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Chapter 8

Organic Chemical Transport to Groundwater[1]

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The use of pesticides in the production of agricultural commodities is widespread. During 1982, 370 000 t of active ingredients were used in the USA (U.S. EPA, 1982) and the use of pesticides is expected to increase in the future (Knusli, 1979).-Since nearly one-half of the U.S. population relies on groundwater as their source for drinking water (McEwen & Stephenson, 1979), contamination potential of groundwater, because of pesticide manufacture and use, must be understood.

The processes of sorption, biotic and abiotic transformation, and vapor transport have been discussed in previous chapters of this book. The objective of this chapter is to integrate the above processes into chemical mass transport models that can be used to forecast environmental exposure.

Almost any modeling activity related to groundwater starts with a water flow model, since, for any significant change to take place in the flow field, flow is an essential ingredient. Van der Heijde et al. (1985) reviewed several hundred groundwater management models from around the world and classified them in a variety of ways. Their review included both saturated and unsaturated flow models along with identifying the source and availability of computer codes for the models. Considering this review and several other reviews (e.g., Rao & Jessup, 1983; Boesten & Leistra, 1983; Addiscott & Wagenet, 1985), the current chapter will emphasize chemical transport rather than mass water flow. For completeness, a brief overview of water flow through saturated and unsaturated soils will be included. Decoupling the water and chemical transport is a major assumption in the following discussion. This means that the influence of the chemical is insignificant on water flow, and properties such as density gradients that can cause fluid movement can

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be ignored. This makes it possible to calculate the water flux independent of the chemical and then use the water fluxes in calculating the chemical flux.

8-1 MASS FLUX OF WATER

Most recharge of groundwater occurs during the-percolation of water through an unsaturated soil. Water movement is controlled by both gravitational and capillary forces.

Capillarity results from two forces: the mutual attraction (cohesion) between water molecules and the molecular attraction (adhesion) between water and solid materials. As a consequence of these forces, water will rise in small diameter glass tubes above the water level in a large container. Most pores in granular material are of capillary size and, as a result, water is pulled upward into a capillary fringe above the water table in the same manner as water would be pulled up into a column of sand whose lower end is immersed in water.

Steady-state water flow in unsaturated soil can be determined from a modified form of Darcy's law (Richards, 1931). Steady state in this context refers to a condition in which the moisture content remains constant, as would be the case under a disposal pond kept at a constant head and separated from the water table by unsaturated soil. The steady-state Darcy flux, V_d (LT^{-1}), is proportional to the effective hydraulic conductivity, $K(\psi)$ (LT^{-1}), which is a function of the water potential, ψ, and gradients because of both capillary and gravitational forces.

$$V_d = -K(\psi) \nabla H \qquad [1]$$

where ∇ is the standard differential operator of vector notation and $H = \psi - z$ is the total potential expressed as total head (L) with the vertical coordinate taken as positive downward. All other components of soil-water potential have been neglected.

If a water-saturated soil could be considered as a bundle of straight and smooth capillary tubes, Poiseuille's and Darcy's equations would be analogous

$$V_d = \frac{-r^2 \rho_a g}{8\gamma} \nabla H \qquad [2]$$

where r is the radius of a tube or pore (L), ρ_a is the density of water (ML^{-3}), g is the gravitational acceleration (LT^{-2}), and γ is the viscosity of water $(MT^{-1}L^{-1})$.

Similarities between these two equations have been used in the development of equations to describe a functional relation between water content and effective hydraulic conductivity (Millington & Quirk, 1961). Under saturated conditions, all of the soil pores are filled with water; thus, the maximum hydraulic conductivity is observed under saturated conditions (note:

water can be assumed to be an incompressible fluid under most environmental conditions). As the soil desaturates (soil-water pressure head decreases), the cross-sectional area of the soil available to conduct water decreases. The first pores to empty during desaturation of a soil are the largest pores in direct connection with the atmosphere. These large pores offer the least resistance to water flow; thus, as the soil desaturates there is a sharp reduction in hydraulic conductivity. Decreases of three or four orders of magnitude are not uncommon in highly structured, well-drained soils (Davidson et al., 1969).

The above two equations imply that soil-water flux vs. hydraulic gradient is a linear relationship. This is true only for laminar flow conditions. At high fluxes, turbulent conditions may exist creating non-Newtonian fluid properties. Similarly, at low gradients water may become non-Newtonian. For most environmental conditions, it is reasonable to assume that water flow is laminar and water behaves as a Newtonian fluid.

The quantitative application of unsaturated water flow theory to field or laboratory soil systems requires a knowledge of the soil hydraulic conductivity [$K(\psi)$] and soil-water characteristic [$\theta(\psi)$] relationships. The soil-water characteristic describes the relationship between water content and water potential. A typical relationship is shown in Fig. 8-1. There are two curves

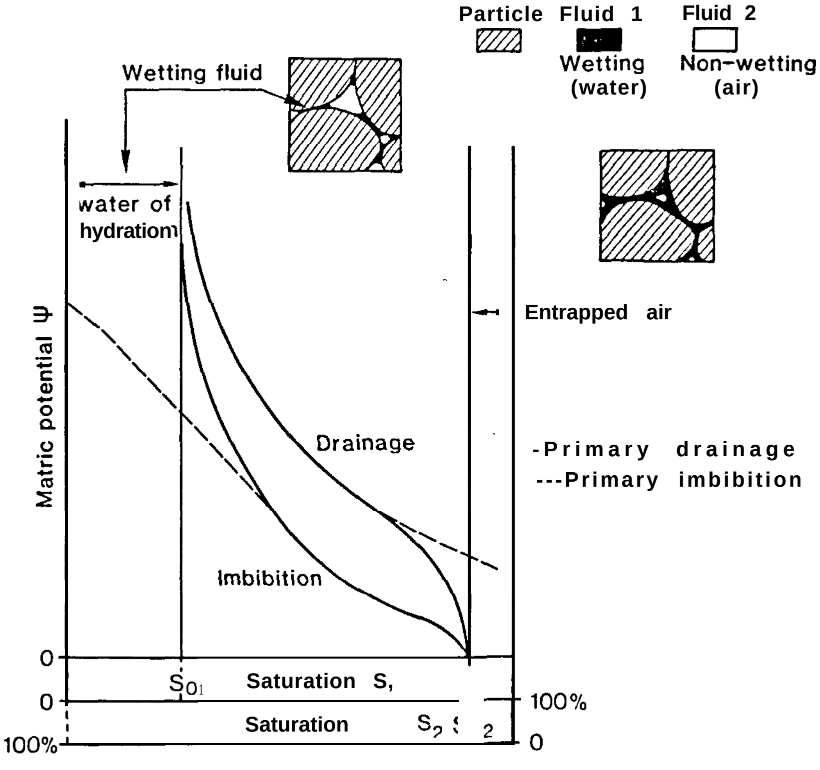

Fig. 8-1. Typical soil-water characteristic curve.

shown: one for drainage and one for imbibition. The soil characteristic can be at any point between the primary drainage and primary imbibition curves depending on past history. In general, flow theory is applied assuming there is a unique function that describes the soil-water characteristic and effects of hysteresis are ignored. Klute (1972) reviewed various methods for measuring hydraulic conductivity and discussed the advantages and disadvantages of each method; methods reviewed included steady-state, unsteady-state, instantaneous profile methods, and those involving the use of soil-water characteristic curves to estimate $K(\psi)$ relationships. Similarly, Heath (1983) reviewed currently used methods in aquifers to determine hydraulic properties.

When evaluating water flow in one dimension under steady-state conditions, once the water flux is known at one of the boundaries, the flow is known throughout the problem domain. Under agricultural conditions, this flux is often approximated from the water balance equation

$$L + P_r = \mathrm{ET} + V_d + \omega. \qquad [3]$$

Precipitation (P_r) and irrigation (L) records are generally available. The net runoff(w) can be estimated from existing watershed models (e.g., Donigian et al,, 1977). Evapotranspiration (ET) has been the subject of numerous reports (e.g., Jensen, 1973; Slatyer, 1967). Many of the methods require considerable input of climatic data, much of which is difficult to obtain and most are semiempirical. One simple approach is to estimate ET from pan evaporation (Jensen, 1973). The approach, which may be adequate for crude estimates, uses the equation

$$E_g = C_{et} E_{pan} \qquad [4]$$

which gives the ET for a turfgrass. To translate from turf to some other crop, one can use the equation

$$\mathrm{ET} = \kappa E_g. \qquad [5]$$

Values for the constants C_{et} and κ are reproduced in Tables 8-l and 8-2. If one assumed there was no runoff, it would be possible to estimate a Darcy flux through the soil.

Many times steady-state conditions are not adequate approximations of water flux. This is particularly true when the temporal distribution of a chemical is wanted near the source of application (near field). As distance and time increase (far field), the variations because of transient climatic activities are minimized. For near-field conditions, Eq. [1] can be combined with the equation of continuity:

$$(\partial\theta/\partial t) = - \nabla V_d \qquad [6]$$

which yields:

$$(\partial\theta/\partial t) = \nabla [K(\psi) \nabla H]. \qquad [7]$$

Table 8-1. Suggested value for C_{et} relating evapotranspiration from a U.S. Class A pan to evapotranspiration from eight 15-cm tall, well-watered grass turf (Jensen, 1973).

	Pan surrounded by short green crop				Pan surrounded by dry surface ground			
	Upwind fetch of	Relative humidity, %†			**Upwind fetch of**	Relative humidity, %†		
Wind	crop, m	20-40	40-70	70	fallow, m	20-40	40-70	70
Light <170 km d^{-1}	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 d^{-1}	0	0.5	0.6	0.65	0	0.65	0.75	0.8
	10	0.5	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 d^{-1}	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 d^{-1}	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.

Equation [7] is appropriate for n-dimensional water flow in a heterogeneous anisotropic soil. The equation for isotropic soils can be written in two dimensions as:

$$\frac{d\theta}{d\psi}\frac{\partial\psi}{\partial t} = \frac{\partial}{\partial x}\left[K(\psi)\frac{\partial\psi}{\partial x}\right] + \frac{\partial}{\partial z}\left[K(\psi)\frac{\partial\psi}{\partial z}\right] - \frac{\partial K(\psi)}{\partial z} . \qquad [8]$$

An alternate form of Eq. [8] is sometimes used by defining a new variable, the soil water diffusivity $D(\theta) = [K(\theta)(d\psi/d\theta)]$ (Childs & Collis-George, 1950). In any event, the dependence of D or K on ψ or θ makes the equation nonlinear. Thus, analytical solutions to Eq. [8] are not available except for simple initial and boundary conditions. According to van der Heijde et al. (1985), there are five supported numerical computer codes available that will handle a saturated-unsaturated water flow as listed in Table 8-3. Four of the five codes listed will handle transient flow conditions and some will also handle anisotropic media.

Table 8-2. Crop coefficient for estimating evapotranspiration (κ) (Jensen. 1973).

Crop	Period	Coefficient, κ
Alfalfa (Medicago sativa L.)	1 Apr.-10 Oct.	0.37
Potato ***(Solanum tuberosum*** L.)	10 May-15 Sept.	0.65
Small grain	1 Apr.-20 July	0.6
Sugarbeet ***(Beta vulgaris*** L.)	10 Apr.-15 Oct.	0.6

Table 8-3. Single-phase saturated-unsaturated flow models. Adapted from van der Heijde et al. (1985).

						Spatial characteristics and dynamics of flow			
Author(s)	Original affiliation	Country	Model name	Completion year (Update)	Model type	Saturated	Unsaturated	System	Process
P.J.M. De Laat	International institute	Netherlands	SUM-2	1972/76 (1980)	Hydraulic	Two-dimensional, horizontal; transient	One-dimensional vertical quasi-steady state	Isotropic heterogeneous porous medium two-layered homogeneous soil	Evapotrans., plant uptake
C.R. Amerman	Federal government	USA	STDY-2	1976	Hydrodynamic	Two-dimensional vertical steady state	Two-dimensional vertical steady state	Anisotropic heterogeneous multi-layered soil	
J.L. Nieber	University	USA	FEATSMF	1979	Hydrodynamic	Two-dimensional vertical transient	Two-dimensional vertical transient	Isotropic homogeneous hill-slope soil	Seepage
G.T. Yeh D.S. Ward	Research laboratory	USA	FEMWATER FECWATER	1981 (1982)	Hydrodynamic	Two-dimensional vertical transient	Two-dimensional vertical transient	Anisotropic heterogeneous porous medium	Ponding
T.N. Narismham	Research laboratory	USA	TRUST	1981	Hydrodynamic	Multi-dimensional steady state or transient	Multi-dimensional steady state or transient	Anisotropic heterogeneous variable saturated deformable porous medium complex geometry	Drainage dewatering hysteresis

8-2 TRANSPORT OF MISCIBLE NONVOLATILE REACTIVE COMPOUNDS

The most common approach to chemical transport is to consider the contaminant to be nonvolatile and miscible in the liquid phase. A solute could then react with the solid phase by sorption and be transformed while sorbed or be transported and transformed in the liquid phase. The vapor phase could be present, but not directly participate in the transport or transformation process. One way of describing the system is to look at each phase independently and mathematically describe the transfer of chemicals between the phases. The aqueous (liquid) phase could be described in one dimension by the equation

$$\frac{\partial(\theta\rho_a C_a)}{\partial t} = D_a \frac{\partial^2(\theta\rho_a C_a)}{\partial x^2} - V_a \frac{\partial(\theta\rho_a C_a)}{\partial x} - k_{as}\theta\rho_a C_a + k_{sa}(1 - n)\rho_s C_s - k_{ta}\theta\rho_a C_a. \quad [9]$$

Equation [9] describes the change in mass, of a contaminant in a unit volume of soil represented in Fig. 8-2, per unit time. The first term on the right-hand side of the equation describes the dispersive flux into the elemental volume. The physical significance of the hydrodynamic dispersion term (D_a) has been the topic of considerable debate. The term is often used to combine the influences of molecular diffusion caused by a concentration gradient

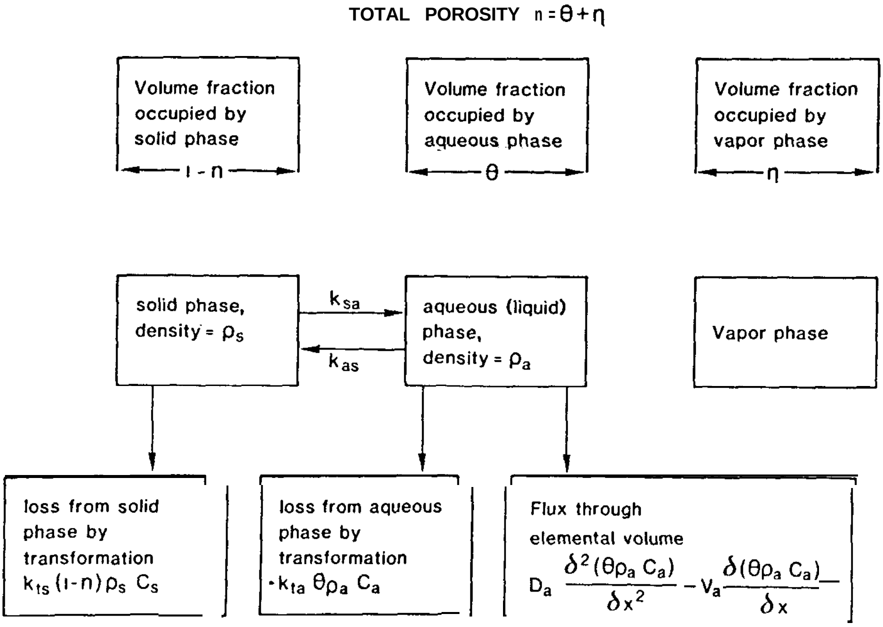

Fig. 8-2. Conceptual drawing of a representative elemental soil volume.

along with dispersion due to mechanical mixing during fluid advection that is a function of the porous media. Many hydrogeologists use the term *dispersivity* (α) with the units of length to describe the porous media and then relate the dispersion coefficient to the fluid velocity by the equation

$$D_a = \alpha V_a + \lambda D \qquad [10]$$

where λ is a constant related to the tortuosity and D is the molecular diffusion coefficient in water. The tortuosity coefficient, with values typically between 0.5 and 0.01 (Freeze & Cherry, 1979), is frequently estimated from empirical relationships such as Millington and Quirk (1961) presented. The molecular diffusion coefficient for dichlorobenzene in water is approximately 0.5 $cm^2 d^{-1}$. With typical values of tortuosity the impact of molecular diffusion is small when there is a significant interstitial velocity. Figure 8-3 shows two experimental breakthrough curves for tritiated water movement through a given experimental column at different flow velocities. Although the interstitial velocity (V_a) and dispersion coefficient (D_a) are significantly different, there is little difference in the dispersivity (α) as seen by the overlap in the experimental data. The experimental data shown in Fig. 8-3 are consistent with Eq. [10]. A difficulty with this concept is the dispersivity appears to be scale dependent. The larger the spatial scale from which measurements are taken, the larger the dispersivity (Smith & Schwartz, 1980). Molz et al. (1983) have postulated, in a field study, that the field-scale dispersivity term represents a lack of understanding of the spatial variability of the hydraulic conductivity in the geohydrologic system. The scale dependence of dispersivity used in groundwater movement studies may, thus, be considered a convenient approach to describing our lack of understanding of the flow system. Bresler and Dagan (1981), Amoozegar-Fard et al. (1982). and Parker and van Genuchten (1984) proposed an alternate approach that describes the spatial variability of the flow system while projecting an average concentration for the chemical in the flow field.

The second term on the right-hand side of Eq. [9] describes the mass transfer of the compound out of the representative elemental volume by fluid flow (often called *advective transport).* The velocity term (V_a) is usually calculated from a saturated-unsaturated flow model that is assumed to be unaffected by the composition of the aqueous phase (i.e., solute concentration gradients do not affect or cause water flow). The interstitial velocity (V_a) is equal to the Darcy velocity (V_d) divided by the volumetric water content (θ). The term may either be a variable that is dependent on the transient nature of the flow field, or a constant if the hydraulic conditions are at steady state. If it is desired to make near-field projections of the concentration distribution (i.e., projections near the source of chemical application), the transient nature of water flow generally must be considered. The greater the time of travel to the point of interest, under most field conditions, the less important the transient nature of the water flow problem.

The third term on the right-hand side of Eq. [9] describes the mass loss rate because of a transfer of molecules from the aqueous phase to the solid

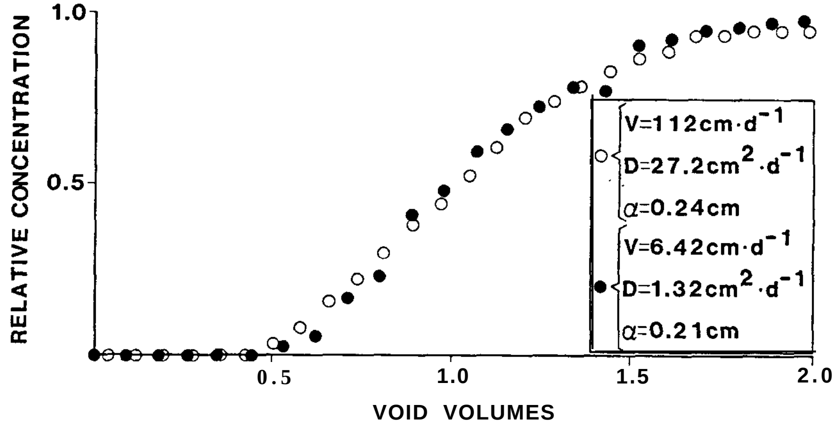

Fig. 8-3. Experimental breakthrough curve for tritium through a sandy soil at two interstitial velocities.

phase. This is written as a first-order kinetic term. It does not attempt to describe the mechanism of the sorption reaction. The term simply states that the higher the activity of a compound in the aqueous phase the higher the probability the molecule can be lost to the solid phase. Similarly, the fourth term describes the mass rate of gain caused by transfer of molecules from the solid phase to the liquid phase.

The final term in Eq. [9] describes the transformation of the compound that takes place in the liquid phase. Overall, the reaction rate is assumed to be a first order. Many different processes can be incorporated in this term. The first-order kinetic model is selected here because it is convenient. When processes other than first order are known to occur, they should be incorporated into transport models.

The contaminant's solid phase concentration can be described by the equation

$$\frac{\partial[(1-n)\rho_s C_s]}{\partial t} = -k_{sa}(1-n)\rho_s C_s + k_{as}\theta\rho_a C_a - k_{ts}(1-n)\rho_s C_s. \qquad [11]$$

As written, Eq. [11] assumes the solid phase is stationary and, therefore, does not include a diffusive or a mass transfer term as included in Eq. [9]. The other three terms have corollaries in Eq. [9]. The change of mass in the total elemental volume is the sum of Eq. [9] and [11] or

$$\frac{\partial(\theta\rho_a C_a)}{\partial t} + \frac{\partial[(1-n)\rho_s C_s]}{\partial t}$$
$$= D_a \frac{\partial^2(\theta\rho_a C_a)}{\partial x^2} - V_a \frac{\partial(\theta\rho_a C_a)}{\partial x} - k_{ta}\theta\rho_a C_a - k_{ts}(1-n)\rho_s C_s. \qquad [12]$$

Equation [12] is written with two dependent variables: the concentration of the contaminant in the aqueous phase (C_a) and the concentration of the contaminant in the solid phase (C_s).

The net rate of change from an individual phase can be written

$$r = k_{as}\theta\rho_a C_a - k_{sa}(1 - n)\rho_s C_s. \qquad [13]$$

Many researchers find equilibrium takes place rapidly with acceptable reversibility (e.g., Schwarzenbach & Westall, 1981 or McCarthy & Jimenez, 1985) while others find minimum reversibility and relatively slow kinetics (e.g., Di Toro, 1985 or Means et al., 1985). Assuming equilibrium exists, the net rate of change from one phase to another would be zero and the mass ratio would be the equilibrium constant

$$C_s/C_a = (k_{as}\theta\rho_a)/[k_{sa}(1 - n)\rho_s] = k_d. \qquad [14]$$

As developed, Eq. [14] leads to a linear sorption partition coefficient with units $M_a M_s^{-1}$, i.e., unitless if phases are not identified. (Note: there are a variety of partition coefficients in the literature; many have associated units. The most common units reported assume that the density of water is 1 Mg m^{-3}; this yields the units $m^3 Mg^{-1}$.)

If we let

$$k'_d = (k_{as}/k_{sa}) \qquad [15]$$

then when local equilibrium exists Eq. [12] can be rewritten in terms of one dependent variable as

$$(1 + k'_d)\frac{\partial C_a}{\partial t} = D_a\frac{\partial^2 C_a}{\partial x^2} - V_a\frac{\partial C_a}{\partial x} - (k_{ta} + k_{ts}k'_d)\,C_a. \qquad [16]$$

Defining a retardation factor as

$$R = 1 + k'_d \qquad [17]$$

and a lumped transformation term as

$$k_t = k_{ta} + k'_d\,k_{ts} \qquad [18]$$

then Eq. [15] becomes

$$R\frac{\partial C_a}{\partial t} = D_a\frac{\partial^2 C_a}{\partial x} - V_a\frac{\partial C_a}{\partial x} - k_t C_a. \qquad [19]$$

Analytical solutions to Eq. [19] have been developed for a variety of boundary conditions and many of these have been compiled by van Genuchten and Alves (1982). In addition to the analytical solutions that are available, several numerical solutions have been presented in the literature. Two numerical codes are available and supported by the International Ground Water Modeling Center, Butler Univ., Indianapolis, IN. These two codes are listed in Table 8-4.

Table 8-4. Distributed nonconservative mass transport models: Miscible (convection and dispersion)—unsaturated and saturated. Adapted from van der Heijde et al. (1985).

Author(s)	Original affiliation	Country	Model name	Completion year (Update)	System	Flow characteristics	Solute transport process	Method
Kaszeta Simmons Cole Ahistrom Foote Serne	Research laboratory	USA	MMT-DPRW (1D/3D)	1976 (1980)	Isotropic, heterogeneous porous medium; confined, semiconfined or water-table aquifer; multi-aquifer system	One- or two-dimensional, horizontal or vertical, or three-dimensional; steady state or transient	Convection, dispersion, adsorption, ion-exchange, radioactive decay, chemical reactions	Discrete parcel random walk
G.T. Yeh D.S. Ward	Research laboratory	USA	Femwaste/ FECWASTE	1981	Anisotropic, heterogeneous porous medium	Two-dimensional, horizontal or vertical; steady state or transient	Convection, dispersion, diffusion, adsorption, first-order decay	Finite element

To illustrate the movement of a retarded compound, where biological transformation is inhibited by sodium azide (0.02%), consider the movement of hexachlorobenzene (HCB) through a soil column. In this experiment, groundwater amended with HCB at 0.013 μM L^{-1} (3.6 μg L^{-1}) was passed through a sandy soil (same soil as illustrated in Fig. 8-3). The porosity of the column was determined from ^{3}H breakthrough curves and assumed to be equal to the water content (θ). The experimental breakthrough curves for HCB through replicate columns are shown in Fig. 8-4. A solution to Eq. [11], assuming $k_t = 0$ with boundary conditions

$$\left(D\frac{\partial C}{\partial x} + V_a C\right)\bigg|_{x = 0} = \begin{cases} V C_o & 0 < t \le t_o \\ 0 & t > t_o \end{cases} \qquad [20]$$

following the development of van Genuchten and Alves (1982), is

$$\frac{C(x,t)}{C_o} = \begin{cases} A(x,t) & 0 < t \le t_o \\ A(x,t) - A(x,t - t_o) & t > t_o \end{cases} \qquad [21]$$

where

$$A(x,t) = \frac{1}{2}\,\mathrm{erfc}\left[\frac{R\,x - V_a t}{2(D_a R\,t)^{1/2}}\right] + \left[\frac{V_a^2\,t}{\pi D_a R}\right]^{1/2} \exp\left[-\frac{(R\,x - V_a t)^2}{4 D_a R\,t}\right]$$
$$- \frac{1}{2}\left[1 + \frac{V_a x}{D_a} + \frac{V_a^2 t}{D_a R}\right] \exp\left[\frac{V_a x}{D_a}\right] \mathrm{erfc}\left[\frac{R\,x + V_a t}{2(D_a R\,t)^{1/2}}\right] \qquad [22]$$

is also presented in Fig. 8-4. The curve presented is a least squares best fit to the experimental data with regression coefficients listed on the figure. Although an attempt was made to maintain a constant water flux through the column throughout the experiment, variations did occur. The projected curve used mean interstitial velocity measured prior to the sampling time. The variation in velocity caused the projected curve to have minor perturbations in the shape of the curve. The same k_d was used to describe the ascending and descending portion of the curve. The agreement between experimental and regressed function indicate the assumption of reversibility is adequate for HCB. The column results are consistent with batch studies shown in Fig. 8-5 where ^{14}C labeled HCB in 30 mL of groundwater was equilibrated with 2 g of soil. The soil partition coefficient obtained from the batch study is not significantly different than the one in the column study. Under appropriate conditions, the analytic solutions currently available in the literature can be a valuable asset to projecting the movement of chemicals through soils and thus contribute to exposure assessments. When the flow conditions are significantly dynamic to make it necessary to consider the temporal and spatial variability in water flow, it is possible to apply one of the numerical models listed in Table 8-4 or other appropriate model to project chemical concentration distributions in environmental situations.

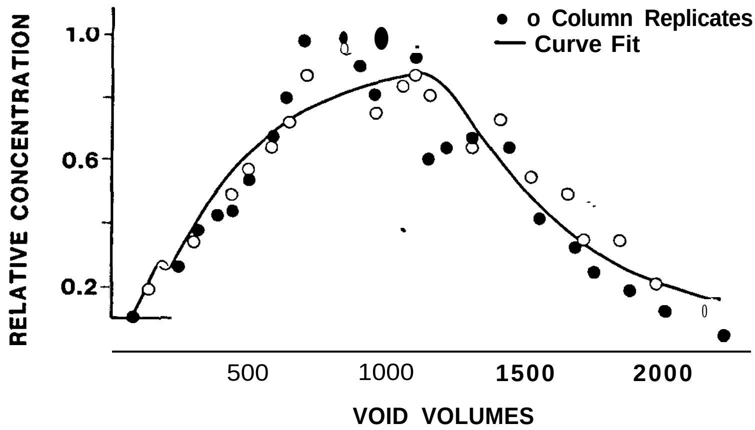

Fig. 8-4. Hexachlorobenzene breakthrough curve for duplicate columns. For col. 1 the following physical parameters apply: $\theta = 0.501$, mean interstitial velocity 112 m d^{-1}. For col. 2, the following physical parameters apply: $\theta = 0.469$, mean interstitial velocity 112 m d^{-1}. The parameters obtained from the least squares analysis are $k_d = 97$ and $\alpha = 2$ m.

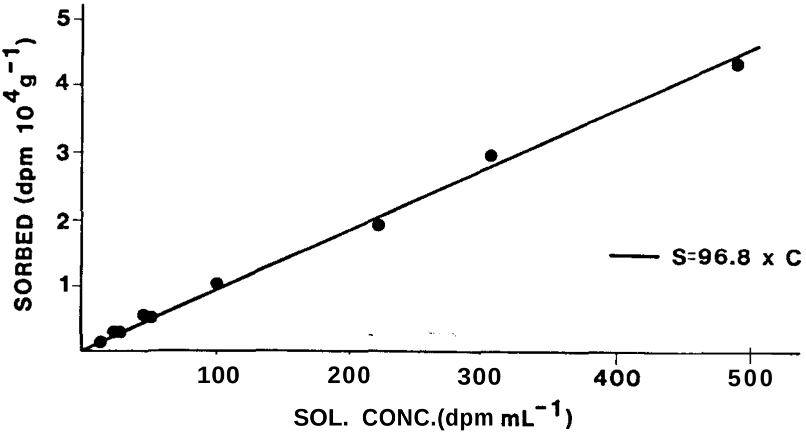

Fig. 8-5. Hexachlorobenzene sorption isotherm.

8-3 TRANSPORT FACILITATED BY COMPLEX FLUIDS

The fluid passing through the soil is not pure water with a single chemical dissolved in the water as assumed in the previous section. There has been an increasing awareness that there are synergistic and antagonistic reactions taking place within the soil system because of the complex nature of the fluid as well as the soil. Two approaches have been proposed to modify the miscible displacement theory of dilute systems to permit consideration of more complex fluids. Nkedi-Kizza et al. (1985) have considered the possibility of mixed miscible solvents. They have shown that it is possible to predict the

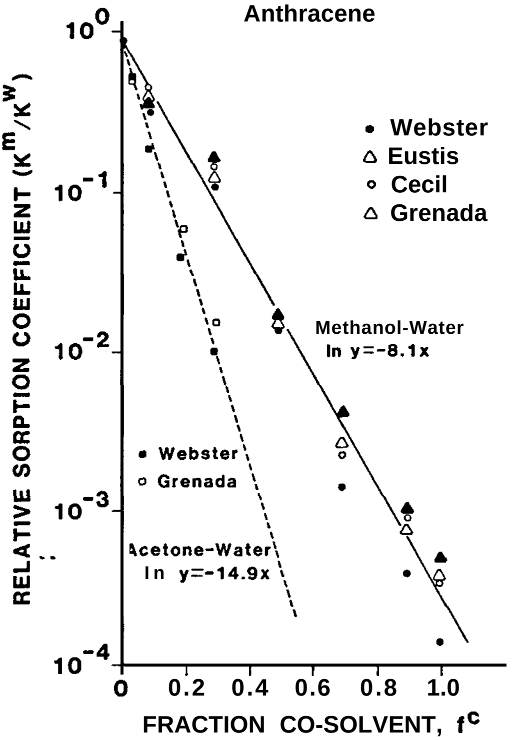

Fig. 8-6. Influence of mixed solvents on solubility in fluid phase. Adapted from Nkedi-Kizza et al. (1985).

enhanced solubility of a chemical because of the chemical properties of the solvents involved. Figure 8-6 shows the impact of the mixed solvents on the retardation factor. The co-solvent can potentially reduce the retardation factor several orders of magnitude. The importance of this phenomenon is particularly significant at municipal or industrial waste sites where there is a potential of co-disposed wastes enhancing the movement of toxic chemicals to groundwater. Nkedi-Kizza et al. (1985) also demonstrated that the impact of the co-solvent is greater the more hydrophobic the chemical. Enfield (1985) proposed that the movement of chemicals can be enhanced by the presence of macromolecules or immiscible fluids that may be moving with the water and acting as surfactants in the soil water system. Enfield (1985) considered the mobile phase to consist of two liquids plus a vapor moving through the soil system as shown in Fig. 8-7. Through a transformation of variables, the form of the equation was shown to be the same as those already solved for a variety of boundary conditions. In the following paragraphs, a similar development is shown with an emphasis on the movement of macromolecules. Change in the aqueous phase follows the same form as Eq. [9] except there are terms to describe the exchange between the aqueous phase and the macromolecule. This results in the one-dimensional equation

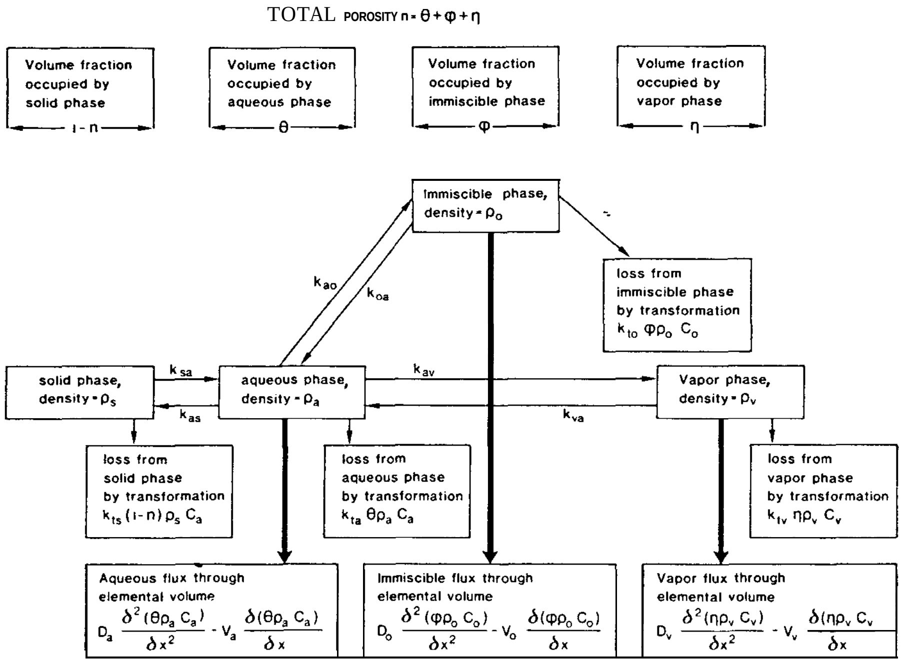

Fig. 8-7. Conceptual model for a representative elemental volume of soil with multiple fluid phases.

$$\frac{\partial(\theta\rho_a C_a)}{\partial t} = D_a \frac{\partial^2(\theta\rho_a C_a)}{\partial x^2} - V_a \frac{\partial(\theta\rho_a C_a)}{\partial x} - k_{ao}\theta\rho_a C_a + k_{oa}\phi\rho_o C_o$$

$$-k_{av}\theta\rho_a C_a - k_{va}\eta\rho_v C_v - k_{as}\theta\rho_a C_a + k_{sa}(1-n)\rho_s C_s - k_{ta}\theta\rho_a C_a. \quad [23]$$

A second equation must be developed to describe the rate of change in concentration associated with the macromolecules.

$$\frac{\partial(\phi\rho_o C_o)}{\partial t} = D_o \frac{\partial^2(\phi\rho_o C_o)}{\partial x^2} - V_a \frac{\partial(\phi\rho_o C_o)}{\partial x}$$

$$- k_{oa}\phi\rho_o C_o + k_{ao}\theta\rho_a C_a - k_{to}\phi\rho_o C_o. \quad [24]$$

The change in the solid phase in this example is identical to Eq. [11]. The vapor phase follows the equation

$$\frac{\partial(\eta\rho_v C_v)}{\partial t} = D_v \frac{\partial^2(\eta\rho_v C_v)}{\partial x^2} - V_v \frac{\partial(\eta\rho_v C_v)}{\partial x}$$

$$- k_{va}\eta\rho_v C_v + k_{av}\theta\rho_a C_a - k_{tv}\eta\rho_v C_v. \quad [25]$$

Equation [25] allows transformations to take place in the vapor phase according to first-order kinetics and partitioning between the liquid and vapor phase. When local equilibrium is assumed,

$$k_{ao}\theta\rho_a C_a = k_{oa}\phi\rho_o C_o \qquad [26]$$

$$k_{av}\theta\rho_a C_a = k_{va}\eta\rho_v C_v \qquad [27]$$

$$k_{as}\theta\rho_a C_a = k_{sa}(1 - n)\rho_s C_s. \qquad [28]$$

By defining a new variable C^* as the total mass concentration of the mobile contaminant over all phases,

$$C^* = \theta\rho_a C_a + \phi\rho_o C_o + \eta\rho_v C_v \qquad [29]$$

or

$$C^* = \left(1 + \frac{k_{ao}}{k_{oa}} + \frac{k_{av}}{k_{va}}\right)\theta\rho_a C_a \qquad [30]$$

and by defining an additional variable

$$\beta = 1 + \frac{k_{ao}}{k_{oa}} + \frac{k_{av}}{k_{va}} \qquad [31]$$

such that

$$C_a = C^*/\beta\theta\rho_a \qquad C_o = k_{ao}C^*/\beta k_{oa}\phi\rho_o$$

$$C_v = k_{av}C^*/\beta k_{va}\eta\rho_v \qquad C_s = k_{as}C^*/\beta k_{sa}(1 - n)\rho_s \qquad [32]$$

then the total change in an elemental volume can be shown to follow the equation

$$\left[1 + \frac{k_{ao}}{k_{oa}} + \frac{k_{av}}{k_{va}} + \frac{k_{as}}{k_{sa}}\right]\frac{\partial C^*}{\partial t} = \left[D_a + \frac{k_{ao}}{k_{oa}}D_o + \frac{k_{av}}{k_{va}}D_v\right]\frac{\partial^2 C^*}{\partial x^2}$$

$$- \left[V_a + \frac{k_{ao}}{k_{oa}}V_o + \frac{k_{av}}{k_{va}}V_v\right]\frac{\partial C^*}{\partial x}$$

$$- \left[k_{ta} + \frac{k_{ao}}{k_{oa}}k_{to} + \frac{k_{av}}{k_{va}}k_{tv} + \frac{k_{as}}{k_{sa}}k_{ts}\right]C^*. \qquad [33]$$

By defining the variables

$$R^* = 1 + \frac{k_{ao}}{k_{oa}} + \frac{k_{av}}{k_{va}} + \frac{k_{as}}{k_{sa}} \quad [34]$$

$$D^* = D_a + \frac{k_{ao}}{k_{oa}} D_o + \frac{k_{av}}{k_{va}} D_v \quad [35]$$

$$V^* = V_a + \frac{k_{ao}}{k_{oa}} V_o + \frac{k_{av}}{k_{va}} V_v \quad [36]$$

$$K_t^* = k_{ta} + \frac{k_{ao}}{k_{oa}} k_{to} + \frac{k_{av}}{k_{va}} k_{tv} + \frac{k_{as}}{k_{sa}} k_{ts}. \quad [37]$$

Eq. [33] becomes

$$R^* \frac{\partial C^*}{\partial t} = D^* \frac{\partial^2 C^*}{\partial x^2} + V^* \frac{\partial C^*}{\partial x} - K_t^* C^* \quad [38]$$

which is the same form as Eq. [19] already discussed. Enfield and Bengtsson (1988) discuss the impact of the macromolecules on the mobility of chemicals. They note that large hydrophilic macromolecules may be excluded by smaller pores in the soil and thus, the macromolecules may actually move more rapidly than the water.

Two theoretical figures (8-8 and 8-9) were developed to elucidate the significance of both the presence of the macromolecule and the impact of differences in interstitial velocities between fluid phases. Several simplifying assumptions were made in the development of the figures. First, dispersion and transformation in Eq. [38] were ignored which yields

$$R^* \frac{\partial C^*}{\;} = V^* \frac{\partial C^*}{\;}. \quad [39]$$

Further, the following assumptions are applied to generate theoretical figures (8-8 and 8-9): (i) the density of the macromolecule equals the density of the water; (ii) the partition coefficient to the macromolecule's organic C is the same as the partition coefficient to the soil's organic C (k_{oc}), $k_p = k_{oc}$ times the weight fraction C occupied by the macromolecules; (iii) the fraction of organic C of the soil (F) is 0.02; (iv) the soil partition coefficient can be described by the equation of Briggs (1981) as

$$\log k_d = 0.52 \log k_{ow} + 0.65 + \log F \quad [40]$$

(v) the total porosity (n) of the soil is 0.5; and (vi) the particle density of the soil is 2.65.

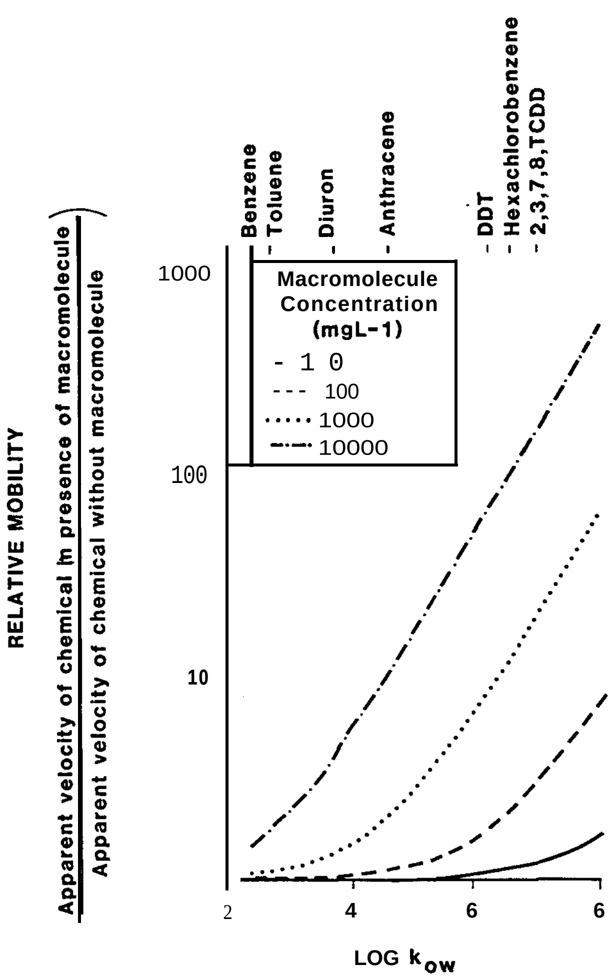

Fig. **8-8.** Mobility of a hydrophobic compound relative to the mobility of the same compound without the presence of a macromolecule as a function of octanol-water partition coefficient (theoretical computation).

The impact of the macromolecule on the mobility of hydrophobic compounds is demonstrated in Fig. 8-8. When one assumes that the interstitial velocity of the macromolecule and the water are the same $(V_a = V_o)$, the octanol/water partition coefficient vs. the relative chemical mobility (mobility in the presence of macromolecule/mobility without macromolecule) can be presented. The macromolecules in the mobile phase can significantly alter the relative mobility of extremely hydrophobic compounds even when the amount of macromolecule is in concentrations typical of groundwater or agricultural soil solution. This might be one explanation why hydrophobic pesticides, such as DDT, have been reported to move farther under field conditions than model projections (e.g., Enfield et al., 1982). The importance

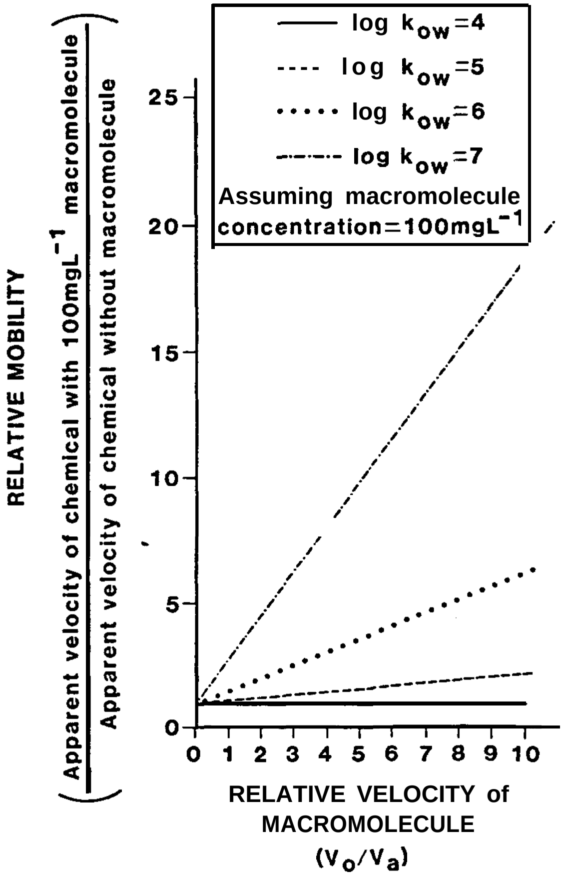

Fig. 8-9. Mobility of a hydrophobic compound relative to the mobility of the same compound without the presence of a macromolecule vs. the velocity of the macromolecule relative to the velocity of the water where the concentration of the macromolecule is 100 mg L^{-1} (theoretical computation).

of the macromolecule rapidly diminishes as the octanol/water partition coefficient goes down. At municipal or industrial waste sites where relatively high concentrations of macromolecule might exist (1 or more g/L of total organic C in the fluid [Williams et al., 1984]) the importance of the macromolecule to chemical mobility could be significant even for chemicals with log k_{ow} of 3 or less. Hydrophilic macromolecules with C concentrations of 100 to 500 mg/L may change the relative mobility of hydrophobic compounds by an order of magnitude in low C soils if the partition coefficient to the macromolecule's C is the same as the partition coefficient to the soil's organic C.

The significance of differences in interstitial velocities of the two mobile phases are shown in Fig. 8-9; it was assumed that the C concentration of the macromolecule was 100 mg/L. By assuming differences in the interstitial velocities of the mobile phases, it is possible to plot relative mobility of the macromolecule (V_0/V_a) vs. the relative mobility of the compound. As the relative mobility of the macromolecule goes down, the importance goes down. By the time the relative velocity of the macromolecule reaches 10% of the velocity of the water, the macromolecule is no longer significant in facilitating chemical transport. Therefore, consideration of a mobile organic phase for accelerating chemical transport is limited to macromolecules that behave as hydrophilic compounds but have the capacity to sorb hydrophobic solutes in groundwater. Examples of this type of macromolecule would be the naturally occurring dissolved organic C (DOC) found in groundwater as well as some of the nonionic or anionic biologically or chemically produced micelle-forming surfactants. The importance of the macromolecule is much more important for chemicals with a high k_{ow} than chemicals with a low k_{ow}. This is similar to the observations Nkedi-Kizza et al. (1985) presented for the presence of co-solvents. For concentrations of dissolved organic C commonly found in most agricultural soils only the hydrophobic compounds will be influenced by the DOC, but in cases where the DOC is greater than normally observed the infuence of the DOC may extend to less hydrophobic chemicals.

8-4 MODEL APPLICATION

The selection and application of a model to an environmental situation depends on the objective of the modeling exercise. There is no one best model for all purposes. Users need to consider their objectives as well as the assumptions in a model prior to implementation of the model. Models might be classified into two or three broad categories (research, screening, and/or educational models). Research models try to accurately describe a portion of the transport processes at a specific site. The models divide the problem domain into elements. Each element is assumed to accurately represent a continuum in the flow field. The models overlook the microscopic flow patterns and attempt to describe some fictious average flow. Model elements are generally much larger than a minimum representative elementary volume defined by Bear (1979), but will be considered the model's representative elemental volume (REV). To calculate the water fluxes in the flow field, the hydraulic properties, which describe the soil-water characteristic and hydraulic conductivity function, are required input for each REV. This information is supplied by either tabular or defined functional relationships. For each REV, the partition coefficient between the solid and liquid phase as well as the transformation rate must be specified to calculate the chemical flux. The user needs to pay particular attention to the units used by the model developer and the assumptions on where the transformation takes place. Some model developers have assumed that the only place transformation will take place is in the bulk liquid. Others have assumed that transformation takes place only when the chemical-is sorbed to the soil. Either of these assumptions can be incorrect descriptions of the processes involved. Nevertheless, it is possible to transform the data such that either of the methods gives a numerically correct presentation of the result using a procedure similar to that described in section 8-3. In addition to describing the properties of each of the elements of the problem domain, boundary conditions must be described either as a potential or flux. Realistic description of the boundary conditions is often the most difficult task for the user of an existing model. This is particularly true for transient flow conditions where boundary conditions change as a function of time.

Research models are used to answer a variety of questions. They are often used in legal actions at hazardous waste sites to help forecast future environmental insult and potential impact of proposed remedial actions. Research models are used in the design of containment systems for landfills and to see if transport processes are understood.

Screening and educational models require much less input data than the research models. As a result, the screening models compromise in the way they describe one or more of the transport processes. Most screening models assume steady-state water flux throughout the problem domain. This is a definite limitation, particularly when the analysis is describing the spatial and temporal distribution of a chemical near the point of application. Other screening models route the water through compartments such that the output of one compartment is the input to the next compartment without maintaining the flow system as a continuum. Even considering the simplifying assumptions in the screening models, they are often as good as the available input data. Screening models are often used where the hydrogeologic system is not well defined. For example, in the past, the potential behavior of a new pesticide has been inferred from a combination of laboratory data and a few field monitoring studies. A major limitation of field studies is that each study represents only one combination of field, climatic, and management factors. Modeling as a preliminary screening and forecasting tool permits extrapolating the limited field data to a variety of conditions. Screening models are often used in developing sampling schemes to minimize the number of compounds quantitatively determined in a sampling train. In this case, even with their inaccurate description of the actual flow process, screening models will often be adequate to determine which chemicals should first arrive at sampling wells and suggest how the sampling wells should be placed to obtain samples of a chemical plume. Examples of models suitable for this purpose are Plume 2D and Plume 3D two- or three-dimensional plumes in uniform groundwater flow presented by Wagner et al. (1984a, b). The model in three dimensions analytically solves the equation:

$$R\frac{\partial C}{\partial t} + V\frac{\partial C}{\partial x} = D_x\frac{\partial^2 C}{\partial x^2} + D_y\frac{\partial^2 C}{\partial y^2} + D_z\frac{\partial^2 C}{\partial z^2} - Rk_tC. \qquad [41]$$

Equation [41] is similar to Eq. [19] except for the way the transformation rate coefficient is defined, but assumes dispersion is in three dimensions rather than in one dimension. The two models assume:

1. The groundwater flow regime is completely saturated.
2. All aquifer properties are constant and uniform throughout the aquifer.
3. The groundwater flow is horizontal, continuous, and uniform throughout the aquifer.
4. The chemical input is a point at the origin of the coordinate system.
5. Mass flow rate of the chemical input is constant.
6. At zero time, the concentration of chemical in the aquifer is zero.
7. The aquifer is infinite in extent.

The models use the principle of superposition to overcome the problem associated with the assumption of an infinite aquifer and to permit multiple sources and variable source rate terms. Input data requirements are listed in Table 8-5. Output from the model is the spatial and temporal distribution for the chemical in tabular format. The models were written in FORTRAN, for interactive use on a microcomputer.

Enfield et al. (1986) presented, with the acronym SWAG (simulated waste access to groundwater), a one-dimensional compartmental screening model developed for use inland treatment of wastewater, where there is an excess of water creating significant amounts of recharge. The compartmental model was developed to describe the movement of volatile or nonvolatile transformable or recalcitrant organic chemicals in rapid-infiltration wastewater treatment systems. The rapid infiltration wastewater treatment system is assumed

Table 8-5. Input data requirements for the screening model Plume 3D.

Title
Units for length
Units for time
Units for concentration
Saturated thickness of aquifer (L)
Aquifer porosity
Seepage (interstitial) velocity (L t^{-1})
Retardation factor
X dispersion coefficient, (sq. L t^{-1})
Y dispersion coefficient, (sq. L t^{-1})
Z dispersion coefficient, (sq. L t^{-1})
Transformation rate (1 t^{-1})
Select transient or steady-state solution
Number of sources
X, Y, and Z coordinates of sources

Starting time, ending time, and mass rates of sources†

Steady-state mass rate of source‡

The remaining input data define the matrix where the concentration is evaluated.

First X. Last X, and Delta X (L)
First Y. Last Y, and Delta Y (L)
First Z. Last Z, and Delta Z (L)
First t, Last t. and Delta t (t)

---

† Input data required for transient solution.
‡ Input data required for steady-state solution.

to operate in a cyclic manner with periods of flooding where the soil surface is covered with water and periods of drying where the soil profile is allowed to dry and re-oxidize. The first compartment describes chemical loss from the infiltration basin when the infiltration basin is flooded with water. The second compartment considers losses because of volatilization and transformation in near-surface soils during periods of drying. The third compartment describes the transport and transformation of the remaining chemical to groundwater. The model was designed to consider an accidental spill of chemical into a treatment system or the constant input of chemical into a system. The theoretical basis for the model is given in brief below.

The model assumes the volume of flow applied to the infiltration basins all passes through the soil profile to groundwater. Precipitation is assumed equal to ET and there is no runoff. The first compartment of the model was considered to be a perfectly mixed container with constant depth with no mass flow. The chemical was allowed to transform by first-order kinetics, and loss to the atmosphere was shown to follow first-order kinetics, based on the Lewis and Whitman (1924) two film model. The chemical remaining after losses in the pond was placed at the bottom of the succeeding compartment that is an unsaturated soil layer. The soil layer acted as a restrictive layer for volatile losses. It was assumed that there was no convective flow through this soil layer and the layer was at a quasi-steady-state condition. First-order transformation was permitted in the soil layer and volatile losses followed Fick's law where the concentration of the chemical in the atmosphere was assumed to be zero. The concentration remaining for input into the third compartment (C_i) was shown to follow the equation:

$$C_i = \frac{C V_d \sinh(\sqrt{\beta}\,\iota)}{(1 - \mathrm{FTF})\; D^* \sqrt{\beta} \cosh(\sqrt{\beta}\,\iota) + V_d \sinh(\sqrt{\beta}\,\iota)}. \qquad [42]$$

Several terms in Eq. [42] have not been defined. The FTF is the fraction of time flooded. This was included to show that volatile losses could take place only during the portion of time the pond was not present. Beta is a temporary variable related to the transformation rate and effective dispersion coefficient. Iota is the thickness of the soil layer restricting volatile losses and is estimated based on the distance a chemical should move during one cycle (wetting and drying) of system operation. The third and final compartment was described in a manner similar to the development in section 8-3 of this chapter ignoring the possibility of an immiscible organic phase.

The output of the model was compared to observations from a replicated laboratory microcosm for 18 organic compounds. Input data requirements are given in Table 8-6 along with the units used in the model. The saturated hydraulic conductivity, total porosity, and Clapp and Hornburger (1978) curve coefficient (6) were used along with the water application rate to describe the hydraulic regime. Given the total porosity (n), the saturated

Table 8-6. Input data requirements for the model SWAG.

Input parameter	1,1,1-Trichloroethane	Bis-(2-chloroethyl)ether
Sat. hydraulic conductivity, m d^{-1}	0.83	0.83
Total porosity, m^3 m^{-3}	0.4	0.4
Clapp & Homburger curve coefficient	0.8	0.8
Dispersivity, m	0.2 . .	0.2
Molecular wt., g	133.41	143.02
Vapor pressure, kPa	16.5	0.19
Solubility in water, mol m^{-3}	5.40	71.32
Temperature, K	293	293
Average water application rate, m d^{-1}	0.044	0.044
Depth of water in pond, m	0.003	0.003
Fraction time flooded	0.1	0.1
Repeat cycle time, d	0.167	0.167
Bulk density of solid, Mg m^{-3}	1.6	1.6
Density of liquid, Mg m^{-3}	1.0	1.0
Density of air at temperature, Mg m^{-3}	1.3 x 10^{-3}	1.3 x 10^{-3}
Ten meter wind speed, m s^{-1}	10-s	10^{-6}
Diffusion coefficient in water, m^2 d^{-1}	5.2 x 10^{-5}	5.2 x 10^{-5}
Diffusion coefficient in air, m^2 d^{-1} at 273	0.6	0.6
Partition coefficient liquid/solid phase	0.052	1.58
Duration of chemical pulse, d	∞	∞
Transformation rate liquid phase, d^{-1}	0	0.06
Transformation rate solid phase, d^{-1}	0	0.2
Constant input conc., mol m^{-3}	1	1
Initial distance, m		
Distance increment, m		
Maximum distance, m		
Initial time, d		
Time increment, d		
Maximum time, d		
Depth to groundwater, m	1.5	1.5

hydraulic conductivity (K_s), the water application rate equivalent to the Darcy velocity (V_d), and a curve coefficient (b). the water content (θ) is calculated from the equation:

$$V_d = K_s(\theta/n)^{2b+3}. \qquad [43]$$

The air-filled porosity (η) is then $n-\theta$, and the interstitial velocity for water $V_a = V_d/\theta$. The effective diffusion coefficient for the vapor phase was approximated from Millington and Quirk's (1961) empirical relationship.

$$D_v = D_o(\eta^{10/3}/\theta_s) \qquad [44]$$

with a knowledge of the diffusion coefficient in air. Projections for volatile losses were within a factor of 2 for slowly transformable compounds. Volatile losses for compounds that would degrade would be over-estimated when degradation is ignored. Independent measurements of transformation rates were not available for most of the compounds used in the study. Although the model could be made to fit the observations by adjusting the transfor-

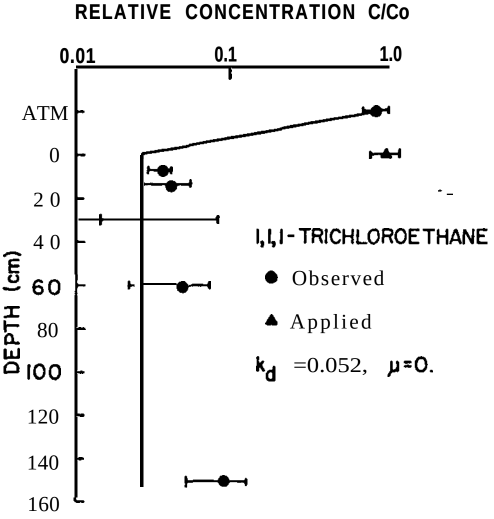

Fig. 8-10. Quasi-steady-state distribution of 1,1,1-trichloroethane in a 1.5-m deep microcosm. The coefficient μ in the figure is the same as K_t^* defined by Eq. [37] where $k_{to} = k_{tv} = 0$.

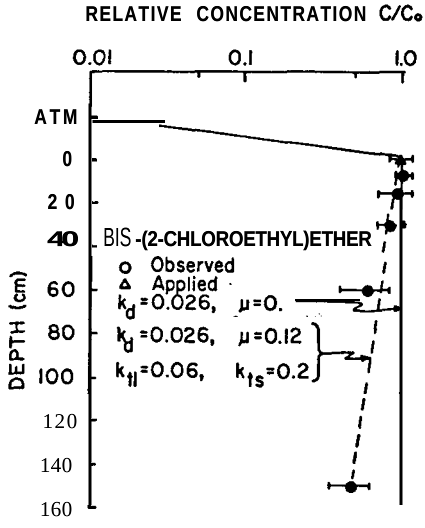

Fig. 8-11. Quasi-steady-state distribution of bis-(2-chloroethyl)ether in a 1.5-m microcosm. The coefficient μ in the figure is the same as K_t^* defined in Eq. [37] where $k_{to} = k_{tv} = 0$.

mation parameters, this does not mean the model adequately describes the processes involved. To illustrate the model's output, results of the output and the measurements from the microcosm are shown in Fig. 8-10 and 8-11. 1,1, I-Trichloroethane was selected because it is a volatile, recalcitrant compound showing little transformation. The figures show the relative concentration applied to the microcosm as a triangle and the relative concentration in the soil solution as a function of depth in the soil profile. The computed and measured relative amounts volatilized are also shown. Bis-(2-chloroethyl)ether (Fig. 8-11) was selected as a transformable, nonvolatile compound. No attempt was made to measure volatile losses from the experimental column. The model projected < 1% of the compound would be lost by volatilization. Bis-(2-chloroethyl)ether is known to hydrolyze, and the transformation rate that best fits the experimental data is close to the hydrolysis rate reported in the literature. The examples presented show conditions where the model estimates are close to the observations. First-order kinetics assumed in the model are not always satisfactory. When processes other than first order are known, appropriate models should be used.

8-5 NEW DEVELOPMENTS AND OUTLOOK FOR USE OF MODELS IN ASSESSING GROUNDWATER CONTAMINATION PROBLEMS

In recent years, researchers have become aware that modeling chemical transport through_soil as an isotropic medium is not always adequate (e.g., Bouma et al., 1982; Smettem & Collis-George, 1985; White, 1985a, b). Many have attempted to consider the medium as anisotropic (Bear, 1979) taking into consideration the stratification of the sediments as they were deposited or developed in layers. This was proposed because when using relatively large REVs the horizontal hydraulic conductivity was generally much greater than the vertical hydraulic conductivity. This approach has been particularly popular in groundwater models. Several researchers have also been trying to integrate soil taxonomy with water and chemical transport. As soils develop a structure, much of the water flow takes place in macropores along the ped faces or worm (Lumbricus spp.) channels bypassing the bulk of the soil. Analytic solutions to chemical transport, considering the soil to be a fractured media where water flows through the macropores and then diffuses into the peds where it may react with the soil particles, have been developed for a variety of boundary conditions (White, 1985a, b; van Genuchten, 1985; Parker & Valocchi, 1986) and shown to fit experimental field data. These ‘are definite advances over the approaches mentioned earlier in this chapter. When using these approaches, the boundary conditions can be difficult to adequately describe, particularly under unsaturated transient flow conditions. For example, if, during a given climatic event, the rainfall or irrigation intensity is less than the saturated hydraulic conductivity of the individual soil peds, flow will not take place along the ped faces as the macropores will remain unsaturated. When the intensity of the climatic event is greater than the saturated hydraulic conductivity of the ped then excess water will flow along the ped faces. This leads to a new problem of requiring a knowledge of how a chemical is applied, when the chemical was applied and a history of climatic events prior to an event where water flows along the ped faces. Dekker and Bouma (1984) studied the flow problem with nitrate (NO_3) and demonstrated large differences in the amount of N lost from a soil profile based on the history of application. White et al. (1986) made similar observations with the movement of the pesticides bromacil and napropamide through undisturbed cores of a structured clay soil. The macropores will also have a dramatic influence on movement of volatile compounds in the vapor phase. Diffusion in the vapor phase is many times greater than diffusion in the liquid phase (see Table 8-6) and the presence of macropores will present a ready conduit for vapor phase movement to the atmosphere. As a result, much of a volatile substance incorporated in surface soils may be lost to the atmosphere. The loss of volatile materials is significant even through several meters of unsaturated soils that were not directly contaminated with the substance. Plumes of chlorinated solvents in groundwater have been monitored by sampling the gas in soil pores several meters above a contaminant plume.

In the presence of macropores, even when the problems associated with the boundary conditions are solved, there will still be problems with describing the number and size of macropores. Soil taxonomists are evaluating geostatistical methods as a possible tool to help describe the macropores. Possibly a stochastic representation of the macropores in a deterministic model will be effective for forecasting the spatial and temporal distribution of chemicals in the environment.

All of the models discussed assume transformation is pseudo first order. This approach is probably adequate as a first approximation. However, many of the reactions will not be first order. For example, oxidation processes in groundwater will likely be second order dependent not only on the concentration of the chemical but on the concentration of O_2. Models have been developed to handle this type of situation (Borden & Bedient, 1986; Yates & Enfield, 1989) and have received limited testing in environmental situations (Borden et al., 1986). Additional work is needed to fully understand the processes and develop rate coefficients as a function of other environmental variables such as O_2, pH, temperature, and nutrients required by the biological population before the implications of second-order reactions can be fully understood.

At the beginning of this chapter, decoupling water flow from chemical transport was assumed. This assumption is not always adequate. For example, in geothermal regions there may be significant temperature gradients such that density variations will have a significant influence on mass flow. Lindstrom and Piver (1985) presented a model for organic transport through unsaturated/saturated soils under nonisothermal conditions addressing such problems. As more is learned about the processes involved and the significance of these processes, approaches similar to that of Lindstrom and Piver will become useful.

The models currently in use have definite limitations and shortcomings. Nevertheless, models are the only rational way to forecast the spatial and temporal distribution of a chemical in the environment. In the registration of pesticides for use in agriculture, the use of field studies gives an excellent way of evaluating the fate of a chemical under a given set of climatic conditions for a given soil. However, to evaluate the fate of a chemical under a variety of climatic conditions for a variety of soils, models must be used with an understanding of their limitations.

In addition to using models for forecasting prior to an environmental problem, models are useful in evaluating alternative reclamation approaches to existing environmental contamination. In the case of an accidental spill, there is a question of how much time is available before a segment of the population is exposed. This type of information can be useful to an emergency response team faced with the responsibility of warning the public of potential exposure. The next question addresses whether human intervention is desirable or if natural physical, chemical, and biological processes will be adequate to sufficiently mediate the problem. Modeling in a forecasting mode is the only current approach to address these problems. When forecasting, the accuracy of model estimates is not good. The modeler rarely has the luxury of calibrating one's model with some past history at the site. The modeler must rely on information in the literature and, hopefully, the experience of a soil taxonomist and hydrogeologist familiar with the area and chemists and microbiologists familiar with the chemicals in question. Even with the limitations on accuracy, the modeler can give a range for the expected spatial and temporal distribution of a chemical in the environment.

Cleanupof soils and geologic materials is an expensive proposition. Often the cleanup procedure is to remove the material and place it in a contained system, potentially, to become a problem at a future date. Models can be used for evaluating in situ reclamation activities such as well placement to capture a contaminant plume, answering such questions as: How many wells are needed? How should each of the wells be pumped? How long will it be necessary to pump a well field to "clean" an aquifer? Other in situ reclamation approaches require the stimulation of naturally occurring organisms in the aquifer. Studies have shown that there is a reasonable population of microorganisms in aquifer materials but their activity is low (Hutchins et al., 1985). Chemical additions may be possible to stimulate the activity. One difficulty with chemical amendments is that they often increase the biological activity within the well and-plug the well screen and aquifer near the well limiting the useful life of the injection system. Models can be used to study alternate schemes of dosing the well, creating "bubbles" of nutrient and giving the well itself a chance to recover its hydraulic properties.

Models are useful in the evaluation of the design of containment systems in both saturated and unsaturated environments. In constructed landfills, barriers to water flow (soils or other materials with low hydraulic conductivity) layered with highly permeable layers are used to divert the water around the waste material. The philosophy is that if water doesn't pass through the material, there will not be contamination of the groundwater. As long as the constructed system remains intact, in theory the system should work and give a long residence time for the chemicals, giving time for chemical and biological transformations.

APPENDIX

Symbol	Description	Units
b	Clapp and Hornburger curve coefficient	
C^*	Concentration in the mobile phase	$\mathrm{M\ M^{-1}}$
C_i	Dependent concentration variable	$\mathrm{M\ M^{-1}}$
C_a	Concentration in aqueous phase	$\mathrm{M\ M^{-1}}$
C_{et}	Evaporation pan coefficient	
C_o	Concentration in immiscible phase	$\mathrm{M\ M^{-1}}$
C_s	Concentration in solid phase	$\mathrm{M\ M^{-1}}$
C_v	Concentration in vapor phase	$\mathrm{M\ M^{-1}}$
D	Soil water diffusivity	$\mathrm{L^2\ T^{-1}}$
d	Molecular diffusion coefficient in water	$\mathrm{L^2\ T^{-1}}$
D^*	Lumped dispersion variable of mobile phase	$\mathrm{L^2\ T^{-1}}$
D_a	Dispersion in aqueous phase	$\mathrm{L^2\ T^{-1}}$
D_o	Dispersion in immiscible phase	$\mathrm{L^2\ T^{-1}}$
D_v	Dispersion in vapor phase	$\mathrm{L^2\ T^{-1}}$
E_g	Evapotranspiration from grass	$\mathrm{L\ T^{-1}}$
E_{pan}	Pan evaporation	$\mathrm{L\ T^{-1}}$
ET	Evapotranspiration	$\mathrm{L\ T^{-1}}$
F	Fraction organic C associated with solid phase	
g	Gravitational acceleration	$\mathrm{L\ T^{-2}}$
H	Total potential head	L
K	Darcy velocity (hydraulic conductivity)	$\mathrm{L\ T^{-1}}$
k_{ao}	First-order transfer coefficient aqueous to immiscible phase	$\mathrm{T^{-1}}$
k_{as}	First-order transfer coefficient aqueous to solid phase	$\mathrm{T^{-1}}$
k_{av}	First-order transfer coefficient aqueous to vapor phase	$\mathrm{T^{-1}}$
k_d	Unitless soil/water partition coefficient	
k_d'	Unitless soil/water distribution coefficient	
k_{oa}	First-order transfer coefficient immiscible to aqueous phase	$\mathrm{T^{-1}}$
k_{ow}	Octanol/water partition coefficient	
K_s	Saturated hydraulic conductivity	$\mathrm{L\ T^{-1}}$
k_{sa}	First-order transfer coefficient solid to aqueous phase	$\mathrm{T^{-1}}$
k_t	Lumped transformation rate	$\mathrm{T^{-1}}$
K_t^*	Lumped transformation variable	$\mathrm{T^{-1}}$
k_{ta}	First-order transformation rate aqueous phase	$\mathrm{T^{-1}}$
k_{to}	First-order transformation rate immiscible phase	$\mathrm{T^{-1}}$
k_{ts}	First-order transformation rate solid phase	$\mathrm{T^{-1}}$
k_{tv}	First-order transformation rate vapor phase	$\mathrm{T^{-1}}$
k_{va}	First-order transfer coefficient vapor to aqueous phase	$\mathrm{T^{-1}}$
L	Hydraulic loading from synthetic sources	$\mathrm{L\ T^{-1}}$
n	Porosity of the soil	$\mathrm{L^3\ L^{-3}}$

(continued on next page)

Symbol	Description	Units
P_r	Precipitation intensity	$L\ T^{-1}$
r	Net rate of change	$M\ L^{-3}\ T^{-1}$
R	Retardation factor	
R^*	Lumped retardation variable	
t	Time	T
V^*	Lumped velocity variable of mobile phase	$L\ T^{-1}$
V_a	Interstitial velocity of aqueous phase	$L\ T^{-1}$
V_d	Darcy velocity	$L\ T^{-1}$
V_o	Interstitial velocity of immiscible phase	$L\ T^{-1}$
V_v	Interstitial velocity of vapor phase	$L\ T^{-1}$
x	Distance along flow path in one-dimensional flow or horizontal distance in two-dimensional flow	L
z	Vertical distance	L
α	Dispersivity	L
β	Temporary variable	
ρ_a	Density of aqueous phase	$M\ L^{-3}$
ρ_o	Density of immiscible phase	$M\ L^{-3}$
ρ_s	Particle density of the soil	$M\ L^{-3}$
ρ_v	Density of the vapor phase	$M\ L^{-3}$
ϕ	Volume fraction occupied by the immiscible phase	$L^3\ L^{-3}$
θ	Volume fraction occupied by the aqueous phase	$L^3\ L^{-3}$
η	Volume fraction occupied by the vapor phase	$L^3\ L^{-3}$
γ	Viscosity of water	
ψ	Water potential	L
τ	Radius of capillary tube or pore	L
κ	Crop coefficient	
λ	Tortuosity constant	
ω	Runoff	$L\ T^{-1}$
ι	Thickness of soil restricting volatilization	L

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