and for which data exists at or near the log Z value being selected. It is strongly recommended that all adsorption data be reported in molar units in order that $(x/m)_y$ data be consistent in the literature.

REFERENCES

1.   B. T. Bowman and W. W. Sans. Soil Sci. Soc. Amer. J. <u>41,</u> 514-519 (1977).

2.   A. B. Filonow, L. W. Jacobs and M. M. Mortland. J. Agric. Food Chem. <u>24</u>, 1201-1204 (1976).

3.   V. H. Freed and R. Haque. Adsorption, movement, and distribution of pesticides in soils. In Pesticide Formulations. Edited by W. Van Valkenburg. Marcel Dekker publ. pp. 441-459 (1973).

4.   S. U. Khan. Can. J. Soil Sci. <u>57</u>, 9-13 (1977).

5.   R. H. Pierce Jr., C. E. Olney and G. T. Felbeck Jr. Geochim. et Cosmochim. Acta <u>38</u>, 1061-1073 (1974).

6.   M. S. Sharom. The behavior and occurrence of some insecticides in aquatic systems. PhD. Thesis, Univ. of Guelph. 158p (1977).

7.   United States Environmental Protection Agency, Federal Register, Vol. 43, No. 132, 29718-29719 (10 July 1978).