A One-dimensional Model of Chemical Diffusion and Sorption in Saturated Soil and Aquatic Systems[1]

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ABSTRACT

A one-dimensional model for chemical diffusion in saturated porous media systems is presented. The one-dimensional diffusion model provides for adsorption-desorption reactions either Freundlich or Langmuir, and both solid and liquid phase first-order chemical degradation under isothermal, water-saturated conditions. Finite-difference solutions to the model which simulate the one-dimensional diffusion of an inorganic/organic chemical from the sediment of an aquatic system into the overlying water are provided for a variety of initial and boundary conditions. Analogous applications to flow processes within a structured soil can be made for the diffusion of an inorganic/organic chemical into and out of saturated planar soil aggregates. The initial and boundary conditions are designed to simulate a variety of aquatic situations: ponds, lakes, streams, rivers and oceans. Both explicit and implicit (i.e., Crank-Nicolson) finite-difference schemes are presented for four different saturated systems. The model provides a means of assessing the physicochemical dynamics of chemical-sediment-water interactions and of assessing the pollution potential of chemicals to plants and animals as determined by their propensity to migrate to different compartments of the aquatic environment. The models can also determine the influence of diffusion processes within planar soil aggregates upon solute flow in saturated structured soils. Various simulations are presented for boron (B), diquat (1,1′-ethylene-2,2′-dipyridilium dibromide), and bromacil (5-bromo-3-*sec*-butyl-6-methyluracil).

Additional Index Words: **movement, finite-difference model, structured soils, soil aggregate.**

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Due to the adsorptive capacity of soil for various organic and inorganic chemicals (e.g., boron [B], pesticides) and to the "piggyback" transport of these adsorbed chemicals upon eroded soil particles, the sediments of some of our water bodies have become unintentional repositories for chemicals potentially harmful to plants and animals. Once these chemicals desorb from the sediment, they can diffuse into the overlying water resulting in a decrease in water quality which could threaten both plants and animals. Analogously, soil aggregates act as sinks or sources of chemicals to the flow process within structured soils due to the diffusion of the chemical into our out of the soil aggregates. This fact is evidenced by the asymmetric displacement patterns often observed for structured soils.

Since very low concentrations of some chemicals are known to be toxic to fish and other aquatic lifeforms, and since irrigation waters containing certain chemicals (e.g., B) are known to produce lower crop yields in certain instances, it is important to have a knowledge of the physicochemical dynamics of inorganic/organic chemical-sediment-water interactions to assess the hazard potential of these chemicals. Similarly, knowledge of the influence of soil aggregate diffusion processes upon solute transport in structured soils is needed to help provide an understanding of the transport of chemicals which may become potential groundwater pollutants, can retard or improve plant growth, or are involved in soil reclamation processes.

Since the aquatic compartment of our environment constitutes a potential sink for various chemicals, increased study of chemical-sediment-water interactions has developed over the years (Lotse et al., 1968; Nicolson and Hill, 1970; Veith and Lee, 1971; Weber, 1972; Pionke and Chesters, 1973; Karickhoff et al., 1979; Peck et al., 1980; Karickhoff, 1981; Goldberg, 1982; Corwin and Farmer, 1984a). In addition, various models describing simple aquatic systems have been presented as a means of assessing the relative importance of the various physico-chemical interactions (Corwin and Farmer, 1984b) and of assessing the pollution potential of hazardous chemicals (Corwin and Farmer, 1985). It is the purpose of this study to present finite-difference solutions to models representing a variety of more complicated aquatic systems such as ponds, lakes, oceans, streams, and rivers. These models also have analogous applications to diffusion within saturated planar soil aggregates of structured soils. The finite-difference schemes describe the one-dimensional diffusion under saturated conditions of any chemical undergoing Freundlich- or Langmuir-type adsorption-desorption reactions with consideration given to simultaneously occurring degradation reactions. A variety of initial and boundary conditions have been imposed to describe likely occurring aquatic systems. The models presented herein provide a means of assessing the pollution potential of chemicals to a variety of aquatic systems more sophisticated than that presented by Corwin and Farmer (1985). With regards to flow processes in structured soils, the models provide a means of determining the extent to which diffusion within planar soil aggregates acts as a source or a sink term to solute transport under saturated conditions.

THEORY

The governing partial differential equation describing one-dimensional diffusion of a chemical under isothermal, water-saturated conditions within a sorbing porous medium is,

$$\theta_v \frac{\partial C}{\partial t} + \varrho_b \frac{\partial S}{\partial t} = D_P \frac{\partial^2 C}{\partial x^2} - \mu_l \theta_v C - \mu_s \varrho_b S \qquad [1]$$

where C and S are the equilibrium solution and adsorbed concentrations, respectively, θ_v is the volumetric water content, ϱ_b is the bulk density, D_p is the porous diffusion coefficient (assumed constant), x is the distance, and t is the time. Negligible solid-phase diffusion is assumed. The coefficients μ_l and μ_s represent the degradation rates of first-order chemical de-

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Table 1. Initial and boundary conditions for potentially existing aquatic systems.

Case	Aquatic system	Initial conditions		Boundary conditions	
I	Well-mixed, fast-flowing rivers	$C(x, 0) = C_0$	$0 \le x \le L_1$	$C(x, t) = 0$	$x = 0, t \ge 0$
				$(\partial/\partial x)C(x, t) = 0$	$x = L_1, t \ge 0$
II	Lakes and oceans with low organic matter sediment (no thin organic film at $x = 0$).	$C_1(x, 0) = 0$	$L_1 \le x < 0$	If volatilization occurs,	
		$C_2(x, 0) = C_0$	$0 \le x \le L_2$	$C_1(x, t) = 0$	$x = L_1, t > 0$
				If no volatilization occurs,	
				$(\partial/\partial x)C_1(x, t) = 0$	$x = L_1, t > 0$
	medium 1 = "stagnant" water			$(\partial/\partial x)C_2(x,t) = 0$	$x = L_2, t > 0$
	medium 2 = sediment			$-D(\partial C_1/\partial x) = -[(D_p/\theta_v)(\partial C_2/\partial x)]$	$x = 0, t > 0$
				$C_1(x, t) = C_2(x, t)$	$x = 0, t > 0$
				where D = aqueous diffusion coefficient	
III	Lakes and oceans with high organic matter sediment (thin organic matter film at $x = 0$).	$C_1(x, 0) = 0$	$L_1 \le x < 0$	If volatilization occurs,	
		$C_2(x, 0) = C_0$	$0 \le x \le L_2$	$C_1(x, t) = 0$	$x = L_1, t > 0$
				If no volatilization occurs,	
				$(\partial/\partial x)C_1(x, t) = 0$	$x = L_1, t > 0$
	medium 1 = "stagnant" water			$(\partial/\partial x)C_2(x, t) = 0$	$x = L_2, t > 0$
	medium 2 = sediment			$-D(\partial C_1/\partial x) = -[(D_p/\theta_v)(\partial C_2/\partial x)]$	$x = 0, t > 0$
				$(\partial/\partial x)C_2(x, t) = \alpha(C_2 - C_1)$	$x = 0, t > 0$
				where $\alpha = h/D_p$	
IV	Poorly-mixed, slow-moving	$C_1(x, 0) = C_0$	$0 \le x \le L_1$	$(\partial/\partial x)C_1(x, t) = \alpha(C_1 - C_s)$	$x = 0, t > 0$
				where $\alpha = h/D_p$	
				$(\partial/\partial x)C_1(x, t) = 0$	$x = L_1, t > 0$

gradation within the liquid and solid phases, respectively. For Freundlich-type equilibrium adsorption, the relation between S and C is given by

$$S = KC^N \qquad [2]$$

where K and N are empirical coefficients representing the strength of adsorption and the degree of nonlinearity of adsorption, respectively. Substituting the differentiated form of Eq. [2] into Eq. [1] results in Eq. [3],

$$\frac{\partial C}{\partial t} = \frac{D_p}{\theta_v R_F}\frac{\partial^2 C}{\partial x^2} - \frac{1}{R_F}\left[\mu_l + \frac{\mu_s}{N}(R_F - 1)\right]C \qquad [3]$$

where the retardation factor R_F is given by

$$R_F = 1 + \frac{\varrho_b}{\theta_v} KNC^{N-1} \qquad [4]$$

for Freundlich-type adsorption. In the case of Langmuir-type adsorption the equation relating S and C is given by

$$S = kbC/(1 + kC) \qquad [5]$$

where k and b represent the Langmuir affinity constant and adsorption maximum, respectively. Similarly, by substituting the differentiated form of Eq. [5] into Eq. [1] results in Eq. [6],

$$\frac{\partial C}{\partial t} = \frac{D_p}{R_L \theta_v}\frac{\partial^2 C}{\partial x^2} - \frac{1}{R_L}[\mu_l + \mu_s(1 + kC)(R_L - 1)]\,C \qquad [6]$$

where

$$R_L = 1 + \frac{\varrho_b kb}{\theta_v(1 + kC)^2} \qquad [7]$$

for Langmuir-type adsorption. The above models represent aquatic systems where no convective-dispersive flow is occurring as would be found in cirque-type water bodies.

Initial and boundary conditions were imposed which simulate those situations which would likely be found in many of our lakes, rivers, streams, and oceans as well as in planar soil aggregates of saturated structured soils. Four basic aquatic situations were envisioned and from these the initial and boundary conditions were drawn. Table 1 outlines the initial and boundary conditions of the four aquatic systems. In all cases an impermeable layer is assumed to exist at some finite depth, $x = L$.

Case I describes an aquatic system in which the sediment has an initial sediment equilibrium solution concentration of C_0 uniformly distributed through the sediment solution from the sediment-water interface at $x = 0$ to the impermeable layer at $x = L$. The chemical equilibrium solution concentration at the sediment-water interface is maintained at zero at all times which would be indicative of a large, fast-flowing, well-mixed river in a pristine condition that removes and dilutes the chemical to essentially zero as soon as it diffuses into the overlying water body.

Case II describes a situation where diffusion occurs from the sediment into a "stagnant" water layer where the flux and concentration are continuous over the sediment-water interface. This set of conditions would likely occur in ponds, lakes, and oceans. The assumption that the concentration is continuous across the surface of composite media separation may not be true in all cases, especially where the sediment is high in organic matter (OM) and a thin film of finely suspended organic material potentially exists at the sediment-water interface (i.e., $x = 0$). This thin layer of organic material is analogous to the nonsettled microparticles or organic macromolecules proposed by Gschwend and Wu (1985) as fundamental in the environmental speciation of hydrophobic organic compounds between three "phases"; dissolved, sorbed to nonsettling particles or macromolecules, and sorbed to settled solids. The thin layer of undisturbed organic material acts as an interface resistance due to its lower effective diffusion coefficient thereby resulting in a discontinuous concentration at the sediment-water interface. In cases such as these, the rate of transfer between the two layers is proportional to their concentration difference as shown by the interface boundary condition of Case III.

Case IV represents an aquatic system where a chemical is diffusing through the sediment into a poorly-mixed flowing fluid with a constant concentration of C_s as might be found in contaminated streams and rivers. Some small lakes may also fall into this category depending on the degree of mixing due to thermal currents. As in Case III, Case IV assumes that the rate of transfer between the two media is a function of the concentration difference at their interface, but unlike Case III the surrounding solution concentration is constant. Case IV is representative of the conditions which would exist in saturated structured soils with planar soil aggregates. The concentration of the fluid flowing through the macropores and cracks surrounding the planar aggregates would be C_s. The interface resistance would be due to an immobile water phase film which exists along the planar aggregates. This effect is often referred to as the "stagnant film concept" (Gottschlich, 1963), and has been used in several models which describe solute transport from a macroscopic point of view (Coats and Smith, 1964; van Genuchten and Wierenga, 1976; Skopp et al., 1981).

Explicit and Implicit Finite-difference Numerical Schemes

Using the method of explicit finite-differences which are forward differenced in time with $C_{xx} \cong$ a second order central difference, Eq. [3] becomes Eq. [8] for $0 < x < L$,

$$C_i^{j+1} = \frac{D_p \Delta t}{\theta_v R_F (\Delta x)^2} [C_{i+1}^j + C_{i-1}^j] + \left\{1 - \frac{1}{R_F}\left[\mu_l + \frac{\mu_s}{N}(R_F - 1)\right]\Delta t - \frac{2D_P \Delta t}{\theta_v R_F (\Delta x)^2}\right\} C_i^j \quad [8]$$

where i refers to position, and j refers to time; and Eq. [6] becomes Eq. [9],

$$C_k^{j+1} = \frac{D_P \Delta t}{\theta_v R_L (\Delta x)^2} [C_{i+1}^j + C_{i-1}^j] + \left\{1 - \frac{1}{R_L}[\mu_l + \mu_s(1 + kC_i^j)(R_L - 1)]\,\Delta t - \frac{2D_P \Delta t}{\theta_v R_L (\Delta x)^2}\right\} C_i^j. \quad [9]$$

R_F or R_L are calculated at the old time step, j. Imposing the initial and boundary conditions for the different aquatic systems results in various explicit numerical solutions.

To ensure stability and convergence in the explicit method, the stability and convergence requirements are $[1/2 - 1/2 (B\Delta t)] \geq r$ *and* $1 \geq B\Delta t$ (assume $B \geq 0$ and $r \geq 0$) where for the Freundlich case

$$B = \frac{1}{R_F}\left[\mu_l + \frac{\mu_s}{N}(R_F - 1)\right] \text{ and } r = \frac{D_P \Delta t}{\theta_v R_F (\Delta x)^2},$$

and where for the Langmuir case

$$B = \frac{1}{R_L}[\mu_l + \mu_s(1 + kC_i^j)(R_L - 1)] \text{ and } r = \frac{D_P \Delta t}{\theta_v R_L (\Delta x)^2}.$$

Accuracy of the explicit method is limited by the truncation error, $e = 0(\Delta t) + 0[(\Delta x)^2]$; therefore, to maintain stability and ensure acuracy Δx and Δt must be sufficiently small.

The numerical solution for Case I was checked against the analytical solution for the same initial and boundary value problem with zero adsorption ($R_F = 1$) and linear adsorption [$R_F = 1 + (\varrho_b k/\theta_v)$, where K = linear adsorption coefficient]. Excellent agreement was obtained between the finite-difference and analytical solutions for both zero and linear adsorption. The overall mass balance error after 10 iterations using space and time grids of 0.5 cm and 0.1 d, respectively, never exceeded 2% and all subsequent iterations were < 1% error on a mass balance basis from the start.

The simplicity of the explicit method is counteracted by the necessity of taking so many time steps that the amount of computation can become unreasonable. For this reason, the Crank-Nicolson implicit finite-difference scheme is a useful alternative numerical approach, though it is somewhat more complicated than the explicit approach. In the Crank-Nicolson method $(C_i^{j+1} - C_i^j)/\Delta t$ is considered as a central-difference approximation to $\partial C/\partial t$ and it is equated to a central-difference quotient for the second derivative with distance, also corresponding to the midpoint in time, by averaging difference quotients at the beginning and end of the time step. By substituting, rearranging, and selecting Δx and Δt such that $[D_P \Delta t/\theta_v (\Delta x)^2] = 1$, Eq. [3] and [6] become Eq. [10] and [11], respectively,

$$-C_{i-1}^{j+1} + 2(R_F + 1)\,C_i^{j+1} - C_{i+1}^{j+1} = C_{i-1}^j + 2\left\{R_F - 1 - \Delta t\left[\mu_l + \frac{\mu_s}{N}(R_F - 1)\right]\right\}C_i^j + C_{i+1}^j \quad [10]$$

$$-C_{i-1}^{j+1} + 2(R_L + 1)\,C_i^{j+1} - C_{i+1}^{j+1} = C_{i-1}^j + 2\{R_L - 1 - \Delta t[\mu_l + \mu_s(1 + kC_i^j)(R_L - 1)]\}C_i^j + C_{i+1}^j \quad [11]$$

Note that the new equilibrium solution concentration, C_i^{j+1}, is not given directly in terms of known concentrations at adjacent positions. This requires a solution to a set of simultaneous equations at each time step. Fortunately, the system is tridiagonal so it is possible to use a LU method and then solve by back-substitution [17].

One advantage of the Crank-Nicolson method is that it is stable for any positive value of B and r, although small values for Δx and Δt produce more accurate results. Furthermore, the truncation error for the Crank-Nicolson method is $e = 0[(\Delta t)^2] + 0[(\Delta x)^2]$, so larger time steps can be taken since the truncation error is smaller and the method is unconditionally stable; as a result, the overall computational time can be reduced.

EXPERIMENTAL PROCEDURE

Representative inorganic and organic chemicals are used to demonstrate and compare the four models. Diquat (1,1′-ethylene-2,2′-dipyridilium dibromide) and bromacil (5-bromo-3-*sec*-butyl-6-methyluracil) are used to represent typical organic herbicides which could be found in the aquatic environment and can effect sensitive, nontarget plants and animals. (Diquat is often used as an aquatic herbicide, while bromacil is used for annual and perennial weed control in citrus groves). Boron represents an inorganic chemical of concern in the aquatic environment since it is an essential element for plants and yet it has a narrow range of tolerance by most plants.

Table 2 summarizes the chemical and physical parameters used in the four models. Representative adsorption and sediment property parameters taken from data presented by Corwin and Farmer (1984a, 1984b) for the adsorption of bromacil and diquat on freshwater sediments are shown. Degradation rates were taken from the literature.

Table 2. Representative physical, chemical, and biological parameters obtained from data presented in the cited literature.

Parameter		Cited literature
Sediment properties		
Volumetric water content (θ_v)	0.5 m^3/m^3	(Corwin and Farmer, 1984a; Corwin and Farmer, 1984b)
Bulk density of sediment (ϱ_b)	0.8 Mg/m^3	(Corwin and Farmer, 1984a; Corwin and Farmer, 1984b)
Organic chemicals–pesticides		
Initial equil. solution conc. (C_0)	0.01 g/L	
Molecular diffusion coefficient (D)	5.0×10^{-10} m^2/s	(Jury et al., 1983)
Porous diffusion coefficient (D_p)	1.9843×10^{-10} m^2/s	
α (h/D_p)	1.00	
Bromacil:		
Freundlich K (L/kg)	3.0	(Corwin and Farmer, 1984a; Corwin and Farmer, 1984b)
Freundlich N	0.9	(Corwin and Farmer, 1984a; Corwin and Farmer, 1984b)
Solution phase degradation rate (μ_l)	0.00347 d^{-1}	(Wolf and Martin, 1974)
Adsorbed phase degradation rate (μ_s)	0	NA†
Diquat:		
Langmuir k (L/kg)	0.0065	(Corwin and Farmer, 1984a; Corwin and Farmer, 1984b)
Langmuir b (mg/kg)	45 000	(Corwin and Farmer, 1984a; Corwin and Farmer, 1984b)
Solution phase degradation rate (μ_l)	0	NA
Adsorbed phase degradation rate (μ_s)	0	NA
Inorganic chemical–boron		
Initial equil. solution conc. (C_0)	0.01 g/L	
Molecular diffusion coefficient (D)	6.1484×10^{-10} m^2/s	(Sulaiman and Kay, 1972)
Porous diffusion coefficient (D_p)	2.44×10^{-10} m^2/s	
α (h/D_p)	100/m	
R-30 sand (No series name):		
Freundlich K (L/kg)	0.162	(Elrashidi and O'Connor, 1982)
Freundlich N	0.843	(Elrashidi and O'Connor, 1982)
Volumetric water content (θ_v)	0.5	(Buckman and Brady, 1969)
Bulk density (ϱ_b)	1.3 Mg/m^3	NA (value assumed)
Glendale clay (fine-silty, mixed thermic typic torrifluvent):		
Freundlich K (L/kg)	3.99	(Elrashidi and O'Connor, 1982)
Freundlich N	0.572	(Elrashidi and O'Connor, 1982)
Volumetric water content (θ_v	0.5	(Buckman and Brady, 1969)
Bulk density (ϱ_b	1.3 Mg/m^3	NA (value assumed)

† NA = Not available.

Under saturated soil conditions, bromacil has been found to have a half-life of 200 d which converts to a solution phase degradation rate of 0.00347 d^{-1} (Wolf and Martin, 1974). There appear to be no quantitative values for the half-life of diquat which is probably due to its cationic nature. As a cationic herbicide, diquat is strongly adsorbed by soils and sediments. Weber and Weed (1974) point out in unpublished work that ^{14}C-diquat adsorbed onto the internal surfaces of montmorillonite clay in aqueous soil-nutrient suspensions was not degraded by microorganisms after 1 yr. For these reasons, diquat was assumed to persist indefinitely. In addition, representative Freundlich adsorption coefficients, and a porous diffusion coefficient for B were obtained from papers by Elrashidi and O'Connor (1982) and Sulaiman and Kay (1972), respectively.

Since similar molecular weight organic chemicals (i.e., pesticides) vary only slightly in the magnitude of their molecular diffusion coefficients, a value of 5.0×10^{-10} m^2/s was selected as a representative value for bromacil and diquat. This value has been used in previous models (Jury et al., 1983). Using the Millington-Quirk relationship (Millington and Quirk, 1961) which under saturated conditions reduces to

$$D_p = \theta_v^{4/3} D, \qquad [12]$$

the porous diffusion coefficient can be determined from the molecular diffusion coefficient, D, if the volumetric water content is known. A saturated volumetric water content of 0.5 m^3/m^3 is assumed since it is a good approximation of saturated water content in most soils (Buckman and Brady, 1969). The representative porous diffusion coefficient for the organic pesticides becomes 1.984×10^{-10} m^2/s.

All simulations were performed using both the explicit and implicit solutions. A spatial mesh within both the water and the sediment of 0.5 cm and a time step of 0.1 d was used for the explicit approach, while Δx and Δt for the implicit approach were selected so that $[D_p\Delta t/\theta_v(\Delta x)^2] = 1$. Since little difference in the results existed between the explicit and implicit approaches, the use of either set of finite-difference solutions is justified although less computational time is needed for the implicit finite-difference scheme since larger time steps are possible. In all cases the results from the implicit approach were those finally used in the illustrations. Simulations involving bromacil and diquat diffusion through a representative sediment (Corwin and Farmer, 1984b), and B through R-30 sand and Glendale clay were performed for each of the four aquatic systems.

RESULTS AND DISCUSSION

The four aquatic diffusion models have been designed to simulate pristine and contaminated lakes/ponds, rivers and streams (Case I and IV), and oceans and deep lakes (Case II and III) where no convective flow is occurring through the sediment, as well as to simulate diffusion in saturated soil aggregates (Case IV).

Case I

Case I is the simplest aquatic system of the four envisioned models. It attempts to simulate an aquatic system where the concentration of the chemical diffusing from a contaminated sediment layer extending from the sediment-water interface (at $x = 0$) to an impermeable layer at some finite depth, $x = L$, is maintained at zero at the sediment-water boundary. This aquatic system would represent a well-mixed lake/pond or fast-flowing river in pristine condition where the diffusing chemical is either quickly removed or diluted to zero concentration as soon as it diffuses into the water body. This particular aquatic system has been previously modelled by Corwin and Farmer (1985) using an explicit finite-difference solution.

Figures 1a–d are the graphic results obtained from using the representative physical and chemical

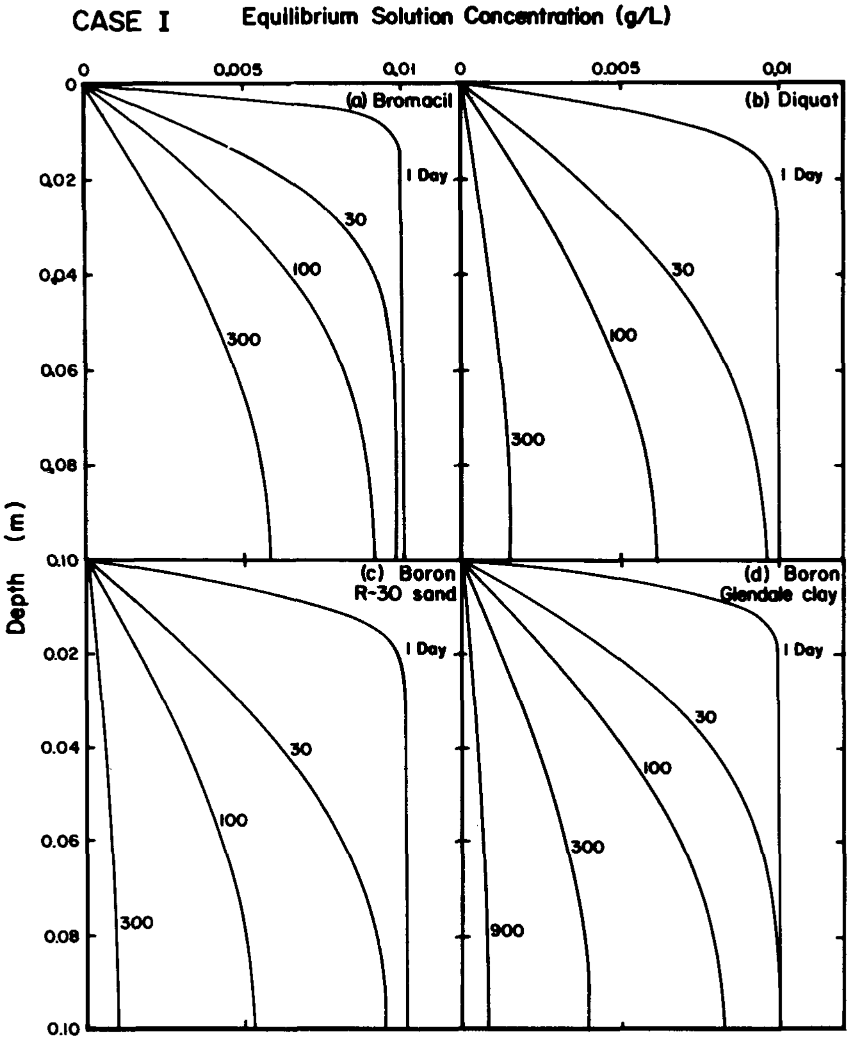

Fig. 1. Sediment equilibrium solution concentration distributions for the Case I diffusion of (a) bromacil, (b) diquat, and (c and d) B (R-30 sand and Glendale clay): C_0 = 0.01 g/L, and L_1 = 0.1 m.

parameters outlined in Table 2 and the solution for Case I. The sediment equilibrium solution concentration distributions at specified time periods are shown for bromacil, diquat and boron (R-30 sand and Glendale clay). Figures 1a and 1b provide the equilibrium distributions of the two chemically dissimilar herbicides. The drastically different physicochemical dynamics involved, due to the radically different adsorption behavior of diquat and bromacil, are apparent from the illustrations. Figures 1c and 1d illustrate the simulated diffusion of B for two dissimilar soils, R-30 and Glendale clay. Since the same physical parameters were assumed for each soil (i.e., same D_p, θ_v, and ϱ_b), the sharply different diffusion rates indicated by the equilibrium solution concentration curves are once again the result of differences in retardation effects due to adsorption capacity and binding strength differences. Since this particular aquatic system has been previously discussed at length (Corwin and Farmer, 1984b; Corwin and Farmer, 1985), there is no need for further discussion. Case I is presented primarily as a reference for comparison to the other aquatic systems and as part of a compendium of aquatic systems.

Case II

Case II is an aquatic system which is analogous to diffusion through a composite medium. In this situation a "stagnant" water body (medium 1) overlies the contaminated sediment layer (medium 2) containing the diffusing chemical. The flux is continuous across the sediment-water interface and the initial chemical concentrations in the "stagnant" water and contaminated sediment layer are 0 and C_0, respectively. If volatilization occurs, as would be expected with many organic compounds, the concentration of the diffusing chemical at the air-water interface can be assumed to be zero at all times. It should be pointed out, however, that in many cases the Henry's Law constant for pesticides is so low that the air would produce a significant boundary layer, therefore, a concentration of zero at the air-water interface due to volatilization may not be likely. More sophisticated volatility models (Jury et al., 1983; Thomas, 1982; MacKay et al., 1983), however, can be coupled to this chemical-sediment-water diffusion model. If no volatilization occurs, as in the case of B, then there would be no change in concentration at

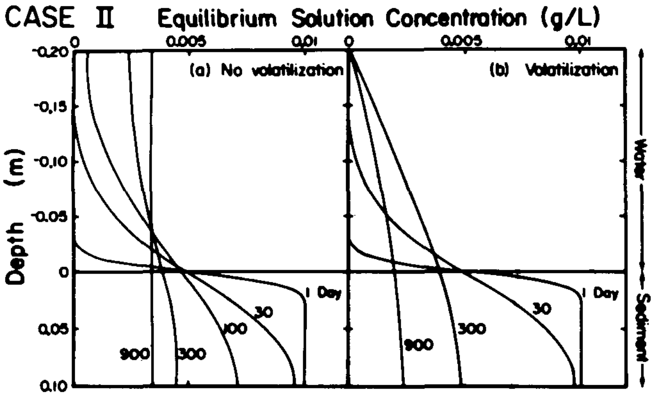

Fig. 2. Equilibrium solution concentration distributions for diffusion in a composite medium (Case II) without adsorption and without degradation/ $C_0 = 0.01$ g/L, $D = 5.0 \times 10^{-10}$ m^2/s, $L_1 = 0.2$ m, and $L_2 = 0.1$ m = equivalent depth of water in the sediment: (a) no volatilization, $(\partial/\partial x)C_1(L_1,t) = 0$. (b) volatilization, $C_1(L_1,t) = 0$.

the air-water interface [i.e., $(\partial/\partial x)C_1(L_1, t) = 0$] although physically there is a step change in concentration across the interface.

Case II would be representative of oceans and deep lakes where the water above the sediment is stagnant. The sediment would be characteristically low in organic matter so that a thin organic matter layer would not exist at the sediment-water interface.

Figures 2a and 2b reveal several interesting results about the diffusion model for Case II. Since no adsorption and no degradation are occurring in Fig. 2, the conservation of mass of material diffusing between the two media is apparent (see Fig. 2a). In other words, the depletion of diffusing chemical from the sediment equals the accumulation of chemical in the "stagnant" water where L_2 in the sediment refers to the equivalent depth of water and not the actual sediment depth. The model accounts for approximately 99.2% of the initial mass of material after 1500 d into the diffusion process. Figure 2 also shows the effect of volatilization on the diffusion process. The complete removal of the chemical at the air-water interface acts as a driving force to remove the chemical from the sediment due to the larger concentration gradient which is maintained within the system. Figure 2 also shows that the diffusion through the "stagnant" water is rapid compared to the sediment. This, of course, is due to the tortuous diffusion path which exists within the sediment.

When adsorption processes do occur the results are more complicated. Due to the retardation effect upon diffusion by the adsorption process and due to the more tortuous pathway followed by diffusing molecules in the sediment, the migration of chemical from the sediment into the "stagnant" water layer is strongly influenced by the sediment. The more adsorptive and tortuous that a sediment is, then the more slowly the chemical moves out into the overlying water body. Furthermore, if the degradation rate is significantly less for the adsorbed phase than the liquid phase, then the adsorptive ability of a sediment not only retains the chemical, but it provides a means by which a chemical may persist for a longer period of time. The persistence may be in a biologically inactive state such as when diquat is adsorbed onto clay surfaces. Nevertheless, this retention and increased persistence may potentially effect organisms which feed upon organic matter that has adsorbed a toxic chemical (e.g., filter-feeding organisms). On the other hand, if the chemical is released quickly into the overlying water then a potential threat exists to organisms residing and feeding immediately above the sediment-water interface.

Figures 3a-d illustrate diffusion into a "stagnant" water layer as simulated for bromacil, diquat, and B. Unlike the results depicted in Fig. 2a where no adsorption occurred, these figures show that as the chemical diffuses into the overlying "stagnant" water the adsorbed phase serves as an additional source of chemical. This is especially apparent in Fig. 3b since the adsorptive capacity for diquat is so high. More specifically, as the chemical diffuses into the "stagnant" water layer and it is depleted from the equilibrium solution of the sediment, adsorption equilibrium adjustments occur so that additional chemical is desorbed from the sediment. The desorption process continues to serve as a source of chemical until depletion or until a system equilibrium is reached, approximately 900 d for the cases simulated in Fig. 3c and 3d. Once a system equilibrium has been reached in Fig. 3c and 3d, approximately 8.7% and 40%, respectively, of the equilibrium solution concentration of B is attributable to desorption from the adsorbed phase.

The same solutions for Case II diffusion can be applied to other situations with adjustments made for different initial conditions. The initial conditions can be varied to describe situations where, (i) a contaminated layer of sediment is buried beneath a thin layer of "clean" sediment, (ii) a thin contaminated layer exists at the sediment-water interface, or (iii) a contaminated sediment layer is sandwiched between two "clean" sediment layers. Figures 4a–c illustrate the equilibrium solution concentration distributions for the three respective variations as simulated for bromacil. A comparison of Fig. 4b and 4c shows that a "clean" layer of sediment overburden can act as a quasi-barrier to the migration of a chemical into the water body. The "clean" layer acts as a quasi-barrier since it retards but does not completely stop the migration of the chemical into the overlying water. The retarded movement of the chemical is due to adsorption and to on-going solid and liquid phase degradation processes. The net effect is that less chemical passes into the overlying water from the sediment. This is the result of the lower rate of migration into the overlying water which increases the residence time within the sediment and permits continued degradation before entering the overlying water.

In comparison to diffusion from a sediment into a fast-flowing water body maintained at zero concentration (Case I), diffusion into a "stagnant" water body (Case II) is significantly slower due to the fact that the concentration gradient through the sediment is less. The concentration gradient for Case II is lower because the chemical is not completely removed at the sediment-water interface as it is for Case I. Rather, the chemical concentration slowly decreases as it diffuses through the "stagnant" water body.

Case III

Case III is actually a specialized form of Case II where there is an interface resistance between the two

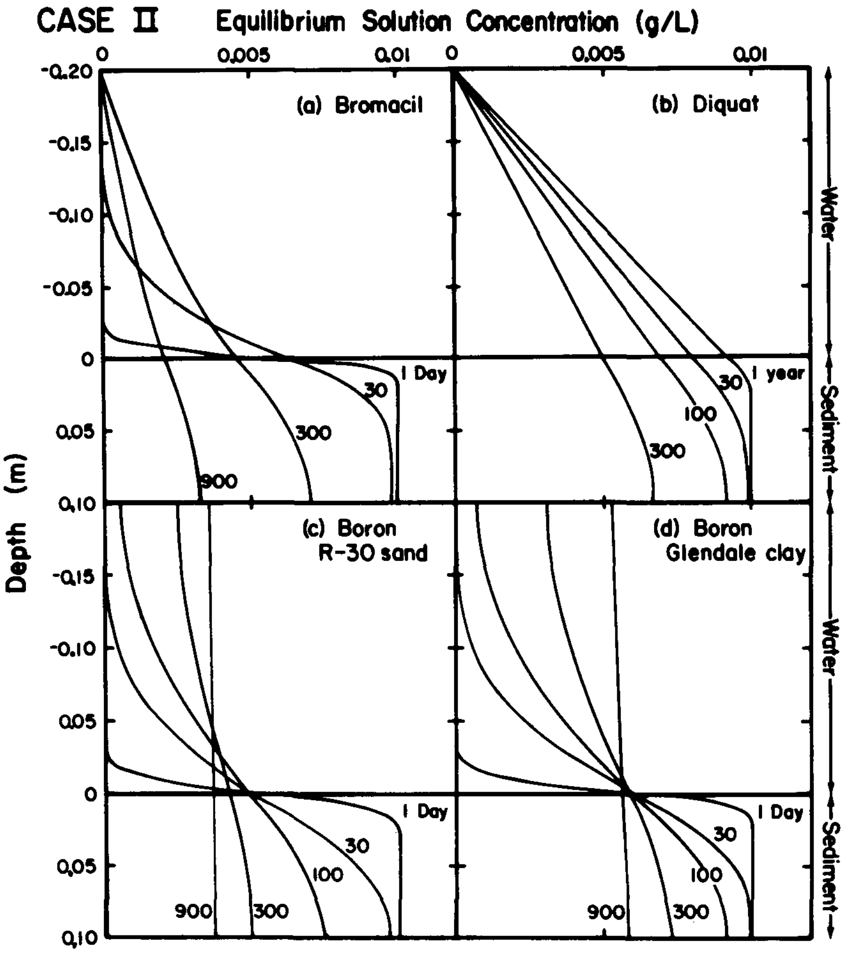

Fig. 3. Equilibrium solution concentration distributions for the Case II diffusion of (a) bromacil, (b) diquat, and (c and d) B (R-30 sand and Glendale clay): $C_0 = 0.01$ g/L, $L_1 = -0.2$ m, and $L_2 = 0.1$ m = equivalent depth of water in the sediment.

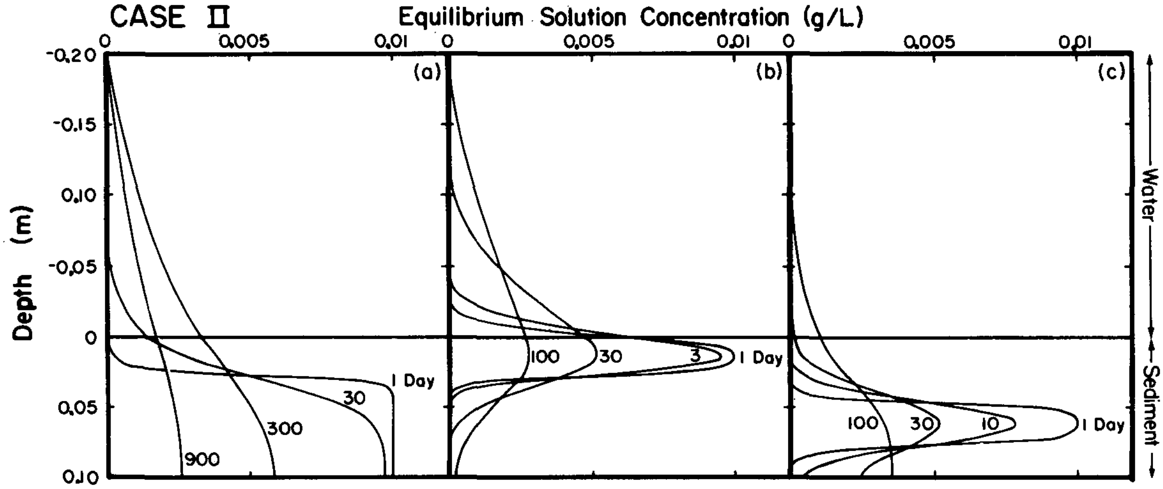

Fig. 4. Equilibrium solution concentration distributions for the Case II diffusion of bromacil using the respective initial conditions outlined in Table 5: $C_0 = 0.01$ g/L. (a) "Clean" sediment overlying contaminated sediment: $L_1 = -0.2$ m, $L_2 = 0.025$ m, and $L_3 = 0.1$ m. (b) Contaminated sediment overlying "clean" sediment: $L_1 = -0.2$ m, $L_2 = 0.025$ m, and $L_3 = 0.1$ m. (c) Contaminated sediment sandwiched between "clean" sediment: $L_1 = -0.2$ m, $L_2 = 0.05$ m, $L_3 = 0.075$ m, and $L_4 = 0.1$ m.

composite media. In high organic matter sediments a thin film of organic matter suspension often exists at the sediment-water interface (Gschwend and Wu, 1985). This film would not have an effective diffusion coefficient similar to either the water or the sediment since as a suspension the pathway through the film is not as tortuous as through the sediment, yet there are still numerous sites for adsorption by the organic material. A means of modeling this essentially dimensionless film is to treat it as an interface resistance between the water

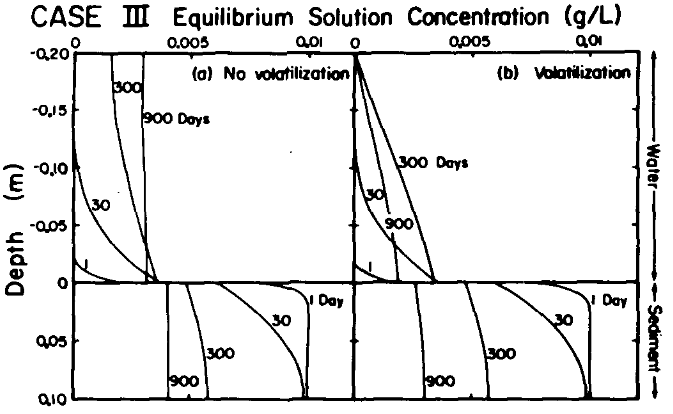

Fig. 5. Equilibrium solution concentration distributions for Case III diffusion without adsorption and without degradation: C_o = 0.01 g/L, $\alpha = 1.0$, $D = 5.0 \times 10^{-10}$ m²/s, $L_1 = -0.2$ m, and $L_2 = 0.1$ m: (a) No volatilization, $(\partial/\partial x)C_1(L_1, t) = 0$, (b) Volatilization, $C_1(L_1, t) = 0$.

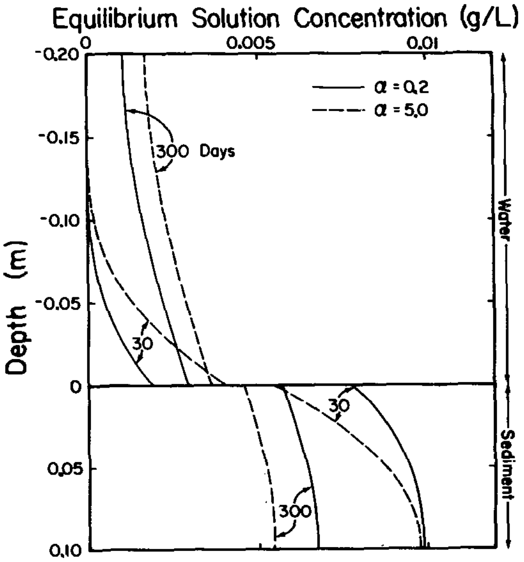

Fig. 6. The effect of α upon Case III diffusion assuming no adsorption by the sediment, no volatilization, and no degradation. C_o = 0.01 g/L, $D = 5.0 \times 10^{-10}$ m²/s, $\alpha = 0.2$ (solid line), and $\alpha = 5.0$ (dashed line).

and sediment. By doing so, the flux of material across a unit area of the interface is proportional to the difference between the surface concentration of the sediment and the concentration in the "stagnant" water immediately across the film,

$$(\partial/\partial x)C_2(0, t) = \alpha(C_2 - C_1) \qquad [13]$$

where $\alpha = h/D_p$, h (in meters per second) is some empirically determined proportionality factor analogous to the coefficient of heat transfer in heat conduction problems having a radiation boundary condition, and C_1 and C_2 are the equilibrium solution concentrations in the "stagnant" water and the sediment, respectively.

The presence of the thin organic matter film creates a discontinuous concentration at the sediment-water interface so that concentrations on either side of the interface are no longer the same (see Fig. 5a and 5b). The net effect of the interface resistance imposed by the organic matter film upon the diffusion process is to further retard the diffusion of the chemical into the water body (compare Fig. 2 and 5). As α decreases the discontinuity of concentration at the sediment-water interface increases which is expected since the resistance across the film has increased (i.e., h is lower) due primarily to greater adsorption, thereby reducing the rate at which the chemical diffuses across the interface into the "stagnant" water (Fig. 6).

Case IV

Case I described the diffusion of a solute from a sediment into a "well-stirred" solution which is analogous to a perfect conductor of heat in heat conduction problems. In heat conduction problems, however, the most usual situation is not that the two media at the interface are held at the same temperature, but that heat is lost by

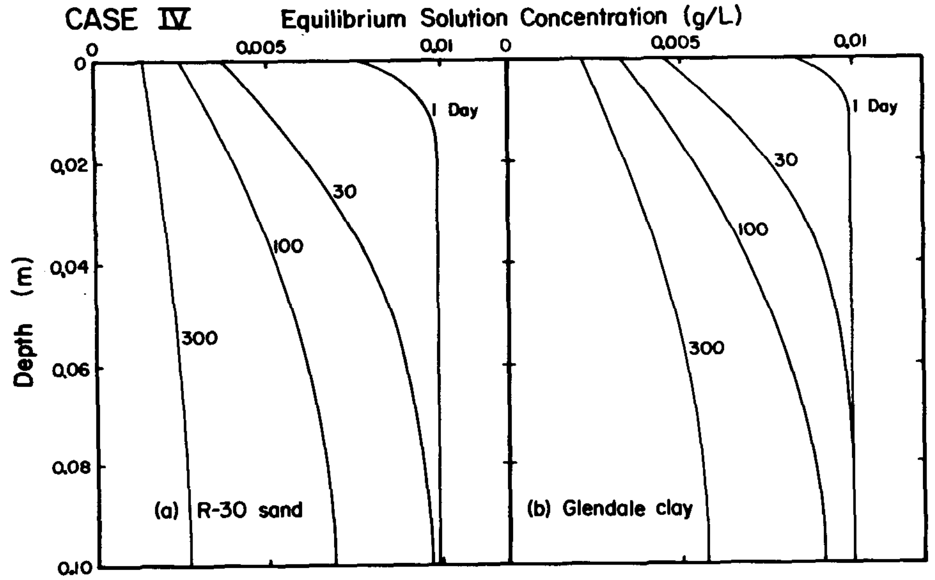

Fig. 7. Sediment equilibrium solution concentration distributions for Case IV diffusion of B from (a) R-30 sand, and (b) Glendale clay. C_o = 0.01 g/L, and C_s = 0.001 g/L.

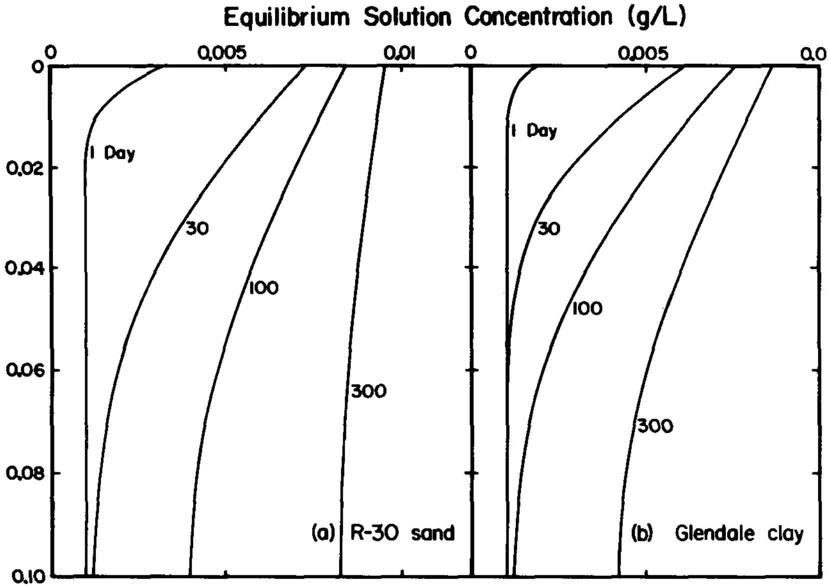

Fig. 8. Sediment equilibrium solution concentration distributions for Case IV diffusion of B into (a) R-30 sand, and (b) Glendale clay. $C_0 = 0.001$ g/L, and $C_S = 0.01$ g/L.

conduction or radiation at a rate proportional to some power of the temperature difference between the surface of the body and its surroundings. An analogous situation would exist for diffusion in an aquatic system where flow is not rapid enough or mixing is not complete enough to create a perfect conductor type of contact. This type of aquatic system, designated Case IV diffusion, would be represented by slow-moving rivers and streams, as well as by irrigation and drainage canals. It is likely that Case IV diffusion would also simulate diffusion in soil aggregates as influenced by a fluid flowing through an aggregated porous medium where the aggregates are thought of as thin sheets of thickness $2L$ and the surrounding fluid solute concentration, C_S, would fluctuate according to convective-dispersive processes.

Since B is often found in the drainage water and sometimes in the soils of the arid southwest, it is likely to exhibit Case IV type of diffusion in irrigation and drainage canals. Figures 7a and 7b illustrate the simulated results of a situation where B is diffusing from the irrigation canal sediment into irrigation water which is at a lower B concentration than that of the sediment equilibrium solution. Diffusion curves for both low (R-30) and high (Glendale clay) adsorptive capacity media with assumed equivalent porous diffusion coefficients are shown in Fig. 7. As expected, B diffuses from the high adsorptive capacity soil more slowly. Agricultural drainage waters are often very high in B; as a result, they produce an opposite situation where boron gradually diffuses into the sediment equilibrium solution which is at a lower B concentration (see Fig. 8a and 8b).

The cycling of high and low B concentration irrigation waters yields interesting equilibrium solution concentration distribution curves for diffusion in sediments of irrigation canals. Figure 9 shows a set of curves for Glendale clay. For the first 200 d the B concentration of the surrounding fluid is maintained at 0.01 g/L after which it is decreased to 0.001 g/L. Since the initial B concentration in the sediment equilibrium solution is 0.001 g/L, B gradually diffuses into the sediment. As soon as the B concentration of the surrounding fluid (C_S) is decreased to 0.001 g/L there is a quick decrease in B within the sediment solution nearest to the sediment-water interface. The B concentration of the sediment near the sediment-water interface continues to decrease and to approach C_S, while at the impermeable layer interface there is initially an increase in concentration due to the redistribution of B from the upper sedi-

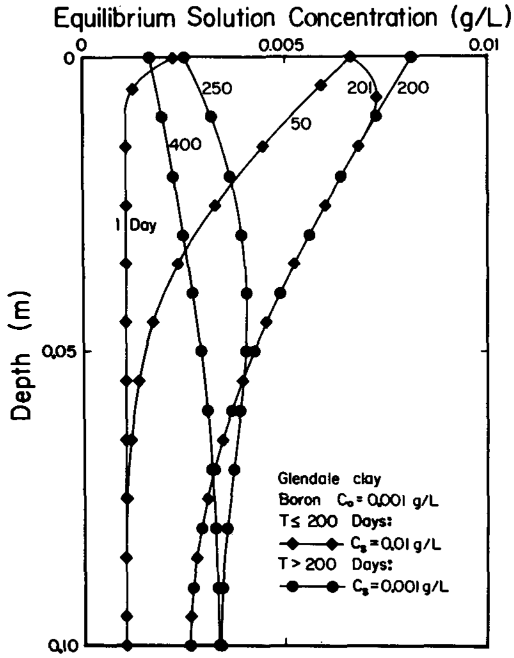

Fig. 9. Sediment equilibrium solution concentration distribution curves for the Case IV diffusion of boron showing the effect of cycling high ($C_s = 0.01$ g/L) and low ($C_s = 0.001$ g/L) B concentration waters.

ment region (0.015-0.04 m). Gradually a uniform sediment solution B concentration of C_s is approached.

As mentioned, this particular model has application to diffusion in soil aggregates. A simulation of diffusion of B through a planar soil aggregate sheet of thickness $2L$ where $L = 0.001$ m shows that as different quality irrigation waters are applied to soils the aggregates can act as reservoirs or sources of B to the soil solution of the large pores and cracks surrounding the aggregates. So, even though a system may appear to be at steady state the diffusion of B into or out of soil aggregates of a structured soil could result in continuing fluctuations in B concentration over extended time periods. This effect has definite ramifications for the agricultural reclamation of high B soils.

SUMMARY

Since organisms within the aquatic environment are often very sensitive to certain organic pesticides and since surface waters serve as irrigation water for crops, it is important to have an understanding of the physicochemical dynamics of chemical-sediment-water systems and of aggregated soil systems. The four models presented provide a means of assessing the various interactions involved in diffusion in simplified aquatic and structured soil systems, as well as a means of assessing the potential threat that a chemical will pose to different compartments of the aquatic and soil environments by providing information concerning their migratory propensity.

As the future demand for water increases, the increased potential for the reuse of high B drainage water as a source of agricultural irrigation water becomes more likely. In order to manage these drainage waters in a way that maximizes their use yet minimizes their deleterious effects to plants, an understanding of the distribution and movement of boron in soils is essential. The modeling of the physical process of solute flow in one-dimension for homogeneous, unstructured porous media is well understood, but aggregated soils present additional complexities as revealed by the asymmetric displacement patterns which are often found in structured soils. In structured soils the bulk of the flow of water and transport of chemicals generally occurs through the cracks between the soil aggregates. The exchange of solutes between the aggregates and these cracks is controlled by diffusion processes. These models, particularly the Case IV model, can assist in determining the contribution which diffusion makes to solute flow in structured soils.

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