

Approximating Pollutant Transport to Ground Water^a

by Carl G. Enfield, Robert F. Carsel, Stuart Z. Cohen,
To Phan, and David M. Walters^b

ABSTRACT

Three simplistic models are developed for evaluating the transport of organic pollutants through soil to ground water. The models consider mobility and first-order degradation. The first calculates linear sorption/desorption of the pollutant and first-order degradation without considering dispersion. The second is similar to the first but also considers dispersion. The third considers nonlinear sorption following a Freundlich equation and first-order degradation but does not consider dispersion. The models are compared to field data for the pesticides aldicarb and DDT. The models projected a lower mobility for DDT than was observed in the field.

Additional index words: pesticides, toxic chemicals, miscible displacement, chemical degradation.

INTRODUCTION

Application of potential organic contaminants to soil is regulated by various laws. A chief concern is the ability of these pollutants to be transported to areas other than their application sites. Such concerns focus on runoff contamination of surface waters and ground-water contamination by transport through the soil matrix. The Federal Water Pollution Control Act of 1972 (PL 92-500) and the Clean Water Act of 1977 (PL 95-217) have encouraged the development of land application of waste water. The EPA policy in this area is to encourage land treatment technology but not at the expense of ground-water quality (Thomas and Reed, 1980). The Toxic Substance Control Act of 1976 (PL 94-469) and the Federal Insecticide, Fungicide and Rodenticide Act of 1978 (PL 95-396) require the development of reliable methods for predicting the probable environmental fate and effect of potentially harmful chemicals prior to their manufacture and use. To this end, EPA has proposed guidelines for registration of pesticides (Blum, 1978) requiring adsorption and leaching studies of pesticides with certain uses.

Recently, EPA has become active in investigating ground-water contamination. Trichloroethylene has been observed in private drinking-water supplies widely distributed in Pennsylvania, New Jersey, New York, and California. Presence of trichloroethylene has necessitated remedial treatment or abandonment of wells (Weimar,

^aContribution from U.S. Environmental Protection Agency, Office of Research and Development, Robert S. Kerr Environmental Research Laboratory, Ada, Oklahoma; and Hazard Evaluation Division, Office of Pesticide Programs, Washington, D.C.

^bSoil Scientist, EPA, Robert S. Kerr Environmental Research Laboratory, P.O. Box 1198, Ada, Oklahoma 74820; Microbiologist, HED, EPA, Washington, D.C.; Environmental Chemist, HED, EPA, Washington, D.C.; Member of Technical Staff, Computer Science Corporation, Huntsville, Alabama; and Research Agronomist, EPA, Ada, Oklahoma, respectively.

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1980). The detection of the pesticide 1, 2-dibromo-3-chloropropane (DBCP) in wells was a major factor in EPA's suspension of most uses of DBCP in the U.S. (Costle, 1979). The presence of the pesticide 2-methyl-2-(methylthio) propionaldehyde O-(methylcarbamoyl) oxime [aldicarb] in Long Island wells (Gatewood, 1979) has led to an intensive study of soil and ground water. Lindane has also been detected in ground water beneath municipal land treatment sites (Leach *et al.*, 1980).

This study was conducted to determine if relatively simple modeling approaches can be used to estimate the impact on ground water of organic chemicals applied to the land. Current field data on aldicarb and historical field data on DDT are used to evaluate three methods for projecting transport and transformation of nonionic organic chemicals through soils.

METHODS FOR CALCULATING TRANSPORT

The transport of a pollutant through soil can be described by the one-dimensional differential equation

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - V \frac{\partial C}{\partial x} - \frac{\rho}{\theta} \frac{\partial S}{\partial t} \quad (1)$$

where:

- C = pollutant concentration in the liquid phase (mg/l),
- t = time (hrs),
- D = dispersion coefficient (cm²/hr),
- V = interstitial pore-water velocity (cm/hr),
- x = distance along the flow path (cm),
- ρ = bulk density (g/cm³),
- θ = volumetric-water content (cm³/cm³) ($0 \leq \theta \leq 1$), and
- S = sink or source term ($\mu\text{g/g soil}$).

A projection of pollutant transport can be made by obtaining a solution to the above equation under the boundary and initial conditions

$$\begin{aligned} C(x=0, t) &= g(t) \\ C(x, t=0) &= 0 \\ C(x=\infty, t) &= 0 \end{aligned} \quad (2)$$

If the actual shape of the breakthrough is not required in the evaluation, dispersion can be ignored. This simplifies equation (1), yielding

$$\frac{\partial C}{\partial t} = -V \frac{\partial C}{\partial x} - \frac{\rho}{\theta} \frac{\partial S}{\partial t} \quad (3)$$

This simplification reduces the input requirements without reducing the accuracy of the projection for total mass moving through the soil profile. However, the concentration at any given time may be in error.

The major input requirement is a method of describing the sink/source term. Often data are available (Reinbold *et al.*, 1979) to describe the sorption of the chemical based on a linear or Freundlich isotherm following the equation

$$S_r = K C^n \quad (4)$$

where:

- K = sorption coefficient,
- n = Freundlich exponent, and
- r = denotes retardation portion of sink/source term.

Research has indicated sorption/desorption kinetics are not the same (e.g. Swanson and Dutt, 1973). However, with the time frame of months for movement in the soil profile under most agronomic conditions rather than hours as in laboratory situations, it is believed sorption and desorption kinetics can be adequately approximated as instantaneous reversible reactions, such as described by equation (4).

Degradation of pesticides occurs in soil systems (Hill and Wright, 1978) with abiotic as well as biological processes being involved. These degradation mechanisms can be considered independently or as one overall reaction. In biological degradation, threshold concentrations must be achieved at times before a population will begin to degrade a compound. For these cases, the sink term may be described as

$$S_d = \int_0^t k_i (C - CE_i) dt \quad (5)$$

where:

- k_i = instantaneous first-order solid phase rate coefficient (hrs⁻¹),
- CE_i = threshold concentration before reaction can proceed (mg/l) (this term usually equals zero for chemical processes), and
- d = denotes degradation portion of sink/source term.

Equation (5) assumes the degradation process

follows first-order kinetics. Most environmental processes are second-order or pseudo first-order. Therefore, there are environmental constraints on the rate coefficient and a single value may not be adequate.

Equations (4) and (5) can then be combined to describe the total sink/source term as

$$S(t) = K C^n + \sum_{i=1}^j \int_0^t k_i (C - CE_i) dt \quad (6)$$

where i is used as an index for multiple degradation processes, and j is the total number of processes. Substituting equation (6) into equation (3), and rearranging terms, yields

$$(1 + \frac{\rho}{\theta} n K C^{n-1}) \frac{\partial C}{\partial t} + V \frac{\partial C}{\partial x} = F(C, x, t) \quad (7)$$

in which

$$F(C, x, t) = -\frac{\rho}{\theta} \sum_{i=1}^j \frac{\partial P_i}{\partial t} \quad (8)$$

where

$$\frac{\partial P_i}{\partial t} = k_i (C - CE_i) \quad 0 \leq P_i \quad (9)$$

The general equations described above can be evaluated in several ways to estimate organic pollutant transport through soils. Three estimation methods are presented below.

METHOD I

This simplified approach is accomplished by solving the problem in two passes. Pass one involves calculating the apparent velocity of the pollutant through the soil. The retardation of the pollutant with respect to water (Hashimoto *et al.*, 1964) (R) is described mathematically by the equation

$$R = \frac{\text{interstitial pore-water velocity}}{\text{apparent velocity of pollutant}} =$$

$$\frac{V}{V_p} = 1 + \frac{\rho}{\theta} \frac{\partial S_r}{\partial C} \quad (10)$$

where just the retardation portion of the sink term is employed. For our example,

$$\frac{\partial S_r}{\partial C} = K n C^{n-1} \quad (11)$$

Since the velocity is a function of concentration, equation (3) is a nonlinear partial differential equation and analytical solutions are difficult to obtain. It can be seen, however, where a linear

function is used to describe the sorption, equation (11) reduces to

$$\frac{\partial S_r}{\partial C} = K \quad (12)$$

When the interstitial pore-water velocity is known it is possible to calculate the apparent velocity of a pulse of pollutant without regard for the concentration applied. Later in the discussion methods of estimating the interstitial pore-water velocity will be addressed. After determining the apparent pollutant velocity

$$\frac{dx}{dt} = V/R \quad (13)$$

the concentration of the pollutant can be evaluated. Substituting equation (6) into equation (3) yields

$$\frac{\partial C}{\partial t} = -V \frac{\partial C}{\partial x} - \frac{\rho}{\theta} (K \frac{\partial C}{\partial t} + \sum_{i=1}^j k_i C) \quad (14)$$

when $n = 1$ and $CE_i = 0$. Substituting equation (13) into equation (14), and rearranging terms gives

$$\frac{\partial C}{\partial t} + \frac{\partial C}{\partial x} \frac{dx}{dt} = -\frac{\rho}{\theta} \frac{C}{R} \sum_{i=1}^j k_i \quad (15)$$

Since C is a function of x and t ,

$$dC = \frac{\partial C}{\partial x} dx + \frac{\partial C}{\partial t} dt \quad (16)$$

Substituting equation (16) into equation (15) and rearranging terms gives

$$\frac{1}{C} dC = -\frac{\rho}{\theta R} \sum_{i=1}^j k_i dt \quad (17)$$

which may be integrated to

$$\ln C = -\tau \frac{\rho}{\theta R} \sum_{i=1}^j k_i + \text{const} \quad (18)$$

by defining the initial concentration at time 0 to be equal to C_o , equation (18) can be rewritten as

$$C_t/C_o = \exp \left(-\frac{\rho}{\theta} \frac{t}{R} \sum_{i=1}^j k_i \right) \quad (19)$$

where

k_i = specific reaction rate constant as described in equation (5) above = $0.693/t_{1/2}$ (hrs⁻¹),

$t_{1/2}$ = half-life of the chemical (hrs),

t = time (hrs) determined from the velocity of pollutant,

C_t = concentration at time t (mg/l), and

C_o = initial concentration (mg/l).

By substituting equation (12) into equation (10) to obtain the resulting pesticide velocity to determine the time in question in equation (19), one can estimate the spatial distribution of a pesticide in the soil profile, provided adequate input data are available. The following input data are required:

- Bulk density of the soil.
- Interstitial pore-water velocity.
- Water content of the soil.
- Sorption coefficients.
- Degradation rate(s).
- Amount of pesticide applied.
- Solubility of pesticide.

Bulk density varies over a reasonably narrow range from about 1.0 to 1.8 g/cm³. If there are no data on the soil, assuming 1.5 g/cm³ will give reasonable projections.

The interstitial pore-water velocity is required in the evaluation. This is equivalent to

$$\text{interstitial pore-water velocity} = \frac{V_d}{\theta} \quad (20)$$

where V_d is the average recharge rate (Darcy velocity cm/hr).

The average recharge rate must be estimated from climatic data or measured in the field. Very

few locations have field-measured recharge rates. The average recharge rate can be estimated from the water balance equation

$$L + P_r = ET + V_d + r \quad (21)$$

where:

L = hydraulic loading of water from man-made sources (e.g., irrigation) (cm/mo),

P_r = precipitation (cm/mo),

ET = evapotranspiration (cm/mo),

V_d = water recharge (cm/mo), and

r = net runoff (cm/mo).

Precipitation and irrigation records are readily available. The net runoff can be calculated from existing watershed models (Donigian *et al.*, 1977) or a generalized estimate such as given in *Control of Water Pollution from Cropland*, Vol. 1 (Stewart *et al.*, 1975) can be used. Assuming the runoff to be equal to zero would be the worst (most conservative) case as far as ground-water protection is concerned. Volumes of data have been generated on the subject of evapotranspiration, and numerous reports written (e.g., Jensen, 1973; Slatyer, 1967). Many of the methods estimating evapotranspiration require considerable input of climatic data, much of which are difficult to obtain. One relatively simple approach is to estimate evapotranspiration from pan evaporation (Jensen, 1973). This approach utilizes the equation

$$E_g = C_{et} E_{pan} \quad (22)$$

**Table 1. Representative Values of Hydraulic Parameters
(Standard Deviation in Parentheses) (Clapp and Hornberger, 1978)**

Soil texture	No. of soils	b	Ψ_s cm	θ_s cm ³ /cm ³
Sand	13	4.05 (1.78)	12.1 (14.3)	0.395 (0.056)
Loamy sand	30	4.38 (1.47)	9.0 (12.4)	0.410 (0.068)
Sandy loam	204	4.90 (1.75)	21.8 (31.0)	0.435 (0.086)
Silt loam	384	5.30 (1.87)	78.6 (51.2)	0.485 (0.059)
Loam	125	5.39 (1.87)	47.8 (51.2)	0.451 (0.078)
Sandy clay loam	80	7.12 (2.43)	29.9 (37.8)	0.420 (0.059)
Silty clay loam	147	7.75 (2.77)	35.6 (37.8)	0.477 (0.057)
Clay loam	262	8.52 (3.44)	63.0 (51.0)	0.476 (0.053)
Sandy clay	19	10.4 (1.64)	15.3 (17.3)	0.426 (0.057)
Silty clay	441	10.4 (4.45)	49.0 (62.1)	0.492 (0.064)
Clay	140	11.4 (3.70)	40.5 (39.7)	0.482 (0.050)

Table 2. Suggested Value for C_{et} Relating Evaporation from a US Class A Pan to Evapotranspiration from 8-15-cm Tall, Well-Watered Grass Turf (Jensen, 1973)

Wind	— Pan surrounded by a short green crop —				— Pan surrounded by a dry surface ground —			
	Upwind fetch of crop (m)	— Relative humidity, %* —			Upwind fetch of dry fallow (m)	— Relative humidity, %* —		
		20-40	40-70	>70		20-40	40-70	>70
Light <170 km/day	0	0.55	0.65	0.75	0	0.7	0.8	0.85
	10	0.65	0.75	0.85	10	0.6	0.7	0.8
	100	0.7	0.8	0.85	100	0.55	0.65	0.75
	1000	0.7	0.85	0.85	1000	0.5	0.6	0.7
Moderate 170-425 km/day	0	0.5	0.6	0.65	0	0.65	0.75	0.8
	10	0.6	0.7	0.75	10	0.55	0.65	0.7
	100	0.65	0.75	0.8	100	0.5	0.6	0.65
	1000	0.7	0.8	0.8	1000	0.45	0.55	0.6
Strong 425-700 km/day	0	0.45	0.5	0.6	0	0.6	0.65	0.7
	10	0.55	0.6	0.65	10	0.5	0.55	0.65
	100	0.6	0.65	0.7	100	0.45	0.5	0.6
	1000	0.65	0.7	0.75	1000	0.4	0.45	0.55
Very strong >700 km/day	0	0.4	0.45	0.5	0	0.5	0.6	0.65
	10	0.45	0.55	0.6	10	0.45	0.5	0.55
	100	0.5	0.6	0.65	100	0.4	0.45	0.5
	1000	0.55	0.6	0.65	1000	0.3	0.4	0.45

* Mean of maximum and minimum relative humidities.

where:

E_g = evapotranspiration for well-watered 8-15-cm tall grass turf,

C_{et} = coefficient for type of pan involved (see Table 2), and

E_{pan} = pan evaporation.

To translate from turf to some other crop, use the equation

$$ET = \kappa E_g \quad (23)$$

where:

ET = evapotranspiration for crop other than turf grass, and

κ = crop coefficient (see Table 3).

This approach is generally adequate ($\pm 25\%$) except when the crops are stressed due to drought, and the estimates are then greater than those which actually occur. The water content is quite variable. There are several methods which could be used to estimate the water content. One approach is to calculate a water content required to conserve mass assuming steady-state water flow. Clapp and Hornberger (1978) developed several empirical equations to describe soil hydraulic properties of soil. If one assumes a unit hydraulic gradient

under steady-state conditions, then V_d , the water recharge rate calculated from equation (21), is equal to the hydraulic conductivity which follows the equation

$$k = (\theta/\theta_s)^{2b+3} \quad (24)$$

where θ_s is the saturated water content or total porosity, and θ is the water content required to satisfy conservation of mass. Both θ_s and the exponent b are empirical and must be estimated. Clapp and Hornberger (1978) evaluated this equation for several soils and the empirical parameters are included in Table 1 along with the standard deviation of the estimate. Using equation (24) and equation (20) permits evaluating the interstitial pore-water velocity.

Table 3. Crop Coefficients for Estimating Evapotranspiration (Jensen, 1973)

Crop	Period	Coefficient (κ)
Alfalfa	April 1-October 10	0.87
Potatoes	May 10-September 15	0.65
Small grains	April 1-July 20	0.6
Sugar beets	April 10-October 15	0.6

The final parameters required to evaluate the movement of the pesticide are the coefficients needed to describe the sorption of the pesticide by the soil. Sorption coefficients have been reported for numerous pesticides (Reinbold *et al.*, 1979; Kenaga and Goring, 1978); however, the method of reporting has been quite variable. Hamaker (1975) reviewed methods of interpreting the data. A common approach is to assume the pesticide partitions between the soil and soil solution. This can be described by the linear form of equation (4)

$$S_r = K_d C \quad (25)$$

where K_d is the soil partition coefficient. Using this approach, each soil will have a different K_d which would have to be determined experimentally. It would be desirable to normalize K_d as a function of some other readily measurable parameter. One approach is to normalize this measurement based on the organic carbon (oc) in the soil (Karickhoff *et al.*, 1979). K_{oc} is then expressed

$$K_{oc} \approx \frac{\mu\text{g pesticide sorbed per g of organic carbon}}{\mu\text{g pesticide in solution per gram of solution}} \quad (26)$$

The soil thin layer liquid chromatography value (R_f) is often reported with respect to pesticides (Helling, 1971). This measurement compares the movement of a solvent to the movement of the pesticide under specific laboratory conditions. Like K_d mentioned earlier these coefficients will vary depending on the soil investigated. Hamaker (1975) has related R_f to K_{oc} by the relationship

$$R_f = \frac{1}{1 + [K_{oc} (\%oc/100) \rho (1/\theta_s^{2/3} - 1)]} \quad (27)$$

$$K_d = K_{oc} \left(\frac{\%oc}{100} \right) \quad (28)$$

When the K_d or K_{oc} for a soil is not known it is possible to estimate the K_{oc} from the water solubility for neutral (nonionic) organic pollutants. Several models have been proposed respectively by Karickhoff *et al.* (1979), Kenaga and Goring (1978), and Chiou *et al.* (1979), as follows:

$$\log K_{oc} = -0.54 \log Ws_1 + 0.44 \quad (29)$$

$$\log K_{oc} = 3.64 - 0.55 \log Ws_2 \quad (30)$$

$$\log G = 4.04 - 0.557 \log Ws_3 \quad (31)$$

where:

Ws_1 is water solubility expressed as a mole fraction,

Ws_2 is water solubility expressed in mg/l,

Ws_3 is water solubility expressed in μ moles/l, and

G is the partition coefficient with organic matter as a base rather than organic carbon ($K_{oc} = G/1.724$).

The degradation rate is a combination of several parameters and refers to the disappearance of the chemical from the subsurface. Degradation as used here refers to a combination of processes including:

1. volatilization,
2. hydrolysis,
3. other abiotic degradation processes, and
4. biotic degradation.

These processes are complex and dependent on the pesticide under evaluation. It is necessary to estimate a loss rate from field or laboratory data. There are several publicized values for hydrolysis and degradation (e.g., Callahan *et al.*, 1979; and Verschuere, 1977). Volatilization from soil surfaces is difficult to measure or predict (Spencer and Cliath, 1975). Kilzer *et al.* (1979) reported volatilization rates from soils at approximately an order of magnitude less than free water. When no value is available, assuming no loss is probably the only conservative approach at the present time. Organic chemists and biochemists can often estimate degradation rates for a chemical structure when the degradation rates of similar compounds are known. This type of estimation is beyond the scope of this paper.

With the rationale presented thus far, it is possible to estimate the velocity of a moving "slug" of pollutant and the concentration of that slug. This would appear as a pulse of chemical with sharp leading and trailing edges. The analysis would yield the correct value for the mass which is contained in the pulse. In actuality, however, water does not flow as a well-defined slug. Some pores carry water at a greater velocity than others and the shape of the slug smears with time. This is a combination of hydrodynamic dispersion which is dependent on the velocity and diffusion. The coefficients that are used to quantify these two processes have the same units and are usually lumped together.

METHOD 2

A second model combining the movement discussed above with dispersion can be written for

the simplified situation with linear sorption.

Kirkham and Powers (1972) presented a solution to describe the equation

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - V \frac{\partial C}{\partial x} \quad (32)$$

using a coordinate system that moved with the water so that equation (32) could be described by

$$\frac{\partial C}{\partial t_1} = D \frac{\partial^2 C}{\partial x_1^2} \quad (33)$$

for a moving pollutant. As discussed earlier for linear absorption, one must substitute equation (4) with $n = 1$ into equation (1) which yields

$$\left(1 + \frac{\rho}{\theta} K_d\right) \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - V \frac{\partial C}{\partial x}$$

$$\text{or} \quad \frac{\partial C}{\partial t} = \frac{D}{R} \frac{\partial^2 C}{\partial x^2} - V_p \frac{\partial C}{\partial x} \quad (34)$$

where $V_p = V/R =$ apparent pollutant velocity. The Kirkham and Powers (1972) solution with boundary conditions (2) can then be solved with a different coordinate system as

$$\frac{C}{C_t} = \frac{1}{2} \left(\operatorname{erf} \frac{x + x_o - V_p t}{2(Dt/R)^{1/2}} - \operatorname{erf} \frac{x - V_p t}{2(Dt/R)^{1/2}} \right) \quad (35)$$

where:

erf = the error function which can be looked up in tables,

x_o = initial length of slug (cm),

V_p = apparent velocity of pollutant from equation (10), and

C_t = concentration as described by equation (19).

x_o can be calculated from the water solubility when the chemical is applied in granular form by determining the equivalent depth of water (from the interstitial pore-water velocity) required to dissolve all of the chemical in water. When the chemical is applied in solution, the depth is calculated using the water content (θ) calculated in equation (24). In either case, the amount adsorbed by the soil in x_o would be included in the calculation for conservation of mass.

To evaluate equation (35), one must also measure the dispersion coefficient or have some way of estimating this parameter. Dispersion has been studied by several investigators, and empirical relationships have been developed based on numerous evaluations. For example, Biggar and

Nielsen (1976) proposed the relationship

$$D = D_p + 2.93 V^{1.11} \quad (36)$$

where D_p = diffusion coefficient for the chemical in the soil (cm^2/day), and V = interstitial pore velocity cm/day . Bresler (1973) reported that D_p could be described by

$$D_p = D_o d \exp(f\theta) \quad (37)$$

where D_o = diffusion in free water, and d and f are empirical constants characterizing the soil. The parameter d ranges from 0.001 to 0.005, and f can be estimated as 10. When no value is available for D_o , D_p can be estimated at .03 (cm^2/hr) (Biggar and Nielsen, 1976). Dispersion is not fully understood. The above discussion is intended only to present one possible method of making estimates of a complex subject.

METHOD 3

Equation (35) is adequate for projecting the concentration of a pollutant where sorption can be described as a linear function. In many cases, describing sorption with a linear function is not adequate. A third model can then be written based on equation (3) which neglects dispersion. The model employed was developed using the method of characteristics to obtain a numerical solution to equation (7). The approach has been used by Enfield *et al.* (1981) to describe phosphate transport and transformation in soil.

From equation (7), the characteristic line can be given by

$$\frac{dx}{dt} = \frac{V}{1 + (\rho/\theta) n K C^{n-1}} \quad (38)$$

Since V is greater than zero, dx/dt is always a positive finite value. Thus, the characteristic curve will not be tangent to the initial curves where $x = 0$ and $t = 0$. The system of equations (7) with boundary and initial conditions of equation (1) will possess a unique solution in the neighborhood of the initial curve (Courant and Hilbert, 1962). Combining equations (7) and (38) yields

$$\frac{dC}{dt} = \frac{F(C, x, t)}{1 + (\rho/\theta) n K C^{n-1}} \quad (39)$$

The total differential in (t) refers to the change in pollutant concentration along the characteristic line. From the initial curve where $t = 0$ and $x = 0$, equation (38) is used to define the marching path, and equation (39) to calculate the change in C .

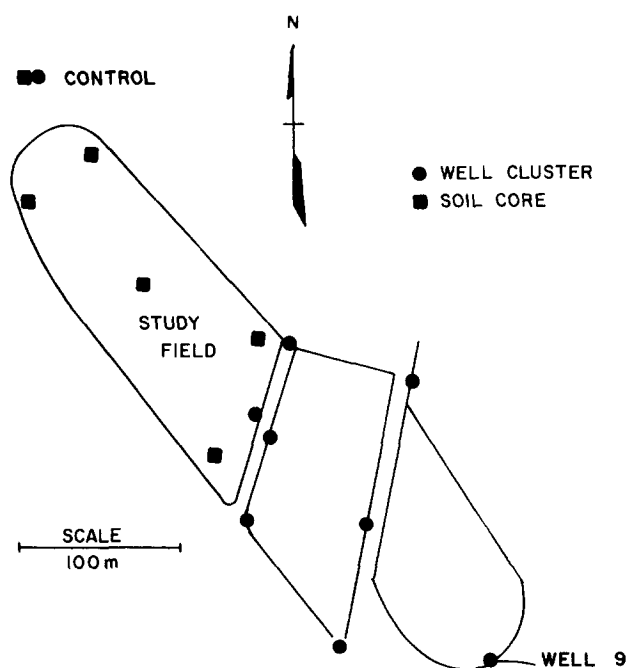


Fig. 1. Test site for aldicarb field study near Cutchogue, New York showing location for soil sampling and ground-water observation wells.

Thus, one can determine $C(x, t)$ throughout the x - t plane.

The stability condition for the numerical scheme with fixed values of Δx and Δt is

$$\frac{\Delta t}{\Delta x} \leq [1 + (\rho/\theta) n K C^{n-1}] / V \quad (40)$$

The function, or the right-hand side of equation (40), is dependent on $C(x, t)$; hence, the stability criterion changes with spatial location and time. The quantity $(\rho/\theta) n K C^{n-1}$ is always positive which permits simplifying equation (40) to

$$\frac{\Delta t}{\Delta x} \leq \frac{1}{V} \quad (41)$$

To avoid overestimation of the pollutant degradation in a single time step, time (t) is subjected to the constraint

$$\Delta t \leq \frac{1}{(\rho/\theta) \sum k_i} \quad (42)$$

The results from the characteristic method were further refined by iteration.

FIELD EVALUATION OF THE MODELS

The models are evaluated by comparing projections for the transport of the pesticides aldicarb and DDT with field measurements. The

aldicarb study field was located approximately 18 miles northeast of Riverhead in Eastern Long Island at Cutchogue, New York. Aldicarb, which has a trade name Temik, was chosen since it and its degradates aldicarb sulphoxide and aldicarb sulphone have been found throughout the North and South Forks of Long Island. The Long Island field site was chosen since:

1. Aldicarb in ground water under the field had been detected.
2. The field was located on a hydrologic divide eliminating confusion caused by potential migration from surrounding fields.
3. There was an accurate history of applications.
4. A shallow water table existed.

The field is about seven acres in size and rectangular in shape as shown in Figure 1. Application of aldicarb to the field was as follows:

1977	May 15 ± 3 weeks	3.59 kg ai/ha
1978	April 15 ± 1 week	2.52 kg ai/ha
	June 10 ± 1 week	2.02 kg ai/ha
1979	April 15 ± 1 week	3.20 kg ai/ha
	June 10 ± 1 week	2.52 kg ai/ha

During December 1979 soil samples from six vertical sections were obtained using a bucket auger. Each section was subdivided into 15-cm (6-inch) increments from the surface to the water table. Of the six sites, five were within the treated field, and one control site was located outside the field. The control site had not received aldicarb. Table 4 shows the results of the sampling. The soil data from this study are used to evaluate the model projections.

Based on the U.S. Soil Conservation Service soil survey map for Suffolk County, the soil at the site is a sand in the Haven soil series with a porosity of 38%, and average of 0.4% organic matter in the surface 180 cm. In this analysis the following reported properties for aldicarb will be used:

Solubility = 7800 mg/l		Goring (1972)	
Degradation rates:			
Aldicarb sulphone	0.0045-0.039	day ⁻¹	Smelt <i>et al.</i> (1978a)
Aldicarb sulphoxide	0.013 -0.034	day ⁻¹	Smelt <i>et al.</i> (1978b)

Table 4. Total Aldicarb as a Function of Depth

Depth cm	Location					
	SW	NE	NW	Center μg/g	SE	Control
0-7.6	20.0	<1	5.8	<1	<1	<1
15	4.3	5.9	2.0	<1	<1	<1
30	1.8	16.0	<1	<1	<1	<1
45	2.7	30.3	2.0	<1	20.0	<1
61	2.8	40.0	<1	<1	118.0	<1
76	8.4	40.0	<1	<1	113.0	<1
91	15.0	34.3	<4.0	<1	38.4	<1
107	19.0	25.8	<1	<1	12.0	<1
122	1.3	27.0	<1	3.9	6.5	<1
137	<1	11.0	<1	<1	4.2	<1
152	<1	<1	<1	<1	2.8	<1
168	<1	<1	<1	<1	<1	<1
183		<1		10.0	<1	<1
198		<1		6.7	1.5	<1
213		4.1			<1	<1
228		5.7			2.7	<1

Detection limit, 1 μg/g.

Table 5. Greenport Powerhouse Gauging Station Data

Year	Month	Precip.† (cm)	E _{pan} † (cm)	Wind† (km/mo)	EST-ET	
					Pan=0.85 Crop, 0.65 (cm)	Rainfall excess (cm)
1977	Nov.	8.2				
	Dec.	16.6				
1978	Jan.	20.9			3.8*	17.1
	Feb.	3.9			3.8*	0.1
	Mar.	6.7			3.8*	2.9
	April	5.4	11.1		6.1	-0.7
	May	13.5	12.6	3924	6.9	6.6
	June	3.1	15.8	3446	8.7	-5.6
	July	16.7	18.2	3338	10.1	6.6
	Aug.	26.6	12.0	2351	6.6	20.0
	Sept.	7.6	10.3	2554	5.7	1.9
	Oct.	8.3	8.7	2349	4.8	3.5
	Nov.	7.3			3.8*	3.5
	Dec.	15.3			3.8*	11.5
1979	Jan.	33.9			3.8*	30.1
	Feb.	11.8			3.8*	8.0
	Mar.	6.4			3.8*	2.6
	April	11.1			6.1	5.0
	May	14.1			6.9	7.2
	June	4.1	16.7		9.2	-5.1
	July	1.8	15.9		8.8	-7.0
	Aug.	10.1	13.4		7.0	3.1
	Sept.	9.7	11.0		6.1	3.6
	Oct.	9.4	7.1		3.9	5.5
	Nov.	10.2			3.8*	6.4
	Dec.	4.9			3.8*	1.1

Average recharge rate April-December 1979 = 0.0034 cm/hr.
Average recharge rate April 1978-December 1979 = 0.0074 cm/hr.

* Estimated.

† Adapted from NOAA (1978, 1979, 1980).

Smelt *et al.* (1978a, 1978b) indicated the degradation of aldicarb to aldicarb sulphoxide and aldicarb sulphone was rapid. The biotic degradation of aldicarb sulphoxide and aldicarb sulphone are the apparent rate limiting steps and further terminal degradates were not considered in the evaluation.

The first step in projecting the aldicarb transport was to determine the net recharge rate using equation (22). The closest NOAA gauging station with a Class A pan was at Greenport Powerhouse, New York. Data on precipitation, pan evaporation and wind speed required for a water balance is given in Table 5. The average relative humidity was estimated to be greater than 70% for the station (Whitting, 1976). Using equations (23) and (24), the evapotranspiration was estimated for potatoes, the crop grown at the site. It was further assumed that a constant 3.8 cm/mo recharge would be maintained for months without record. The time available for flow since the 1979 application was approximately 240 days before sampling on December 27. The average recharge rate is estimated at 0.0034 cm/hr which considers the rainfall excess flowing at a constant rate during the months of April through December 1979. The water content is estimated to be 0.24 from equation (24) and Table 1 ($b = 4.05$, $\theta_s = 0.395$). From equation (20), the interstitial pore-water velocity is estimated to be 0.013 cm/hr. To calculate the apparent velocity of the pollutant, one also needs a sorption or partition coefficient. Knowing the water solubility of 7800 mg/l, K_{oc} was determined to be 31.6. The organic matter is reported as 0.4% average for a 180-cm profile. This must be translated to organic carbon to obtain soil partition coefficient. Using the relationship,

$$1.724 \text{ oc} = \text{OM} \quad (43)$$

we obtain an equivalent of 0.23% oc in the profile. Then, from equation (28) the K_d used in this projection is 0.073. The apparent pollutant velocity can be determined by substituting equation (12) into equation (10) and rearranging terms to yield

$$V_p = V/[1 + (\rho/\theta) K] \quad (44)$$

$$V_p = 0.009 \text{ cm/hr}$$

where ρ was assumed to be 1.5 g/cm³. Knowing the velocity (0.009 cm/hr) and the time for travel (240 days), one would anticipate the slug to have traveled approximately 52 cm (1.7 ft).

To calculate the concentration of the slug, some additional assumptions are required. First, the initial concentration in the soil solution must

be estimated. A logical assumption would be to assume the applied concentration, or that it is equal to the solubility of the compound in water (7800 mg/l) if the chemical were applied in granular form. At the site the pesticide was applied in two applications in 1979, once in April and once in June. For simplicity, it was assumed the total application was made in May, and there were a total of 240 days for the degradation to proceed. Based on equation (19) the concentration of the slug at $t = 240$ days would then be 5×10^{-14} to 71 mg/l based on the range of degradation rates [K_d in equation (19)] 0.0016 to 0.00019 hrs^{-1} , respectively. Without a better understanding of the degradation rates, one has little confidence in the concentration which might be contaminating the ground water.

A solution to equation (35) and equations (38) and (39) are presented in Figure 2 where the dispersion coefficient is assumed to be 0.06 cm^2/hr , and the degradation rate assumed to be 0.00011 hr^{-1} . Two peaks are shown, one resulting from the pesticide application in 1978 and the other from the application in 1979. Also included in the

Figure is one set of field data for comparison from Table 4. Both of the projections estimate the peak concentration at the same location. The degradation rate assumed is in the range observed by Smelt *et al.* (1978a). The value was selected to yield the best match for the projected peak concentration as calculated from equation (35) with those measured in the soil. It was shown earlier that the concentration is extremely sensitive to degradation rates. Without accurate rates the utility of predicting a projected concentration is questionable. The apparent dispersion observed from the solution of equations (38) and (39) is due to the truncation of values in the numerical scheme. The similarity of the shape of the curves in Figure 2 having the numerical dispersion is approximately equal to 0.0006 cm^2/hr .

DDT was selected to evaluate the modeling approach representing compounds with very low mobility. DDT transport has been evaluated by several researchers. The data presented by Lichtenstein *et al.* (1971) were selected for the evaluation. The study was conducted on a Miami silt loam in Madison, Wisconsin. Vertical distribution of DDT was measured for an application of 4.5 kg ai/ha (4 lbs ai/acre) ten years after application. The recharge in the area was estimated at 12.7 cm/yr (Stewart *et al.*, 1975), the degradation rate 0.000034 hr^{-1} (Lichtenstein *et al.*, 1971), the solubility for the degradate DDE 0.001 mg/l (Kenaga and Goring, 1978), and $K_d = 478$ from equations (28) and (30) based on a range of organic matter from 0.5-3% for the Miami Soil Series. Figure 3 presents a projection based on equation (35) and field observations adapted from data of Lichtenstein *et al.* (1971). For DDT the approach underestimates the transport of the chemical. Based on the very low solubility of DDT, the model did not allow all of the DDT to go into solution. Therefore, projected transport into the soil was not complete after ten years. There is a potential for transport by mechanisms other than miscible displacement. These mechanisms could be used to explain a greater observed transport than those projected.

CONCLUSIONS

Three methods have been presented for estimating transport of organic chemicals through soils. Based on the correlation between field data and model projections the approach should be adequate to make environmental decisions evaluating the potential hazard of nonionic organics to the ground water. Modifications to

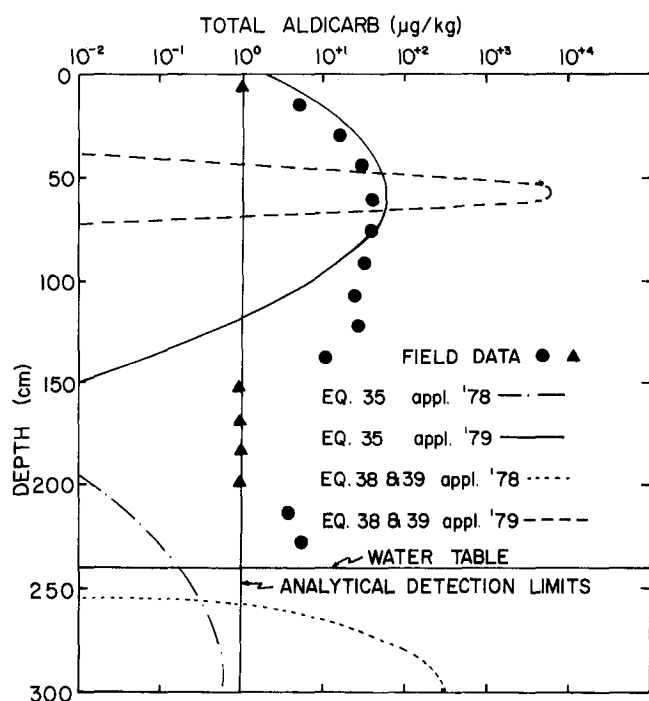


Fig. 2. Projected and observed distribution of aldicarb at sampling data as a function of depth. The analytical solution is based on equation (35) and the numerical solution is based on a solution of equations (38) and (39). The experimental data presented as triangles refer to concentrations below detectable limits. Field data is from NE sampling point.

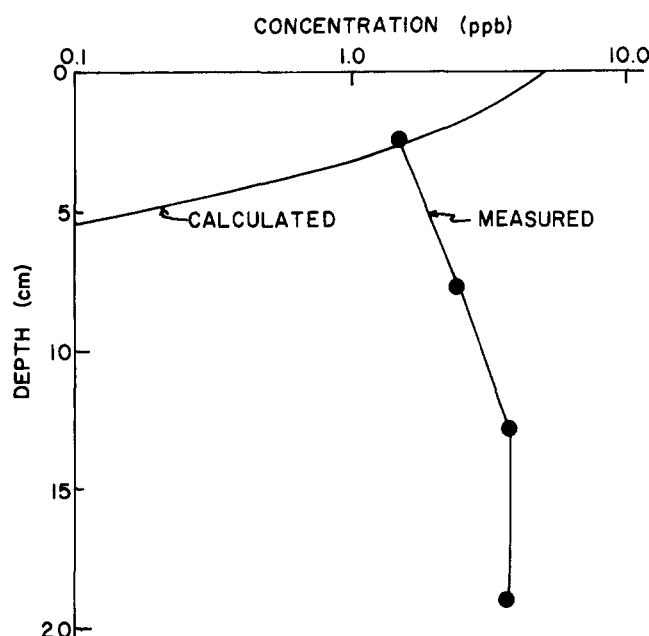


Fig. 3. Projected and observed distribution of DDT ten years after application using equation (35).

equation (6) would be required to evaluate ionic or charged compounds. The sensitivity of the model(s) to degradation rate shows the need to describe degradation and the parameters affecting degradation accurately. Each of the models have certain advantages, and the appropriate model should be selected based on individual need.

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Carl G. Enfield earned his B.S.C.E. in Civil Engineering and M.S. in Agronomy at Purdue University, and Ph.D.

in Agricultural Chemistry and Soils at the University of Arizona. He currently is a Soil Scientist involved in the transport and transformation of chemicals within soil systems. He has published in the areas of environmental chemistry, environmental physics, and field instrumental methods.

Robert F. Carsel's professional training includes a B.S. degree in Environmental Health Science and M.S. degree in Microbiology from the University of Georgia. He is currently active in development of guidelines for the registration of pesticides and modeling the transport and fate of pesticides through the soil matrix and within ground water, with publications in various soil/hydrology journals.

Stuart Cohen earned his B.A. in Chemistry at the University of Maryland—Baltimore County, and is completing the requirements for a Ph.D. in physical organic chemistry at George Washington University. He currently is a chemist in EPA's Hazard Evaluation Division and a Guest Worker at the National Institute of Health. He has published in the areas of environmental chemistry, pesticide product chemistry and immunochemistry.

To Phan received the B.S.E.E. from National Taiwan University, M.S. in Nuclear Engineering from National Tsing Hua University, and M.S.E. in Mechanical Engineering from University of Alabama, Huntsville. Since 1978, he has been with Computer Sciences Corporation, Huntsville, Alabama.

David M. Walters earned his B.S.F. in Forest Management and M.S. in Agronomy at West Virginia State University. He currently is a Research Agronomist involved in optimizing land application waste-water treatment using remote digital process control. He has published in the area of transport processes in soil systems.