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proper value for q, in this case 2.326. The solution for distance travelled by vapor diffusion is then:

$$x_v = q\sqrt{4Dt} = w\sqrt{t} \qquad (36)$$

$$\text{where } w = q\sqrt{4D} \qquad (36a)$$

6). The time in days is calculated to reach an arbitrary 3-meter deep groundwater with c/c_0 of 0.000001 to 0.8 by adding equations (35) and (36). The combined movement with water and as vapor is approximated as:

$$xx = w\sqrt{t} + uu \cdot t = 3 \text{ m} \qquad (37a)$$

letting $$z^2 = t \qquad (37b)$$

$$wz^2 + w \cdot z - xx = 0 \qquad (37)$$

solving for z gives: $$z = \{-w + \sqrt{[w^2 - (4\,xx \cdot uu)]}\}/2\,uu \qquad (38a)$$

or $$t = z^2/(60 \cdot 60 \cdot 24) \qquad (38)$$

CONCLUSIONS

1). This PC computer program provides an easy way to estimate the potential of a chemical for migration in soil or groundwater.

2). It requires as data only

a. aqueous solubility (and if cpd is a solid, then preferably a MP)

b. vapor pressure

c. molecular weight

3). It derives several simple parameters such as KOW, KOC, Rf, and a soil vapor diffusion coefficient, D_S.

4). Migration patterns and fluxes for several simple situations are calculated.

5). Because of the widely varied migration properties of different chemicals, it provides for consideration of both aqueous migration and vapor diffusion. This should be done in general.

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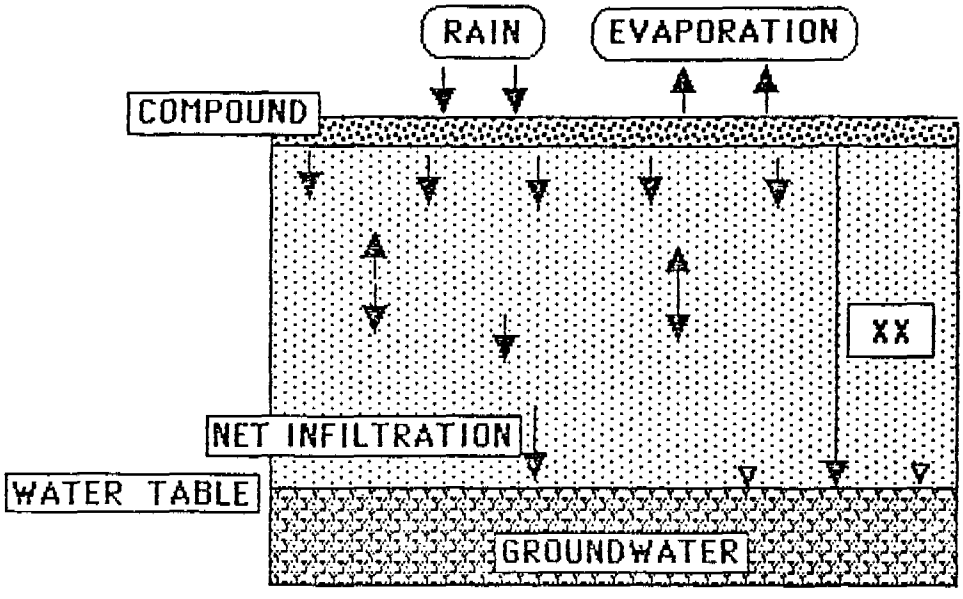
Figure 6. Time for Compound to Reach Groundwater Scenario.



The assumptions and derivation are as follows:

1). The compound is initially in the surface zone.

2). Intermittent rainfall totalling 88 cm/y drives the compound downward according to the Rf value and Ø.

3). Back movement of 48 cm/y of water with evaporation moves the compound back upward according to Rf and Ø. (Actually desorption is slower and less effective than adsorption and material left adsorbed for some time is more firmly bound).

4). We simplify the outcome of 2) and 3) as simply the net downward movement of water x Rf/Ø.

Darcy velocity	$v = 40$ cm/y = 1.27E-6 cm/s	(35a)
Compound velocity	$uu = Rf \cdot (1.27E-6)/\emptyset$	(35b)
Compound travel by water	$x_W = uu \cdot t$	(35)

5). Vapor phase diffusion is simply included as an additive value. (This is certainly not strictly so, but gives some measure of overall effect).

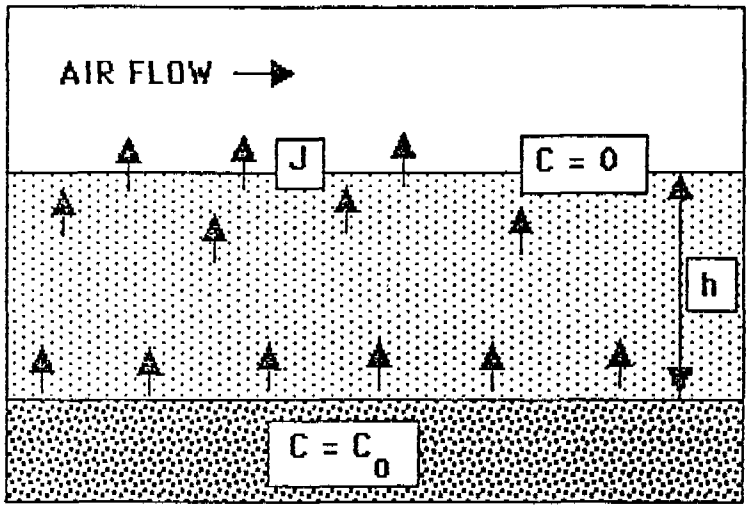
We need the value of $x_v/\sqrt{4Dt}$ such that

$$1 - erf(x_v/\sqrt{4Dt}) = C/C_0 \qquad (36a)$$

We then define a value $q = x_v/\sqrt{4Dt}$ (36b)

For any given value of C/C_0, e.g., 0.001, we can obtain from a table of the error function, erf, the

Figure 5. Steady State Flux Through a Soil Layer.



This solution is based on Fick's law and follows a similar treatment by Farmer et al (19xx) for hexachlorobenzene loss through a landfill cover of clay.

$$J = -D\Delta c/h \quad (33)$$

but $D = D_S$ (33a)

and $\Delta c = 0 - c_0 = (WS/KWA)\,\sigma_\theta$; let COV = Δc (33b)

but $h = 1\ m = 100\ cm$ (33c)

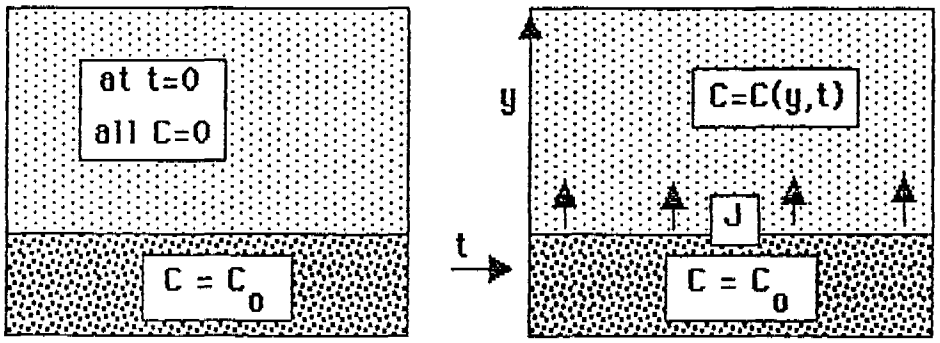
Converting from seconds to days we get:

$$J = 864 \cdot D_S \cdot COV \quad \mu g/(cm^2 \cdot d) \quad (34)$$

Time to Reach 3-meter Deep Groundwater

This example deals with the movement of a compound initially present in surface layers of the soil and subject to downward movement along with infiltrating water from rain and also by superimposed vapor diffusion.

Figure 4. Total Depletion from a Plane Source by Vapor Migration from Initial Exposure to Given Time, t.



It is calculated by: $J_{av}\, t = c_0\sqrt{4\,Dt/\pi}$ (24)

This is derived from Fick's law: $J = -D\,\partial c/\partial y$ (25)

coupled with the solution of the diffusion equation :

$c/c_0 = 1 - \mathrm{erf}(y/\sqrt{4\,Dt})$ (26)

where $\mathrm{erf}(q) = 2/\sqrt{\pi}\int_0^q \exp(-n^2)\,dn$ (26a)

with $q = y/\sqrt{4Dt}$ (26b)

then $d(c/c_0)/dq = (-2/\sqrt{\pi})\exp(-q^2)$ (27)

or $\partial c/\partial y = (-1/\sqrt{Dt\pi})\exp(-y^2/4Dt)\cdot c_0$ (28)

Therefore an instantaneous flux value is:

$J = (\sqrt{D/\pi t})\exp(-y^2/4Dt)c_0$ (29)

The average value of flux over time at y=0 is then

$J_{av} = \int_0^t J\,dt/\,t = (c_0/t)\int_0^t \sqrt{D/\pi t}\,dt$ (30)

or $J_{av} = c_0\sqrt{4D/\pi t}$ (31)

therefore $J_{av}t = c_0\sqrt{4Dt/\pi}$ (32)

Steady State Flux Through 1 Meter of Soil

For the situation where a zone of soil with a concentration of the compound at a concentration, $c=c_0$ is covered with 1 meter of soil, such as, for example, clay, the program calculates an estimated steady state flux passing through the soil. This could be illustrated as shown in Figure 5.

the solution of equation (10a) is:

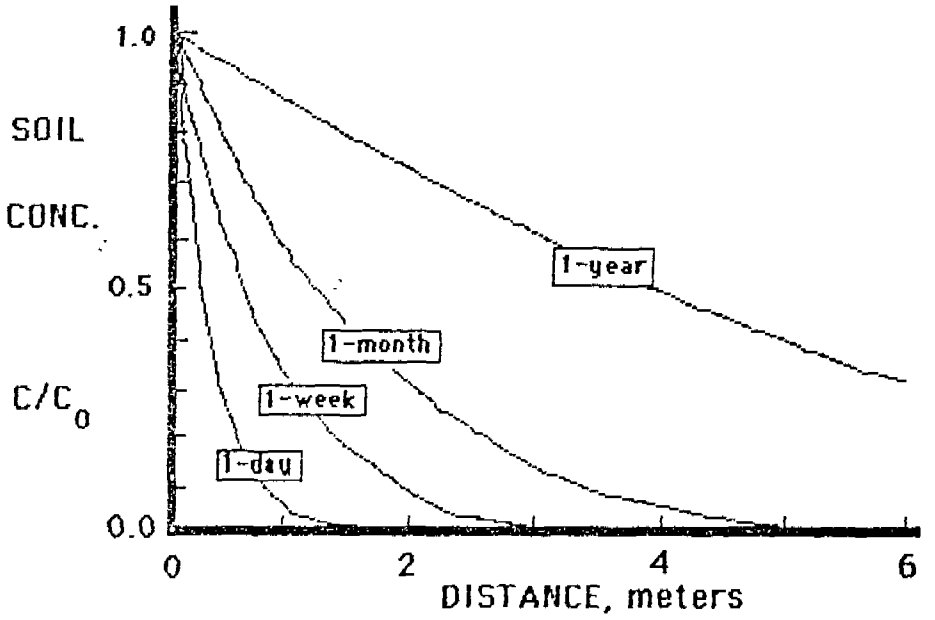
$$c/c_0 = 1 - \mathrm{erf}(q) \qquad (23)$$

where $$q = x/\sqrt{4 D_s t} \qquad (23a)$$

and $$\mathrm{erf}(q) = (2/\sqrt{\pi})\int_0^q \exp(-y^2)dy \qquad (23b)$$

Using the estimated value of D_s from equation (22), we can solve for x at any time t, or for t for any penetration distance, x. The program calculates values for this simple example one-dimensional migration from a large planar source, giving solutions of x for c/c_0 of 0.000001 to 0.8, at times of 1,7,30, and 365 days. If these data are plotted they appear as follows:

Figure 3. Vapor Diffusion Migration Distances.



Vapor Migration, Zero Time to Given Time

This example represents material depleted from a plane layer, with a concentration $c=c_0$, into an adjacent region from an initial exposure time to any given time, t, as indicated in Figuyre 4. The derivation is similar to one given by Thibodeaux (19xx) for upwelling of nutrients from a lake bottom.

To estimate the diffusion coefficient of a compound in air, Shen gives an equation 3:

$$D' = D(M/M')^{1/2} \quad (18)$$

This leads here to $D_{cpd} = D_{air}\sqrt{MW_{air}}/\sqrt{MW_{cpd}}$ (19)

$$= 0.1849\,(\sqrt{28.8})/(\sqrt{MW}) \quad (19a)$$

or: $$D_a = D_{cpd} \approx 1/\sqrt{MW} \quad (20)$$

D_S, Soil Diffusion Coefficient

The program calculates a soil vapor diffusion coefficient, D_S, following the general lines of the treatment of Goring and Hamaker (1972). It is simply the air diffusion coefficient reduced by the fraction of compound in the soil air space and by a tortuosity factor (Hemwall in G&H).

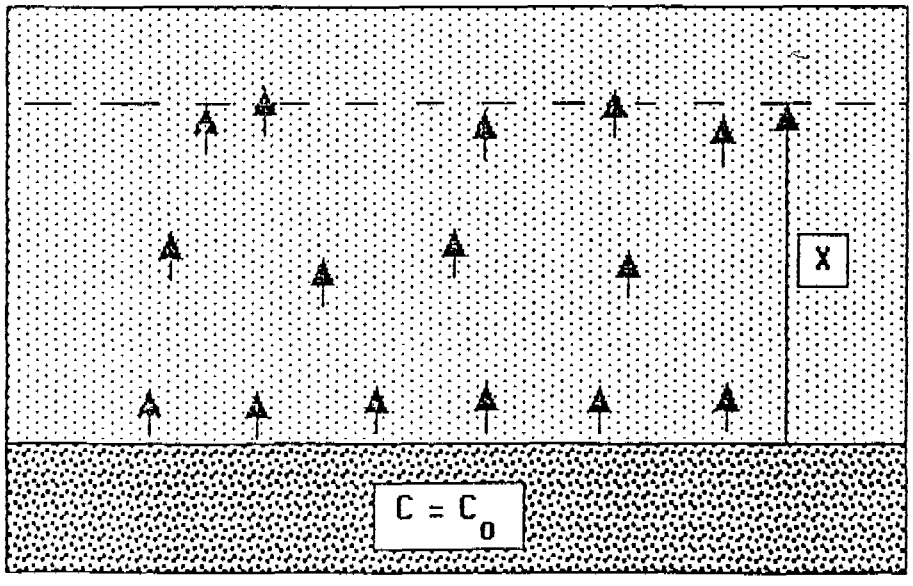
$$D_S = 0.66\, F_a \cdot D_a \quad (21)$$

$$D_S = \frac{(0.66)\,\emptyset \cdot D_a}{\emptyset_a + BD \cdot KOC \cdot OC \cdot \emptyset_W + \emptyset_W \cdot KWA} \quad (22)$$

A Vapor Diffusion Application

The diffusion equation (10), if restricted to one dimension, for a situation such as indicated below, becomes: $(\partial c/\partial t)_x = D_S \cdot (\partial^2 c/\partial x^2)$ (10a)

Figure 2. One-Dimensional Vapor Diffusion.



VAPOR DIFFUSION

The equation governing movement as vapor in the air pososity of the soil is the general diffusion equation:

$$\partial c/\partial t = D\cdot\partial^2 c/\partial x^2 + \partial^2 c/\partial y^2 + \partial^2 c/\partial z^2 \qquad (10)$$

An appropriate D value and 5 typical applications are generated by the program. Movement can be 1000 to 10000 times faster than the diffusion of a few cm/month observed in liquids.

Fraction in the 3 Soil Phases

Following the general treatment in Goring & Hamaker (1972), the amount of compound/ml of soil for each phase can be expressed as:

$$\text{in water, } x_w = c_w \phi_w \qquad (11a)$$

$$\text{in air, } x_a = c_a \phi_a = (c_w/KWA)\cdot\phi_a \qquad (11b)$$

$$\text{in solids, } x_s = c_s\cdot \phi_s\cdot d_s = KOC\cdot OC\cdot c_w(d_s\phi_s) = c_w\cdot KOC\cdot OC\cdot BD \qquad (11c)$$

$$TOTAL = x_w + x_a + x_s = c_w\cdot TOT \qquad (11)$$

$$\text{where} \quad TOT = \phi_w + \phi_a/KWA + KOC\cdot OC\cdot BD \qquad (11d)$$

The fraction of compound in each phase is then given by:

$$\text{in water, } F_w = x_w/TOTAL \qquad (12)$$

$$\text{in air, } F_a = x_a/TOTAL \qquad (13)$$

$$\text{in solids, } F_s = x_s/TOTAL \qquad (14)$$

C_0-Soil, maximum soil concentration without a 2nd liquid phase.

$$C_0\text{-Soil} = WS\cdot TOT \qquad (15)$$

DIF-AIR, an air diffusion coefficient

This is estimated simply as $D_a \approx 1/\sqrt{MW}$; the derivation is as follows:

An equation for estimating the diffusion of one gas in another is given by T. T. Shen (Shen, 1981, eqn 2):

$$D = 0.001T^{1.75}\sqrt{(1/M_1 + 1/M_2)}\,/\,\{P[(\Sigma V_1)^{1/3} + (\Sigma V_2)^{1/3}]^2\} \qquad (16)$$

For air in air using $V_1 = V_2 = 20.1$ (Shen), $M_1 = M_2 = 28.8$, and $T = 20$ °C gives:

$$D_{air} = 0.1849\ cm^2/sec \qquad (17)$$

ASSUMED TYPICAL SOIL PROPERTIES

The following typical soil properties are used by the program:

	CLAY	LOAM	SAND	GRAVEL
Porosity, Ø	0.40	0.50	0.30	0.50
Air fraction, $Ø_a$	0.20	0.25	0.15	0.25
Water fraction, $Ø_w$	0.20	0.25	0.15	0.25
Bulk density, BD, g/ml	1.50	1.25	1.75	1.25
Permeability, k, cm/s	1.0e-7	1.0e-4	1.0e-3	1.0
% Organic carbon, OC · 100	0.10	1.45	0.10	0.01

AQUEOUS MIGRATION

The program estimates the movement of a compound through the soil by water convection as modified by adsorption. It does this by combining a water velocity from Darcy's law and an estimated Rf for the compound vs the water.

Rf-Soil Column

This is estimated by use of an equation given by J. W. Hamaker (1975) (his equation #4):

$$1/Rf = 1 + K_{OC}(\%\ OC/100)d_S(1/Ø^{2/3}-1) \qquad (6)$$

where d_S=soil particle density=2.50 g/ml= BD/Ø. This equation was derived by Hamaker for soil TLC. He gave a slightly rearranged equation expressed as an "R" value giving the compound movement in the soil relative to the water entry rate into the soil for soil columns. The latter showed excellent agreement with experimental values for flow rates of <0.1 in/hr. The single form used here seems appropriate for both situations.

Migration, meters

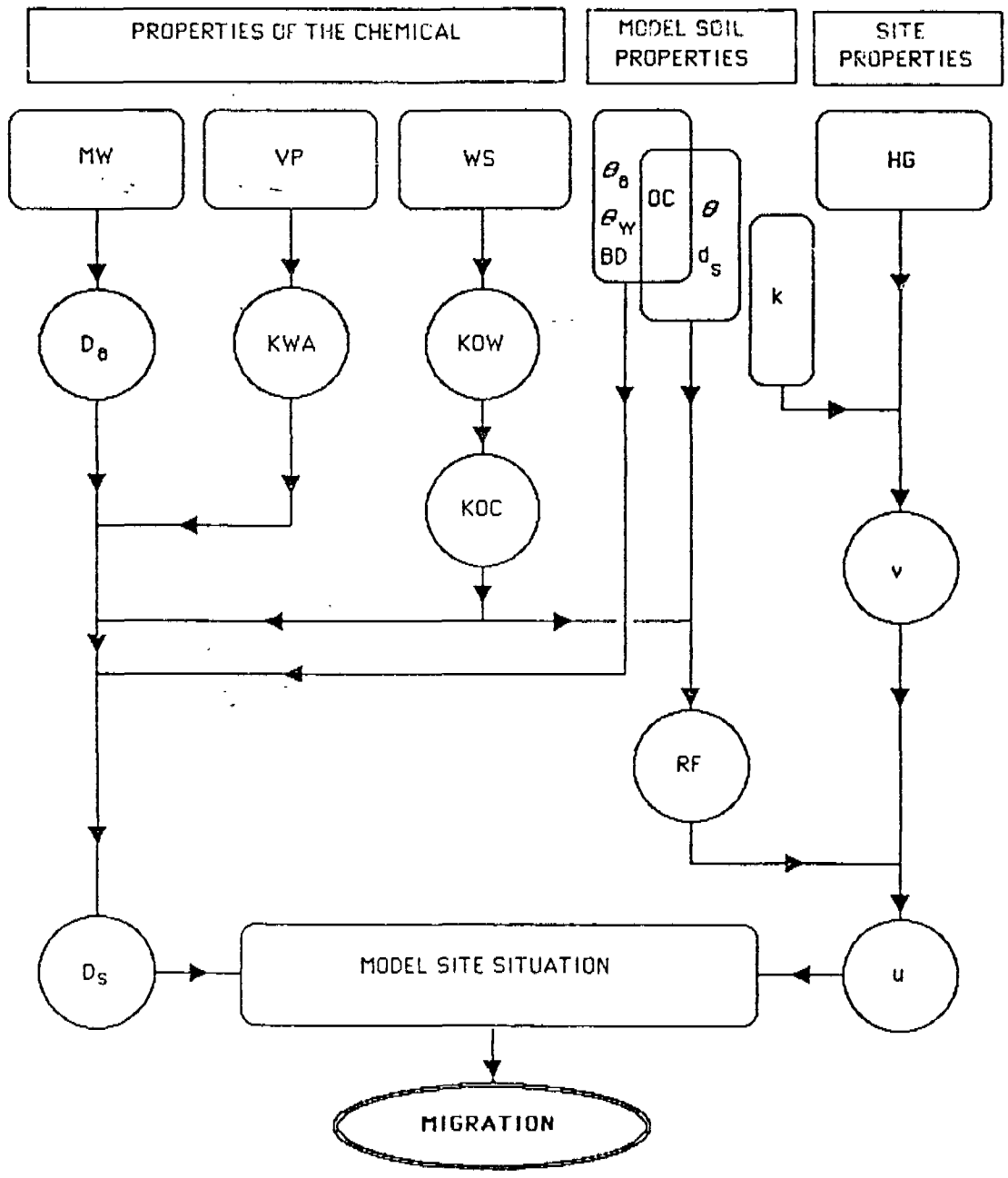
The distance travelled by the center of mass of the concentration for several times (1,7,30, and 365 days), three typical hydraulic gradients (HG)(0.001, 0.01, and 0.10), for 4 soil types (clay, loam, sand, gravel) are estimated for a no dispersion condition. The equations used are:

$v = -k \cdot HG$ Darcy velocity (7)

$u = Rf \cdot v/Ø$ Compound velocity (8)

$XAQ = u \cdot (t\ sec)/100$ cm/m Compound travel (9)

FIGURE 1. MIGRT DATA FLOW SHEET



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If the chemical is a solid with unknown MP, the Chiou relation (Chiou, 1977) is used:

$$\log KOW = 5.00 - 0.67 \log S \quad (2)$$

or $$\ln KOW = 11.513 - 0.67 \times \ln S \quad (2a)$$

An option is provided in the input prompts to allow the bypass of the correlation equations and directly enter a known KOW.

KOC, the soil adsorption coefficient.

This is obtained from KOW by the Karickhoff/Brown relation, their eqn 5 (Karickhoff/Brown, 1979):

$$KOC = 0.63 \times KOW \quad (3)$$

BCF, Bioconcentration Factor

While not directly involved in the partitions that are used in groundwater calculations, this partition coefficient is readily available from KOW, and is useful in environmental evaluations. The equation is from Veith/Defoe, 1979.

$$\log BCF = 0.85 \log KOW - 0.70 \quad (4)$$

or $$\ln BCF = 0.85 \ln KOW - 1.612 \quad (4a)$$

KWA, water to air partition coefficient

This is the reciprocal of the dimensionless Henry's Law constant, i.e.:

$$KWA = c_w/c_a \quad (5a)$$

where c_w is the saturation concentration in water at, say 20° C,

or: $$c_w = (WS\ mg/L)/((1000\ mg/g)(MW)) \quad (5b)$$

and c_a is the saturation concentration in air at, say 20 °C,

or: $$c_a = (VP, mm\ Hg/760)/((0.082\ L\ atm\ mol^{-1} \cdot K^{-1})(293\ K)) \quad (5c)$$

or: $$KWA = 18.26\ WS/(VP \times MW) \quad (5)$$

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MIGRT, a Computer Program to Estimate Migration Properties of Chemicals in Soil and Groundwater

F.A.Blanchard
Anal & Env Chem, H & ES, Dow USA

Has program for this

For meeting regulatory requirements and for doing an adequate job of product stewardship, including both proper use as well as proper disposal, it is vital to be able to make reasonable estimates of the migration potential of chemicals.

This report describes a simple PC computer program which requires as input only the physical chemical properties of molecular weight (MW), water solubility (WS), vapor pressure (VP) and melting point (MP) to make such estimates. Correlation equations provide the partition coefficients KOW, KOC, and KWA. An air diffusion coefficient is estimated from MW. When these are combined with typical assumed soil hydrogeological properties we can obtain estimates of the fractional distribution of a chemical among the air, water, and solids fractions of the soil. These also lead to an estimated soil column Rf (or its reciprocal, a retardation coefficient), and a soil vapor diffusion coefficient. Several different scenarios are then used to indicate the potential for migration by vapor diffusion through the soil and by movement along with water movement in the soil. These steps are illustrated as a flow sheet in Figure 1.

To operate the program itself, after placing the diskette into an operating PC, simply type in : BASICA A:MIGRT.BAS, (assuming the diskette is in the A drive), Then respond to prompts. An example printout is given as Appendix A. The program itself is given as Appendix B.

PARTITION COEFFICIENTS

KOW, the octanol/water partition coefficient

If a MP is provided or if the compound is a liquid at 25° C, the program uses the Banerjee/Yalkowsky Eqn 6 (Banerjee/Yalkowsky, 1980):

$$\log KOW = 6.5 - 0.89 \log S - 0.015 \times MP \qquad (1)$$

where S, in $\mu mol/L = 1000\ WS/MW$ (1a)

The calculation is actually done with natural logs:

$$\ln KOW = 14.97 - 0.89 \ln S - 0.035 \times MP \qquad (1b)$$