DIVISION S-1—SOIL PHYSICS

Two-Site/Two-Region Models for Pesticide Transport and Degradation: Theoretical Development and Analytical Solutions

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ABSTRACT

Analytical solutions are presented for two convection-dispersion type transport models useful for studying simultaneous pesticide sorption and degradation. One solution is for the familiar two-site sorption model in which adsorption-desorption proceeds kinetically on one fraction of the sorption sites, and at equilibrium on the remaining sites. Another solution holds for two-region (or mobile-immobile liquid phase) transport appropriate for aggregated or fractured media. The transport models account for degradation in both the solution and sorbed phases. The dimensionless analytical solutions for the two-site and two-region models are shown to be identical; they contain up to six independent dimensionless parameters: a column Peclet number, a retardation factor, a coefficient partitioning the soil/chemical system in equilibrium and nonequilibrium parts, a rate coefficient, and two dimensionless degradation coefficients. One of the two independent degradation coefficients may be eliminated when the solution and sorbed phase degradation rate coefficients are assumed to be identical, or when, with additional but reasonable assumptions, adsorbed phase degradation is assumed to be negligible.

CONCERN about the fate of chemicals introduced into soil-water systems has recently intensified. It is often necessary to estimate the behavior of a chemical in the field without substantial knowledge of the interaction of the chemical with the solid phase or its degradation rate. As new chemicals are proposed for future use, or as closer scrutiny is given to those already in use, it is necessary to utilize scientifically sound, comprehensive tools to evaluate the potential behavior of these chemicals in the environment. Well-constructed tools in the form of models describing transport in soil-water systems also serve the complementary purpose of increasing our understanding of basic processes affecting chemical fate.

Analytical solutions of the classical convection-dis-

persion equation (CDE), or of alternative equations, have been widely used as models of chemical transport and transformation in soil-water systems. Although such models are limited to conditions of steady-state water flow in homogeneous soils, and hence are primarily useful only for interpreting laboratory experiments, valuable information has been gained through their use. The application of analytical models to the study of pesticide transport in soils has actually been a standard practice for many years (Lindstrom et al., 1967; Kay and Elrick, 1967; Davidson et al., 1968; Davidson and McDougal, 1973; O'Connor et al., 1976; Rao et al., 1979; Enfield and Carsel, 1981; Jury et al., 1983, 1984; Zhong et al., 1986). Models of this type have been reviewed a number of times (van Genuchten and Cleary, 1979; Nielsen et al., 1986), and have recently been placed within the perspective of other approaches to describe solute transport (Addiscott and Wagenet, 1985; Jury, 1984). A variety of analytical solutions are currently available (e.g., van Genuchten and Alves, 1982; Javandel et al., 1984), some of which have now been included into optimization packages usable on a routine basis for interpretation of laboratory or field tracer experiments (Parker and van Genuchten, 1984).

Pesticide transport is influenced by a large number of simultaneous processes and properties. Among the nonequilibrium processes influencing transport is the possible division of sorption sites into two types. The two-site sorption concept presumes that sorption or exchange sites in soils can be classified into two fractions: one fraction (Type-1) on which sorption is assumed to be instantaneous, and another fraction (Type-2) on which sorption is considered to be time-dependent. The resulting two-site model has been successfully used to describe the transport of a number of solutes (Selim et al., 1977; Cameron and Klute, 1977; Rao et al., 1979; DeCamargo et al., 1979; Hoffman and Rolston, 1980; Parker and Jardine, 1986) that interact with a solid phase composed of such different constituents as soil minerals, organic matter and various oxides. Studies of the sorption of 2,4-D (2,4-dichlorophenoxy acetic acid) and atrazine (2-chloro-4-ethylamine-6-isopropylamino-1,3,5 triazine)

(Rao et al., 1979) indicate that the two-site model may well be suitable for these pesticides.

Another nonequilibrium model that has been found useful for modeling solute transport is the "two-region' or "bi-continuum" transport model (Coats and Smith, 1964; Gaudet et al., 1977; van Genuchten and Cleary, 1979; Nkedi-Kizza et al., 1984) in which the sorption rate is thought to be limited by the rate at which solutes are transported by diffusion to the exchange sites. This conceptualization has led to physical nonequilibrium models that partition soil water into mobile (flowing) and stagnant (immobile or nonflowing) regions. The approach in effect assumes that the pore-water velocity distribution is bimodal: convective-dispersive transport is confined to only a fraction of the liquid-filled pores, while the remainder of the pores have stagnant water (e.g., dead-end pore water, intra-aggregate water, thin liquid films around particles). In models of this type, solute exchange between the two liquid phases is frequently considered to be a first-order rate process. We note that similar "mobile-immobile" type two-region transport models have also been used for modeling solute transport in river systems containing dead zones (Bencala and Walters, 1983; LeGrand-Marcq and Laudelout, 1985).

Microbial degradation is another process of importance to pesticide transport. Biodegradation of organic chemicals has classically been presumed to occur primarily in the liquid phase of the soil. Whereas degradation in the sorbed phase has at times been measured (Marshman and Marshall, 1981; Moyer et al., 1972; Scott et al., 1983), other studies with such herbicides as 2,4-D (Ogram et al., 1985), diquat (1,1'-ethylene-2,2'-bypyridylium ion) (Weber and Cole, 1968) and triazine (Moyer et al., 1972) indicate that the sorbed phase may not always be available for degradation. Thus, the separation of pesticide degradation into relative contributions of the sorbed and solution phases is a continuing concern for soil scientists and soil microbiologists dealing with the environmental fate of pesticides.

Analytical solutions of two-site and two-region type models with solution and sorbed phase degradation are needed to fully interpret pesticide transport experiments involving laboratory soil columns. Such experiments in turn are designed to estimate future pesticide behavior in field soils (e.g., Zhong et al., 1986). In this paper we shall develop the governing equations and relevant analytical solutions for these two-site and two-region transport models with degradation. For completeness, we shall also formulate the classical equilibrium and one-site kinetic transport models with degradation. In a later study (Gamerdinger et al., 1989) we will use the analytical models to analyze a set of column displacement experiments with atrazine and 2,4,5-T (2,4,5-trichlorophenoxy acetic acid).

LINEAR EQUILIBRIUM SORPTION

We first derive the governing equation for classical "Fickian"-based, deterministic solute transport with degradation. Consider a soil system (Fig. 1) composed of a liquid phase involving convective and diffusive/dispersive transport, and a solid phase subject to chemical sorption or exchange. The continuity equation for the liquid phase is

$$\frac{\partial(\theta c)}{\partial t} = -\frac{\partial J_s}{\partial x} - J_a - \theta \mu_l c \qquad [1]$$

where c is the volume-averaged solution concentration (with units M L^{-3}), θ is the volumetric water content (L^3 L^{-3} or L^0), μ_l is a first-order decay coefficient for degradation from the liquid phase (T^{-1}), x is distance (L), t is time (T), J_a is a transfer rate from the solution to the sorbed phase due to sorption (M L^{-3} T^{-1}), and J_s is the solute flux density (M L^{-2} T^{-1}),

$$J_s = -\theta D \frac{\partial c}{\partial x} + qc, \qquad [2]$$

in which D is the dispersion coefficient (L^2 T^{-1}) and q the volumetric water flux density (L T^{-1}). Combining Eq. [1] and [2] gives

$$\frac{\partial(\theta c)}{\partial t} = \frac{\partial}{\partial x}\left(\theta D \frac{\partial c}{\partial x} - qc\right) - J_a - \theta \mu_l c. \qquad [3]$$

Equation [1] is based on a mass balance of input and outputs for the solution phase. A similar mass balance for the sorbed phase leads to

$$\rho \frac{\partial s}{\partial t} = J_a - \rho \mu_s s, \qquad [4]$$

where s is the sorbed concentration (M^0), ρ is the soil bulk density (M L^{-3}), and μ_s is the first-order sorbed phase degradation coefficient (T^{-1}). Equation [4] states that the change in sorbed concentration equals the transfer rate (J_a) from the solution to the sorbed phase minus decay from the sorbed phase. We will further use the term "sorption rate" when referring to J_a.

Equation [3] and [4] hold for the solution and sorbed phases, respectively. Adding the two equations eliminates J_a and leads to a transport equation for the soil system as a whole

$$\frac{\partial(\theta c)}{\partial t} + \rho \frac{\partial s}{\partial t}$$
$$= \frac{\partial}{\partial x}\left(\theta D \frac{\partial c}{\partial x} - qc\right) - \theta \mu_l c - \rho \mu_s s. \qquad [5]$$

This equation is valid irrespective of whether sorption is an equilibrium or kinetic process. Equilibrium sorption presumes that solute exchange between the liquid and solid phases occurs at such a rate that at all times the sorbed concentration, s, is uniquely related algebraically to the so-
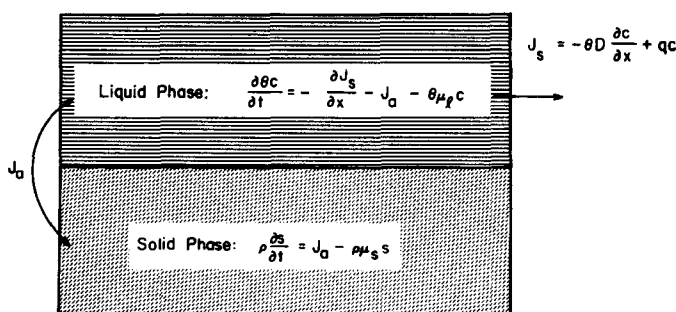
Fig. 1. Schematic of the one-site equilibrium and kinetic sorption transport models with degradation.

lution concentration, c. If the sorption process is linear, this leads to

$$s = kc \qquad [6]$$

where k is an empirical distribution coefficient ($M^{-1}\ L^3$). Substituting Eq. [6] in [5] gives

$$\frac{\partial(\theta Rc)}{\partial t} = \frac{\partial}{\partial x}\left(\theta D\frac{\partial c}{\partial x} - qc\right) - \mu\theta c \qquad [7]$$

where R and μ are the retardation factor and total (or effective) degradation constant, respectively

$$R = 1 + \rho k/\theta \qquad [8]$$

$$\mu = \mu_l + \rho\mu_s k/\theta . \qquad [9]$$

Note that when the two degradation constants μ_l and μ_s are identical (e.g., for radioactive decay), Eq. [9] reduces to $\mu = \mu_l R$. For chemical or microbial degradation, however, the two rate coefficients likely have different values.

Equation [7] holds for transient fluid flow. For steady-state flow in a uniform medium (constant θ and ρ), the transport equation becomes

$$R\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - v\frac{\partial c}{\partial x} - \mu c \qquad [10]$$

where $v = q/\theta$ is the average pore water velocity. Analytical solutions of this model for various initial and boundary conditions are given elsewhere (van Genuchten and Alves, 1982).

ONE-SITE KINETIC ADSORPTION

Assuming linear kinetic sorption, the sorption rate, J_a, from the solution to the sorbed phase is given by

$$J_a = \alpha\rho(kc - s) , \qquad [11]$$

where α is a first-order kinetic rate coefficient. Equations [3] and [4] become now respectively,

$$\frac{\partial(\theta c)}{\partial t} = \frac{\partial}{\partial x}\left(\theta D\frac{\partial c}{\partial x} - qc\right) - \alpha\rho(kc - s) - \theta\mu_l c \qquad [12a]$$

$$\frac{\partial s}{\partial t} = \alpha(kc - s) - \mu_s s , \qquad [12b]$$

which is the one-site kinetic model for transient flow. For steady-state water flow in a uniform medium, Eq. [12a] reduces to

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - v\frac{\partial c}{\partial x} - \frac{\alpha\rho}{\theta}(kc - s) - \mu_l c . \qquad [13]$$

It is important to recognize that Eq. [13] holds only for the liquid phase, and as such only contains a decay term for the liquid phase (last term of Eq. 13). By making use of Eq. [12b], the sorption rate term may be eliminated from Eq. [13] to give

$$\frac{\partial c}{\partial t} + \frac{\rho}{\theta}\frac{\partial s}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - v\frac{\partial c}{\partial x} - \mu_l c - \frac{\rho\mu_s}{\theta}s . \qquad [14]$$

This equation holds for the soil system as a whole and is identical to Eq. [5] for steady-state water flow. Hence, the one-site kinetic model is also given by Eq. [12b] and [14]. Note that the sorbed phase decay term appears now in Eq. [12b] as well as [14]. This decay term was ignored by Lindstrom (1976) in his classical derivation of the analytical solution for first-order kinetic solute transport with decay (see Eq. [1] of Lindstrom, 1976). We conclude from the above
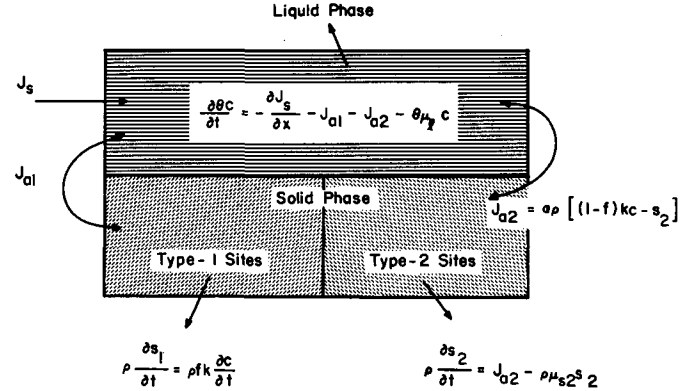

Fig. 2. Schematic of the two-site partial equilibrium, partial kinetic sorption transport model with degradation.

step-by-step development that Lindstrom's 1976 formulation is incomplete.

The one-site model is a special case of the two-site transport model to be discussed next. Thus, analytical solutions for the two-site model are directly applicable also to the above one-site kinetic model.

TWO-SITE EQUILIBRIUM/KINETIC SORPTION

Governing Equations

The derivation for this case proceeds in the same fashion as for the one-site model. Since the two-site model itself has been explained in detail elsewhere, only a capsulized derivation is presented here to indicate the treatment of the degradation terms. Following the notation of van Genuchten (1981) and Parker and van Genuchten (1984), we have at equilibrium for the Type-1 (equilibrium) and Type-2 (kinetic) sites, respectively

$$s_1 = fkc \qquad [15a]$$

$$s_2 = (1-f)kc \qquad [15b]$$

where f is the fraction of exchange sites assumed to be at equilibrium, and where the subscripts 1 and 2 refer to the two Type-1 and Type-2 sorption sites, respectively. Total adsorption, s, is given by

$$s = s_1 + s_2 \qquad [16]$$

which at equilibrium becomes equivalent to Eq. [6].

Figure 2 shows schematically a soil made up of the liquid phase, a Type-1 solid phase, and a Type-2 solid phase. Both J_{a1} and J_{a2} are the sorption rates from the liquid into the Type-1 and Type-2 regions, respectively. Mass transport in the liquid phase is still described by Eq. [3], given that J_a now becomes the sum of J_{a1} and J_{a2}. The mass balances for the Type-1 and Type-2 are similar to Eq. [4]

$$\rho\frac{\partial s_1}{\partial t} = J_{a1} - \rho\mu_{s1}s_1 \qquad [17a]$$

$$\rho\frac{\partial s_2}{\partial t} = J_{a2} - \rho\mu_{s2}s_2 . \qquad [17b]$$

The mass transport equation for the system as a whole follows by adding the contributions of Eq. [3] and [17a,b], and noting that $J_a = J_{a1} + J_{a2}$

$$\frac{\partial(\theta c)}{\partial t} + \rho\frac{\partial(s_1 + s_2)}{\partial t} = \frac{\partial}{\partial x}\left(\theta D\frac{\partial c}{\partial x} - qc\right)$$

$$- \theta\mu_l c - \rho\mu_{s1}s_1 - \rho\mu_{s2}s_2 . \qquad [18]$$

Because Type-1 sites are always at equilibrium, sorption onto these sites is also given by the time-derivative of Eq. [15a]

$$\frac{\partial s_1}{\partial t} = fk \frac{\partial c}{\partial t}. \qquad [19]$$

By using a first-order kinetic sorption rate law analogous to Eq. [11], and by making use of Eq. [15b], the mass balance equation for the Type-2 sites becomes

$$\frac{\partial s_2}{\partial t} = \alpha[(1 - f)kc - s_2] - \mu_{s2}s_2. \qquad [20]$$

Substituting Eq. [19] and [20] into Eq. [18] and using Eq. [15a] to eliminate s_1 from the equilibrium sorbed phase degradation term leads to

$$\frac{\partial(\theta + f\rho k)c}{\partial t} = \frac{\partial}{\partial x}\left(\theta D \frac{\partial c}{\partial x} - qc\right) -$$

$$\alpha\rho[(1 - f)kc - s_2] - \theta\mu_l c - f\rho k\mu_{s1} c. \qquad [21]$$

Hence, the complete two-site model is given by Eq. [20] and [21].

Analytical Solution

For steady-state flow in a uniform system, Eq. [21] reduces to

$$\left(1 + \frac{\rho fk}{\theta}\right)\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - v\frac{\partial c}{\partial x} -$$

$$\frac{\alpha\rho}{\theta}[(1 - f)kc - s_2] - \mu_l c - \frac{f\rho k\mu_{s1} c}{\theta}. \qquad [22]$$

Equations [20] and [22] are solved for an initially solute-free, semi-infinite soil profile subject to a pulse-type input boundary condition. Thus, the auxiliary conditions are of the form

$$c(x,0) = s_1(x,0) = s_2(x,0) = 0 \qquad [23]$$

$$\frac{\partial c}{\partial x}(\infty,t) = 0 \qquad [24]$$

$$\left(-D\frac{\partial c}{\partial x} + vc\right)\Big|_{x=0} = \begin{cases} vC_0 & 0 < t \leq t_0 \\ 0 & t \geq t_0 \end{cases} \qquad [25]$$

where C_0 is the input concentration, and t_0 is the time duration of the applied solute pulse. To obtain a convenient dimensionless system of equations consistent with those of van Genuchten (1981, p. 27), the following variables are introduced

$$T = vt/L \qquad z = x/L \qquad [26a,b]$$

$$P = vL/D \qquad \beta = \frac{\theta + f\rho k}{\theta + \rho k} = \frac{R_m}{R} \qquad [27a,b]$$

$$R = 1 + \rho k/\theta \qquad R_m = 1 + f\rho k/\theta \qquad [28a,b]$$

$$\omega = \alpha(1 - \beta)RL/v, \qquad [29]$$

where L is an arbitrary distance from the input boundary (e.g., column length). We also define the dimensionless concentrations c_1 and c_2

$$c_1 = \frac{c}{C_0} \qquad c_2 = \frac{s_2}{(1 - f)kC_0}. \qquad [30a,b]$$

Equations [22] and [20] become then respectively,

$$\beta R \frac{\partial c_1}{\partial T} = \frac{1}{P}\frac{\partial^2 c_1}{\partial z^2} - \frac{\partial c_1}{\partial z} - \omega(c_1 - c_2) - \xi c_1 \qquad [31a]$$

$$(1 - \beta)R \frac{\partial c_2}{\partial T} = \omega(c_1 - c_2) - \eta c_2 \qquad [31b]$$

where

$$\xi = \frac{\mu_l L}{v} + \frac{\mu_{s1}(\beta R - 1)L}{v} = \frac{(\theta\mu_l + f\rho k\mu_{s1})L}{q} \qquad [32a]$$

and

$$\eta = \frac{(1 - \beta)R\mu_{s2}L}{v} = \frac{(1 - f)\rho k\mu_{s2}L}{q}. \qquad [32b]$$

Analytical solutions of Eq. [31a,b] can be derived using Laplace transforms as shown in detail, among others, by Lindstrom and colleagues (Lindstrom and Narasimhan, 1973; Lindstrom and Stone, 1974; Lindstrom, 1976). We omit here the relatively straightforward but extremely lengthy derivation. The general analytical solution for our problem is

$$c_1(z,T) = \begin{cases} c_a(z,T) & 0 < T \leq T_0 \\ c_a(z,T) - c_a(z,T - T_0) & T > T_0 \end{cases} \qquad [33a]$$

$$c_2(z,T) = \begin{cases} c_b(z,T) & 0 < T < T_0 \\ c_b(z,T) - c_b(z,T - T_0) & T > T_0 \end{cases} \qquad [33b]$$

where

$$c_1(z,t) = \int_0^T g(z,\tau) J(a,b) d\tau \qquad [34a]$$

$$c_2(z,t) = \frac{\omega}{\omega + \eta} \int_0^T g(z,\tau) [1 - J(b,a)] d\tau \qquad [34b]$$

$$T_0 = vt_0/L \qquad [35]$$

$$J(a,b) = 1 - e^{-b} \int_0^a e^{-\lambda} I_0[2\sqrt{b\lambda}] d\lambda \qquad [36a]$$

$$a = \frac{\omega^2\tau}{(\omega + \eta)\beta R} \qquad b = \frac{(\omega + \eta)(T - \tau)}{(1 - \beta)R} \qquad [36b,c]$$

and

$$g(z,\tau) = \frac{\partial G}{\partial \tau}(z,\tau) \qquad [37]$$

in which $G(z,t)$ represents the analytical solution of

$$\beta R \frac{\partial G}{\partial T} = \frac{1}{P}\frac{\partial^2 G}{\partial z^2} - \frac{\partial G}{\partial z} - \left(\xi + \frac{\omega\eta}{\omega + \eta}\right)G \qquad [38]$$

for the same initial and boundary conditions as before. For volume-averaged resident concentration (Kreft and Zuber, 1978; Parker and van Genuchten, 1984), $g(z,\tau)$ is given by

$$g(z,\tau) = \exp\left[-\left(\frac{\xi}{\beta R} + \frac{\omega\eta}{(\omega + \eta)\beta R}\right)\tau\right]$$

$$\left\{\left(\frac{P}{\pi\beta R}\right)^{1/2} \exp\left[-\frac{P(\beta Rz - \tau)^2}{4\beta R\tau}\right]\right.$$

$$\left. - \frac{P}{2\beta R} \exp(Pz) \, erfc\left[\left(\frac{P}{4\beta R\tau}\right)^{1/2}(\beta Rz + \tau)\right]\right\}. \qquad [39]$$
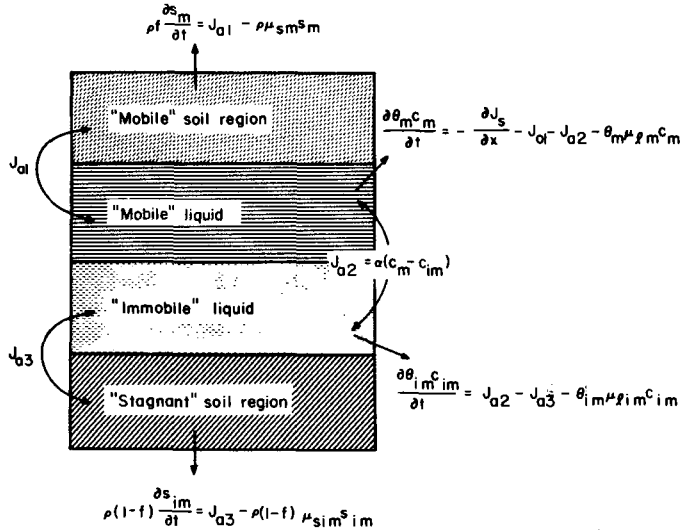
Fig. 3. Schematic of the two-region (mobile-immobile) transport model with degradation.

For flux-averaged or flowing concentrations, which are characteristic of column effluent curves (van Genuchten and Parker, 1984), $g(z,\tau)$ becomes

$$g(z,\tau) = \exp\left[-\left(\frac{\xi}{\beta R} + \frac{\omega\eta}{(\omega + \eta)\beta R}\right)\tau\right]$$

$$\left\{\frac{z}{\tau}\left(\frac{P\beta R}{4\pi\tau}\right)\exp\left[-\frac{P(\beta Rz - \tau)^2}{4\beta R\tau}\right]\right\}. \qquad [40]$$

TWO-REGION TRANSPORT MODEL WITH DEGRADATION

Governing Equations

The derivation of the two-region model with first-order degradation also parallels the no-decay case (van Genuchten, 1981; p. 12–16). The inclusion of degradation into the two-region model appears somewhat more complicated than for the two-site model. This is because local degradation rates inside aggregates can be radically different from those occurring at aggregate edges due to varying O_2 and/or microbial activities. To keep the formulation general, we need provisions for different degradation coefficients in the mobile and immobile liquid phases, as well as for different degradation coefficients for the mobile and immobile sorbed phases of the soil. Thus, a total of four degradation rate coefficients are possible in the two-region model, as compared to three for the two-site model.

Figure 3 shows again schematically the most important fluxes in a "two-region" soil system with decay. Convective-dispersive transport is confined to a mobile liquid region (subscript m) while the presence of solute in an immobile region (subscript im) depends on liquid diffusion from the mobile to the immobile liquid. The solid phase is also partitioned, in this case into a fraction f that equilibrates instantaneously with the mobile fluid, and another fraction $(1 - f)$ that equilibrates with the immobile liquid. Using the same notation as before, the transport equation for the mobile liquid phase (subscript m) is

$$\frac{\partial(\theta_m c_m)}{\partial t} = \frac{\partial}{\partial x}\left(\theta_m D_m \frac{\partial c_m}{\partial x} - qc_m\right)$$

$$- J_{a1} - J_{a2} - \theta_m\mu_{lm}c_m \qquad [41]$$

where μ_{lm} is the mobile liquid phase degradation coefficient, J_{a1} is the transfer rate from the liquid to the solid phase of the "mobile" region, while J_{a2} is due to diffusion-like exchange between the mobile and stagnant liquid zones. Analogous to Eq. [4], the mass balance for the "mobile" sorbed concentration (s_m) is

$$f\rho \frac{\partial s_m}{\partial t} = J_{a1} - f\rho\mu_{sm}s_m \qquad [42]$$

where μ_{sm} is the sorbed phase degradation coefficient for the mobile region. Adding Eq. [41] and [42] gives the transport equation for the mobile region as a whole

$$\frac{\partial(\theta_m c_m)}{\partial t} + f\rho \frac{\partial s_m}{\partial t} = \frac{\partial}{\partial x}\left(\theta_m D_m \frac{\partial c_m}{\partial x} - qc_m\right)$$

$$- J_{a2} - \theta_m\mu_{lm}c_m - f\rho\mu_{sm}s_m. \qquad [43]$$

A similar mass balance without the convection-dispersion terms holds for the stagnant region as a whole (subscript im)

$$\frac{\partial(\theta_{im}c_{im})}{\partial t} + (1 - f)\rho \frac{\partial s_{im}}{\partial t} = J_{a2}$$

$$- \theta_{im}\mu_{lim}c_{im} - (1 - f)\rho\mu_{sim}s_{im}. \qquad [44]$$

Solute exchange between the mobile and immobile liquid regions is approximated by the expression

$$J_{a2} = \alpha(c_m - c_{im}) \qquad [45]$$

in which the model-specific α is a first-order mass transfer coefficient describing the rate of transfer between the mobile and immobile liquid phases. Sorption in the inter- and intra-aggregate regions of the soil is described with linear isotherms of the form

$$s_m = kc_m \qquad s_{im} = kc_{im}. \qquad [46a,b]$$

Substituting Eq. [45] and [46a,b] into [43] and [44] gives finally the transient-flow two-region transport model with degradation

$$\frac{\partial(\theta_m + f\rho k)c_m}{\partial t} = \frac{\partial}{\partial x}\left(\theta_m D_m \frac{\partial c_m}{\partial x} - qc_m\right)$$

$$- \alpha(c_m - c_{im}) - (\theta_m\mu_{lm} + f\rho k\mu_{sm})c_m \qquad [47a]$$

$$\frac{\partial[\theta_{im} + (1 - f)\rho k]c_{im}}{\partial t} = \alpha(c_m - c_{im})$$

$$- [\theta_{im}\mu_{lim} + (1 - f)\rho k\mu_{sim}]c_{im}. \qquad [47b]$$

Analytical Solution

Assuming steady-state flow in uniform soil, Eq. [47a,b] reduce to

$$(\theta_m + f\rho k) \frac{\partial c_m}{\partial t} = \theta_m D_m \frac{\partial^2 c_m}{\partial x^2} - q \frac{\partial c_m}{\partial x}$$

$$- \alpha(c_m - c_{im}) - (\theta_m\mu_{lm} + f\rho k\mu_{sm})c_m \qquad [48a]$$

$$[\theta_{im} + (1 - f)\rho k] \frac{\partial c_{im}}{\partial t} = \alpha(c_m - c_{im})$$

$$- [\theta_{im}\mu_{lim} + (1 - f)\rho k\mu_{sim}]c_{im}. \qquad [48b]$$

We use the same initial and boundary conditions as for the two-site model (replace c by c_m in Eq. [23] through [25]). Introduce further the model-specific dimensionless parameters (T and z are as before)

Table 1. Expressions for the dimensionless parameters ξ and η in Eq. [31a,b] for the one-site, two-site and two-region transport models.

	One-site model	Two-site model	Two-region model†
Solution and sorbed phase degradation rates are independent	$\xi = \psi_l$ $\eta = (R-1)\psi_s$	$\xi = \psi_l + (\beta R - 1)\psi_{s1}$ $\eta = (1-\beta)R\psi_{s2}$	$\xi = \phi_m\psi_{lm} + (\beta R - \phi_m)\psi_{sm}$ $\eta = \phi_{im}\psi_{lim} + [(1-\beta)R - \phi_{im}]\psi_{sim}$
Degradation everywhere the same	$\xi = \psi$ $\eta = (R-1)\psi$	$\xi = \beta R\,\psi$ $\eta = (1-\beta)R\,\psi$	$\xi = \beta R\,\psi$ $\eta = (1-\beta)R\,\psi$
Degradation only in the liquid phase	$\xi = \psi_l$ $\eta = 0$	$\xi = \psi_l$ $\eta = 0$	$\xi = \phi_m\psi_l$ $\eta = \phi_{im}\psi_l$
Degradation only in the sorbed phase	$\xi = 0$ $\eta = (R-1)\psi_s$	$\xi = (\beta R - 1)\psi_{s1}$ $\eta = (1-\beta)R\,\psi_{s2}$	$\xi = (\beta R - \phi_m)\,\psi_{sm}$ $\eta = [(1-\beta)R - \phi_{im}]\,\psi_{sim}$

† $\phi_m = \theta_m/\theta$, $\phi_{im} = \theta_{im}/\theta$.

$$P = v_m L/D_m \qquad [49]$$

$$\beta = \frac{\theta_m + f\rho k}{\theta + \rho k} \qquad \omega = \alpha L/q \qquad [50a,b]$$

$$c_1 = c_m/C_0 \qquad c_2 = c_{im}/C_0 . \qquad [51a,b]$$

The dimensionless transport equations become then identical to Eq. [31a,b], provided ξ and η are now defined as

$$\xi = \frac{L}{q}(\theta_m\mu_{lm} + f\rho k\mu_{sm}) \qquad [52a]$$

$$\eta = \frac{L}{q}[\theta_{im}\mu_{lim} + (1 - f)\rho k\mu_{sim}] . \qquad [52b]$$

The dimensionless initial and boundary conditions for the two-site and two-region models are easily shown to be identical also. Thus, the analytical solution for the two-site model also applies to the above two-region mobile-immobile transport model with degradation.

DISCUSSION

The above formulations for the two-site and two-region models were obtained without making any assumptions about possible values of the degradation coefficients μ_l, μ_{s1}, μ_{mb} etc. While at least in theory it is possible that the degradation coefficients in any particular model will attain different values, in practice it may be nearly impossible to distinguish between them, with concomitant problems of parameter identification. This is especially true for the two-region model which contains four potentially different degradation coefficients. Thus, the number of degradation terms needs to be reduced where possible. Fortunately, it is possible to make several simplifications of the most general case of unequal solution and sorbed phase degradation rates.

One simplification results when all rate coefficients are the same, e.g, $\mu_l = \mu_{s1} = \mu_{s2} \equiv \mu$ for the two-site model, or $\mu_{lm} \equiv \mu_{lim} = \mu_{sm} = \mu_{sim} \equiv \mu$ for the two-region model. The otherwise independent parameters ξ and η for the two-site (Eq. [32a,b]) and the two-region (Eq. [52a,b]) models reduce then to (see also Table 1)

$$\xi = \beta R\,\psi \qquad \eta = (1 - \beta)R\psi \qquad [53a,b]$$

where the dimensionless parameter ψ is defined as

$$\psi = \mu L/v . \qquad [54]$$

Another significant simplification is possible when degradation is assumed to be limited to the solution phase, a situation that seems to hold for at least some pesticide-soil combinations (Weber and Cole, 1968; Moyer et al., 1972; Ogram et al., 1985). The solid phase degradation coefficients are then zero ($\mu_{s1} = \mu_{s2} = 0$) and ξ and η reduce to

$$\xi = \psi_l \qquad \eta = 0 \qquad [55a,b]$$

where, similar to Eq. [54] and other cases shown in Table 1, $\psi_l = \mu_l L/v$.

Table 1 summarizes the expressions for ξ and η for the most general case of unequal degradation rates in the solution and sorbed phases, as well as for several limiting cases involving the one-site, two-site and two-region transport models. Note that for the general two-site and two-region formulations, ξ includes all or part of the effects of both solution and sorbed phase degradation. The same is true for η in the general two-region formulation. The parameters ξ and η in both models are in that case independent, leading to a total of six independent dimensionless parameters: the column Peclet number P, the retardation R, a dimensionless partitioning coefficient β, a dimensionless rate coefficient for kinetic sorption or mobile-immobile type exchange ω, and the two degradation rate coefficients ξ and η. For equal degradation in the solution and sorbed phases, ξ and η become dependent, and only five independent variables can be identified (see also Table 1): P, R, β, ω and ψ.

Five independent parameters also result when degradation in the one-site and two-site models is limited to the solution phase. Note that $\xi = \psi_l$ ($= \mu_l L/v$) in that case, while η becomes zero (Table 1). However, ξ and η for the two-region model remain theoretically independent because of the inclusion of the mobile (ϕ_m) and immobile water (ϕ_{im}) fractions in ξ and η. These fractions are not independently included in any other dimensionless variable (including β as shown by van Genuchten and Cleary, 1979), and hence must be considered separately. This could pose considerable problems, especially when some of the parameters are estimated from measured breakthrough data. Curve-fitting is often necessary since the partitioning of the liquid phase into mobile and immobile parts is generally not known a priori. We can avoid this problem by assuming that the sorption sites and the mobile
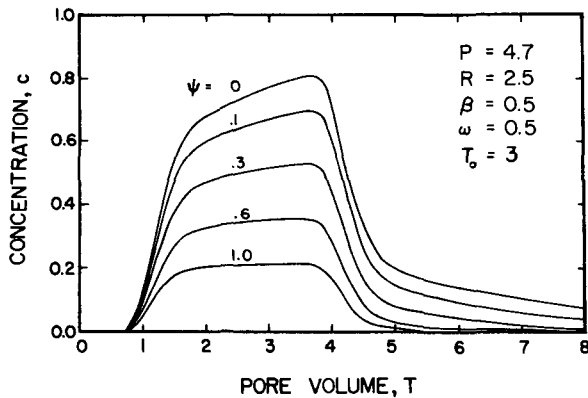
Fig. 4. Effect of the dimensionless degradation coefficient, ψ, on the shape of effluent curves calculated with the two-region model.

water fractions are distributed in the same manner throughout the soil system, that is (Nkedi-Kizza et al., 1984)

$$\phi_m = \theta_m/\theta = f = \beta \qquad [56]$$

so that the ξ and η parameters become

$$\xi = \beta \psi_l \qquad \eta = (1 - \beta) \psi_l. \qquad [57a,b]$$

Note that ξ and η are now the same as Eq. [53a,b] for equal degradation in the solution and sorbed phases, except that R now has been dropped.

Figure 4 illustrates the effect of degradation on calculated effluent curves. All parameter values are the same as used previously by van Genuchten and Cleary (1979) to demonstrate the effects of the dimensionless variables P, R, β and ω on calculated effluent curves. The one additional degradation parameter ψ in this example assumes that degradation is everywhere the same (Table 1). Given the assumption inherent in Eq. [56], the curves also apply to the special case of solution phase degradation only, provided the ψ's in Fig. 4 are multiplied by the value of R ($= 3.0$). Numerous effluent curves were also calculated with the general two-site/two-region model assuming unequal solution and sorbed phase degradation coefficients. The curves so obtained (not further shown here) behaved qualitatively very similar to those plotted in Fig. 4.

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