NUMERICAL TECHNIQUE FOR ESTIMATING EQUILIBRIUM CONCENTRATIONS FROM INITIAL CONCENTRATIONS WHEN USING THE FREUNDLICH ADSORPTION EQUATION

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ABSTRACT

The Freundlich equation, $X/m = K C_e^N$, is frequently used to express the partitioning of pesticides between solid (soil, sediment) and aqueous phases. When designing adsorption-desorption experiments, it would be useful to be able to estimate the equilibrium concentration, C_e, in terms of the initial concentration, C_e, if reasonable estimates of K and N can be made. Because of the usual non-integer nature of N, only a numerical solution of the Freundlich equation is possible for C_e in terms of C_e. A simple computer program is presented which produces almost an exact solution for the value of C_e.

INTRODUCTION

The Freundlich equation, $X/m = K C_e^N$, is perhaps the most commonly used expression for describing pesticide partitioning between aqueous and solid (soils, sediment) phases. In batch-type adsorption studies in the laboratory, it would be very useful to have a prior estimate of pesticide concentrations existing at equilibrium on the solid and in the liquid phases, so as to facilitate experimental design and analysis. In desorption studies it also would be useful to estimate in

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advance what partitioning will be so that an appropriate combination of solution volumes, adsorbent weights and dilution factors can be selected. Should desorption hysteresis occur, the calculated solution concentrations would be the maximum possible, and actual values would decrease with increasing hysteresis. The ability to predict equilibrium solution concentrations based on amount of solute present, amount of adsorbent and partitioning constants (K, N) would be most useful for modeling studies. There has been a tendency to assume linear adsorption of pesticides ($X/m = K_P C$, $N = 1$) (Karickhoff *et al.,* 1979, Roberts *et al.,* 1981), perhaps because only a numerical solution of the Freundlich equation is possible for equilibrium concentration expressed in terms of initial concentration (C_e). The purpose of this communication is to introduce a simple iterative routine using a microcomputer that will quickly give solution concentration estimates, if reasonable estimates of K and N can be made.

THEORY

In an adsorption or desorption experiment, the adsorbent weight, m, and total amount of pesticide, X_T, are always known, and if prior knowledge of, or reasonable estimate of K and N can be made, then it should be possible to express the solution concentration (C_e) in terms of the initial concentration (C_o). In the following derivation, the amount of pesticide in solution, X_s, will be expressed as a function of the total amount of pesticide in the system, X_T.

$$X_T = X_a + X_s \tag{1}$$

where X_T and X_s have been defined above (µg)

X_a = amount of pesticide adsorbed (µg)

The Freundlich equation can be rewritten as:

$$X_a/m = K (X_s / V)^N \tag{2}$$

where the equilibrium concentration, $C_e = X_s/V$

   V = aqueous phase volume (mL)

Solving for X_a in Eq. 1 and substituting into Eq. 2

$$(X_T - X_s)/m = K(X_s/V)^N \tag{3}$$

Solving for X_S and rearranging

$$mK\,X_s^N + V^N X_s - V^N X_T = 0 \tag{4}$$

Since N is usually a non-integer value that can experimentally range from about 0.4 to 1.7, there does not appear to be a simple analytical solution for X_s, and in order to solve it, numerical techniques must be employed.

   A simple computer program (in BASIC), which uses a slightly modified Newton method (Smail, 1953), has been written to make a close numerical approximation to the exact solution for X_s. Initially, an estimate of X_s is made assuming a linear isotherm (i.e., N = 1). Thus,

$$X_a/m = K(X_s/V) \tag{5}$$

Substituting for X_a, using Eq. 1, and solving for X_s

$$X_s = V\,X_T/(V + mK) \tag{6}$$

In the Newton method, the ratio of the function F(x)(i.e., Eq. 4) to its first derivative, $F^1(x)$, is subtracted from the initial estimate, X_s(Eq. 6) and this value becomes the second estimate. This process is repeated until there is little or no difference in successive estimates. The first derivative of Eq. (4) is:

$$F^1(X_s) = N\,m\,K\,Xs^{N-1} + V^N$$

The program is listed in Appendix I.

RESULTS AND DISCUSSION

   The Program outputs include estimates of both amounts of solute in solution (X_s) and on the adsorbent (X_a), as well as their respective concentrations in solution (C_e) and on the adsorbent (X/m). The following examples demonstrate how the program is used in experimental design and analysis of adsorption-desorption systems.

EXAMPLE 1. PARATHION ADSORPTION ISOTHERM FOR AN ORGANIC SOIL

   Since the water solubility of parathion is about 12.5µg mL^{-1}, the five initial concentrations (five adsorption points) must be selected over the 0-10 g mL^{-1} range.

The only adsorption information available was from the literature where $K = 700$ $\mu g^{1-N} g^{-1} mL^N$, $N = 0.95$. However, in that study, the author used 1.0 g soil in a 200 mL volume. In this experiment, the solution volume was to be 30 mL. It was necessary to establish a suitable ratio between adsorbent weight and the lowest initial concentration, such that the equilibrium concentration would be within the analytical range of the gas chromatograph, which in this study was at least 0.1 μg mL^{-1}. Table 1 shows the predicted partitioning for several combinations of initial concentrations and adsorbent weights. The lowest initial concentration selected was 1.0 μg mL^{-1} using an adsorbent weight of 0.2 g (oven-dry basis). Having selected the adsorbent weight of 0.2 g, predicted equilibrium concentrations were then computed for four other initial concentrations including 10 μg mL^{-1} (i.e., 2.0, 4.0, 6.5 μg mL^{-1}). Although not shown here, the Program was used to select the other initial concentrations such that the equilibrium concentrations were fairly evenly spaced.

Despite the fact that this organic soil sample (Table 2) adsorbed somewhat less than that in the literature citation, the resulting solutions were still within the analytical range. Usually the lowest concentration sample would be analyzed first, and if its concentration is much different from the predicted value, proportional adjustments can be made to either the dilution factors of higher concentration samples, or to the standards selected to embrace the unknown samples.

EXAMPLE 2. DESORPTION ISOTHERM

A desorption isotherm was constructed for the parathion-organic soil system described in Example 1. The dilution method for desorption was used, where five adsorption samples (triplicate) were prepared (0.2 g soil + 30 mL of 10 g mL^{-1} parathion solution) and equilibrated for 24 hr. At that time one sample was selected for analysis of the supernatant and different volumes of distilled water were added to the four other samples, which were then equilibrated for a second 24 hr period prior to analyzing the supernatant. The computer program was used in selecting

TABLE 1. Estimation of Equilibrium Concentrations of Parathion in Aqueous Slurry of an Organic Soil for Various Soil Weights and Initial Starting Concentrations Using Computer Program.

Initial Conc. ($\mu g\ mL^{-1}$)	Total Solute (μg)	Adsorbent Weight (g)	Predicted C_e * ($\mu g\ mL^{-1}$)	Predicted X/m* ($\mu g\ g^{-1}$)
1.5	45	0.50	0.11	84
		0.20	0.25	188
		0.10	0.44	319
1.0	30	0.50	0.07	56
		0.20	0.16	125
		0.10	0.29	214
0.5	15	0.50	0.034	28
		0.20	0.079	63
		0.10	0.140	108

* Predictions made using N = 0.95; K = 700 $\mu g^{1-N} g^{-1} mL^{N}$; V = 30 mL

TABLE 2. Comparison of Predicted and Actual Equilibrium Concentrations Obtained for Parathion Adsorption by an Organic Soil.

Initial Conc. ($\mu g\ mL^{-1}$)	Adsorbent Weight (g)	Predicted C_e * ($\mu g\ mL^{-1}$)	Actual C_e ** ($\mu g\ mL^{-1}$)
1.0	0.2273	0.146	0.199
2.0	0.2276	0.301	0.433
4.0	0.2271	0.622	0.942
6.5	0.2268	1.03	1.62
10.0	0.2273	1.62	2.62

* Prediction made using N = 0.95; K = 700 $\mu g^{1-N} g^{-1} mL^{N}$; V = 30 mL

** Measured isotherm constants: N=0.86; K=425 $\mu g^{1-N} g^{-1}\ mL^{N}$

the volumes of water used to dilute the adsorption samples such that the desorption points would be somewhat evenly spaced and analyzed above detection limits. In Table 3, a series of dilution volumes were used in computing the partitioning of parathion. The last column shows the various volumes selected, which would produce somewhat evenly spaced equilibrium concentrations.

TABLE 3.   Selection of Appropriate Dilution Volumes for Parathion-Organic Soil Desorption Isotherm.

Vol. Added (mL)	Total Vol. V_T (mL)	Predicted* C_e ($\mu g\ mL^{-1}$)	Predicted X/m ($\mu g\ g^{-1}$)	Chosen Volumes
-	30	2.77	1020	Adsorption
30	60	2.10	805	1
70	100	1.60	636	2
90	120	1.43	578	
150	180	1.09	457	3
220	250	0.85	320	
370	400	0.58	268	4

* based on: N = 0.86; K = 425 $mg^{1-N}\ g^{-1}\ mL^N$; m = 0.2 g; X_T = 287 g

TABLE 4.   Comparison of Predicted and Actual Equilibrium Concentrations Obtained for Parathion Desorption From an Organic Soil.

Desorp. Sample	Ads. Weight (g)	Predicted C_e * ($\mu g\ mL^{-1}$)	Actual C_e ($\mu g\ mL^{-1}$)
1	0.2277	1.94	1.85
2	0.2285	1.42	1.50
3	0.2281	1.04	0.97
4	0.2275	0.57	0.54

* based on: N = 0.86; K = 425 $\mu g^{1-N}\ g^{-1}\ mL^N$; X_T = 287 g; volumes as indicated in Table 3.

Hysteresis effects will result in somewhat lower-than-predicted equilibrium concentrations and therefore the dilution volumes must be chosen with this factor in mind.

Table 4 shows excellent agreement between predicted and actual equilibrium concentrations, indicating a minimal amount of hysteresis for this system. Agreement between predicted and actual values was much better than in the first example because accurate K and N values were available.

This program is also adaptable to the successive removal-resuspension technique for desorption where aliquots of supernatant are replaced with distilled

water, and then the sample is re-equilibrated. In this case the volume is constant, and the total solute present, X_T, is decreased by (C_e x V) following each desorption step. Again, when predicting desorption equilibrium, hysteresis effects must be compensated for as discussed earlier.

With a few minor syntax changes, this computer program will run on any microcomputer, and would, as a sub-routine in modeling programs, allow the use of the Freundlich equation, rather than assuming linear pesticide partitioning between soil and water phases. Because of the short running time, it is possible to quickly examine the effect that changing adsorbent weights or solution volumes has on the equilibrium concentration. The use of this program has: 1) saved considerable time in that samples are seldom wasted or discarded because equilibrium concentrations are below detectable limits, or outside limits of standards being used, and 2) resulted in isotherms with more uniformly spaced data points.

If a microcomputer is not available, it is possible to adapt this program for manual use on an advanced scientific calculator since the iterative procedure rapidly converges (usually within two cycles). In lines 50 and 60, four different calculator memories could store B1, B2, B3 and X, and one could manually step through lines 70 to 110 and recycle to line 70 as required. At line 110, the new estimate, X1, would be entered into Memory 4 to replace X for the second cycle.

APPENDIX I
PROGRAM LISTING FOR PREDICTING FREUNDLICH PARTITIONING

```
10:      CLEAR
20:      INPUT "K(µg-mL) = "; K, "SLOPE (N) = "; N
30:      INPUT "VOL(mL) = "; V
40:      INPUT "SOIL WT.(g) = "; M, "TOTAL SOLUTE(µg) = "; A
50:      B1 = M*K : B2 = V ^ N :B3 = B2*A
60:      X = V*A / (V+B1)
70:      F1 = B1*X^N+B2*X-B3
80:      F2 = N*B1*X^(N-1)+B2
```

```
85:        IF F1/F2>=X LET X = X/10: GO TO 70
90:        X1 = X-F1/F2
100:       IF ABS(X1-X)<1E-09*X1  GO TO 120
110:       X = X1 : GO TO 70
120:       X2 = M*K*(X1/V)^N : USING "##.#####^"
130:       PRINT "AMT(soln) = "; X1: PRINT "CONC.(soln) = "; X1/V
140:       PRINT "AMT(ads.) = "; X2: PRINT "CONC.(ads.) = "; X2/M
150:       PAUSE "END OF PROGRAM" : END
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Program Notes:

1. The Newton method fails for certain combinations of small N values (<1.0) with large K values, if too large an initial estimate is made (as per Eq. 6). This occurs when the $F(X_s)/F^1(X_s)$ ratio $>X_s$, the initial estimate. (In the program $F1 = F(X_s)$, $F2 = F^1(X_s)$.) Consequently the second estimate of X_s is negative (X1, line 90). When the program recycles to line 70 for the next estimate, an error results because it is impossible to take a root of a negative number, *i.e.*, $N<1$, $X_s<0$, thus X^N is imaginary. To correct for this large initial estimate, line 85 was inserted where X_s is repeatedly reduced by a factor of 10 until $X_s > F(S_x)/F^1(X_s)$. The program then rapidly converges to an answer, usually within three cycles.

2. In line 100, the computer is directed to make further estimates of X_s until two successive estimates differ by less than ($Xs *10^{-9}$). This happens to be one digit less than the accuracy (10 digits) forthe pocket computer for which the program was written.

3. Care should be taken that consistent units are used throughout, especially the units for K (Bowman, 1981; Bowman, 1982), if literature values are being used as estimates. Units other than those shown for Input values (Lines 30, 40) may be used providing they areconsistent with those used in obtaining the K value.

4. Required Inputs: Solution Volume, Adsorbent Weight, Freundlich constants K and N, and Total Amount of pesticide (initial concentration x volume).

5. If a number of successive estimates are being made using the same K, N, and/or volume inputs (Lines 20 and 30), then Line 150 can be changed to "GO TO 20", or "GO TO 30" as is appropriate.

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