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AN ASSESSMENT OF THE SIGNIFICANT PHYSICOCHEMICAL INTERACTIONS INVOLVED IN PESTICIDE DIFFUSION WITHIN A PESTICIDE-SEDIMENT-WATER SYSTEM

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ABSTRACT

Using the explicit method of finite differences, a one-dimensional numerical model for the diffusion of pesticides through a sorbing porous medium under saturated conditions has been developed to assess the significant physical and chemical properties which influence the diffusion process in an aquatic system. The model quantitatively demonstrates in which area of the aquatic environment a given pesticide will principally reside, as well as providing a means of indicating to what degree various sediment and pesticide chemical and physical properties will influence the migration of the pesticide.

INTRODUCTION

Because of the ability of soil to adsorb a variety of organic and inorganic chemicals (e.g., pesticides, fertilizers, etc.) and their subsequent "piggyback" transport via erosion processes into aquatic systems, sediments of various water bodies have become unintentional repositories for many chemicals that are harmful to both plants and animals. Since the aquatic environment constitutes a potential sink for many pesticides, a growing interest has developed by environmentalists in the area of pesticide-sediment-water interactions (Lotse et al., 1968; Nicolson and Hill, 1970; Veith and Lee, 1971; Weber, 1972; Pionke and Chesters, 1973; Karickhoff, Brown and Scott, 1979; Peck et al., 1980; Karickhoff, 1981; Goldberg, 1982; Corwin and Farmer, 1983).

Once pesticides enter the aquatic compartment of the environment by way of adsorption onto eroded particles, they eventually settle to the bottom with the sediment. Desorption of these chemicals from sediments and subsequent diffusion into overlying surface waters may lead to a significant decrease in the quality of lakes, streams and ponds. Though at first thought insignificant in scale as far as solute transport is concerned, the diffusion from contaminated sediments is potentially a primary source of aquatic pollution particularly in situations where surface waters have received effluent containing pesticides for relatively long periods of time. This can become especially apparent when the water itself has returned to nearly pristine conditions.

Because very low concentrations of certain chemicals are known to be toxic to fish and other forms of aquatic life, and because polluted irrigation waters may produce lower crop yield, it is important to have an understanding of the basic physicochemical processes that affect chemical-sediment-water interactions. This study formulates various numerical models describing one-dimensional diffusion under saturated conditions of a pesticide undergoing linear, Freundlich or Langmuir-type adsorption-desorption. It will be the object of this paper to utilize these numerical models to assess the significance of the various physicochemical interactions to the diffusion of pesticides from sediments into overlying water bodies. The models are specifically designed, therefore, to highlight the influence of adsorption-desorption reactions upon the diffusion process in order to provide insight into the significant physicochemical properties and their interrelationship to better assess pollution potential rather than to provide an accurate quantitative projection of pollutant movement. Future work is anticipated in the development of refined models to reflect more complicated situations.

PROCEDURE AND THEORY

Four models have been formulated to describe the diffusion under saturated conditions of a herbicide through sediment into an overlying water body. Each model differs in the type of adsorption-desorption process which could occur depending on the chemical involved: single-valued linear adsorption-desorption, single-valued Freundlich adsorption-desorption, single-valued Langmuir adsorption-desorption, and nonsingle-valued linear/Freundlich or Langmuir adsorption-desorption.

Isothermal conditions, a constant molecular diffusion coefficient, no degradation and instantaneous adsorption-desorption reactions were assumed in all cases. The assumption that isothermal conditions exist seems valid since the high heat capacity of water tends to moderate temperature changes at the sediment-water interface in all but shallow water bodies. In situations where the pesticide concentration is low (as in most natural systems), the molecular diffusion coefficient in aqueous solution is in many cases independent of concentration and can be assumed constant (Scott and Phillips, 1972; Graham-Bryce, 1969). The reason for assuming no degradation or other sink terms was to highlight the significance of the adsorption-desorption reactions in the diffusion process to better understand the physicochemical dynamics of pesticide-sediment-water interactions. From rate of reaction studies performed on pesticide adsorption onto a variety of porous media, it appears that an instantaneous adsorption-desorption reaction rate is in most cases a reasonable assumption especially for sediments with low organic matter fractions (Hamaker and Thompson, 1972).

Several relationships between the molecular diffusion coefficient in porous media and the molecular diffusion coefficient in aqueous solution have been developed (Buckingham, 1904; Call, 1957; Marshall, 1959; Millington and Quirk, 1961; and Shearer et al., 1973). The Millington-Quirk model was used since under saturated conditions only values of the volumetric water content and the molecular diffusion coefficient in aqueous solution are required. The Millington-Quirk model is written,

$$D_P = \left(\frac{\Theta_v}{P_T} \right)^2 \Theta_v^{4/3} D \tag{1}$$

where Θ_v is the volumetric water content (cm^3/cm^3), P_T is the total porosity (cm^3/cm^3), D is the molecular diffusion coefficient in aqueous solution and D_P is the porous molecular diffusion coefficient. Under saturated conditions $\Theta_v = P_T$ and Equation 1 reduces to,

$$D_P = \Theta_v^{4/3} D \tag{2}$$

Since similar molecular weight organic compounds seem to vary little in the magnitude of their molecular diffusion coefficients, the value of $D = 2.5 \times 10^{-6}$ cm^2/sec = 0.2160 cm^2/day has been selected as a representative value and is a slightly conservative estimate of values used in previous models (Jury et al, 1983). For ease of comparison, Θ_v was assumed to be 0.5 in all modeling situations which is a representative approximation of the saturated volumetric water content in most soils (Buckman and Brady, 1969); therefore, the "representative" porous molecular diffusion coefficient became 0.0857 cm^2/day.

The general mathematical equation describing one-dimensional diffusion through a sorbing porous media disregarding sink terms (e.g., degradation) is

$$\Theta_v \frac{\partial C}{\partial t} = D_P \frac{\partial^2 C}{\partial x^2} - \rho_b \frac{\partial S}{\partial t} \tag{3}$$

where C is the equilibrium solution concentration (μg/ml), S is the amount of herbicide adsorbed per unit weight of sediment (μg/g), Θ_v is the volumetric water content (cm^3/cm3), ρ_b is the bulk density (g/cm^3), t is the time (days), x is the depth (cm) and D_P is the porous molecular diffusion coefficient (cm^2/day). Figure 1 provides a schematic representation of the proposed problem with the appropriate initial and boundary conditions:

Initial conditions: $C(x,0) = C_o$ [4a]

Boundary conditions: $C(0,t) = 0$ [4b]

$$\frac{\partial}{\partial x} C(L,t) = 0 \qquad [4c]$$

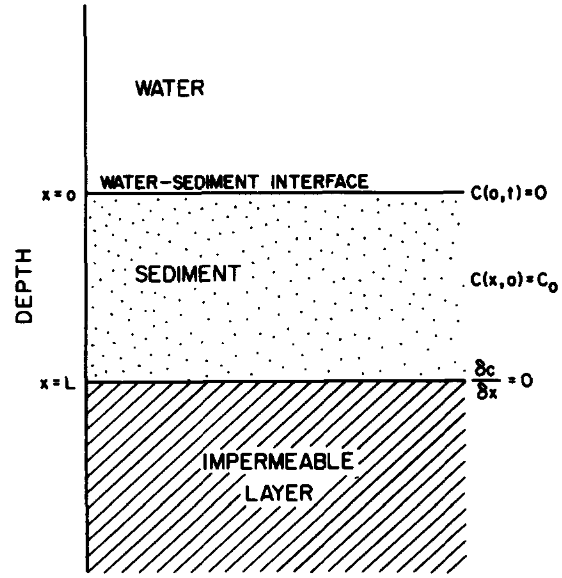

Figure 1: A schematic illustrating the initial and boundary conditions envisioned for the diffusion of a pesticide through sediment with an impermeable layer into an overlying water body.

It is assumed that the sediment is a homogeneous medium with an initial pesticide equilibrium solution concentration of C_o uniformily distributed throughout the sediment. At a finite depth x=L, which for all modeling situations was arbitrarily set to 10 cm, there exists an impermeable layer (e.g., bedrock) while at the sediment-water interface (i.e., x=0) the concentration of pesticide is at all times maintained at zero. These conditions would be most representative of a flowing stream.

In the case of linear adsorption-desorption, an analytical solution to Equation [3] was obtained for the initial and boundary conditions outlined in Equations [4a-c]. For nonlinear Freundlich and Langmuir adsorption-desorption, however, the explicit method of finite differences was utilized. Though the explicit method is simple, it suffers from inherent instability problems; consequently, the time, Δt, and depth increments, Δx, were selected to be sufficiently small to maintain stability and acceptable accuracy, but not too small to be impractical in regard to computation time on a computer. The accuracy of the explicit finite difference scheme which depends upon the truncation error, $O(\Delta t) + O[(\Delta x)^2]$, was checked by comparing the numerical and analytical solutions for similar conditions (i.e., zero and linear adsorption).

DIFFUSION MODELS

Model 1: Diffusion with Linear Single-valued Adsorption-desorption

The simplest diffusion model is envisioned to be that of the instantaneous linear single-valued adsorption-desorption of a diffusing herbicide from sediment into an overlying water body. The general equation for linear adsorption is,

$$S = KC \qquad [5]$$

where S is the amount adsorbed per unit mass of sediment (μg/g) and K is the adsorption or partition coefficient. By taking the partial derivative of Equation [5] with respect to time and substituting into Equation [3], the diffusion equation for Model 1 becomes,

$$\frac{\partial C}{\partial t} = \frac{D_p}{\theta_v}\frac{\partial^2 C}{\partial x^2} - \frac{\rho_b K}{\theta_v}\frac{\partial C}{\partial t} \qquad [6]$$

or rearranging,

$$\frac{\partial C}{\partial t} = \frac{D_p}{\theta_v(1+R)}\frac{\partial^2 C}{\partial x^2} \qquad [7]$$

where $R = \frac{\rho_b K}{\theta_v}$, and 1 + R is known as the retardation factor (Hashimoto et al., 1964).

The analytical solution to Equation [7] can be found in Carslaw and Jaeger (1959) for an analogous problem of heat conduction. The solution is in the form of an infinite series:

$$\frac{C}{C_o} = \frac{4}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{(2n+1)}\{\exp[-\frac{D_p}{\theta_v(1+R)}(2n+1)^2\pi^2 t/4L^2]\}\cos\frac{(2n+1)\pi(L-x)}{2L} \qquad [8]$$

where C_o represents the initial pesticide equilibrium solution concentration.

For comparison purposes the analytical solution to Equation [7] for the case of an infinite layer of "contaminated" sediment (i.e., boundary condition [4c] becomes $\frac{\partial}{\partial x}C(\infty,t)=0$) was found by separation of variables,

$$\frac{C}{C_o} = \text{erf}\left\{ \frac{x}{2 \frac{D_P}{\theta_v(1+R)} t} \right\} \quad . \qquad [9]$$

Model 2: Diffusion with Nonlinear Single-valued Freundlich Adsorption-desorption

Freundlich adsorption is characterized by the equation,

$$S = KC^N \qquad [10]$$

where K is the Freundlich adsorption partition coefficient and N is the coefficient of adsorption (N<1) which indicates the degree of nonlinearity. Once again the partial derivative of the adsorption model is taken and then substituted into Equation [3] resulting in the following model,

$$\frac{\partial C}{\partial t} = \frac{D_P}{\theta_v(1 + RNC^{N-1})} \frac{\partial^2 C}{\partial x^2} \qquad [11]$$

where $R = \frac{\rho_b K}{\theta_v}$, and $1 + RNC^{N-1}$ is often referred to as the retardation factor.

In cases where N=1, Equation [11] reduces to that of diffusion with linear adsorption.

By utilizing the explicit method of finite differences Equation [11] becomes,

$$\frac{C_i^{j+1} - C_i^j}{\Delta t} = \frac{D_P}{\theta_v[1+RN(C_i^j)^{N-1}]} \left[\frac{C_{i+1}^j - 2C_i^j + C_{i-1}^j}{(\Delta x)^2} \right] \qquad [12]$$

where Δt is the time increment (days), Δx is the depth increment (cm), i refers to position and j refers to time. Solving for C_i^{j+1}, Equation [12] becomes,

$$C_i^{j+1} = \frac{D_P \Delta t}{\theta_v[(\Delta x)^2 + RN(C_i^j)^{N-1}(\Delta x)^2]} [C_{i+1}^j + C_{i-1}^j] + [1 - \frac{2D_P\ t}{\theta_v[(\Delta x)^2 + RN(C_i^j)^{N-1}(\Delta x)^2]}] C_i^j \qquad [13]$$

for all x < L, and satisfying the boundary condition of $\frac{\partial C}{\partial t} = 0$ at x=L we get,

$$C_i^{j+1} = C_i^j + \frac{2D_P \Delta t}{\theta_v[(\Delta x)^2 + RN(C_i^j)^{N-1}(\Delta x)^2]} [\ C_{i-1}^j - C_i^j\ ] \qquad [14]$$

for x = L. In order for Equations [13] and [14] to be stable it is necessary to select Δt and Δx such that for all C_i^j,

$$\frac{D_p \Delta t}{\theta_v[(\Delta x)^2 + RN(C_i^j)^{N-1}(\Delta x)^2]} < \frac{1}{2} \quad . \qquad [15]$$

Consequently, for all cases involving Model 2, Δt was taken to be 0.1 days and Δx was 0.5 cm.

The accuracy of the explicit finite scheme was determined by comparing the finite difference solution of diffusion for zero and linear adsorption with the analytical solutions of the same problem. Good agreement was obtained between the finite difference and analytical solutions. An overall error of less than 2% was found for all calculations beyond the first 10 time steps (i.e., after 1 day).

Model 3: Diffusion with Single-valued Langmuir Adsorption-desorption

Langmuir adsorption is represented by the general equation,

$$S = \frac{kbC}{1+kC} \qquad [16]$$

where k is the affinity constant and b is the adsorption maximum. Using the quotient rule of differentiation to take the partial derivative of Equation [16] with respect to time and substituting into Equation [3], the following diffusion equation is obtained,

$$\frac{\partial C}{\partial t} = \frac{D_p(1+kC)^2}{\theta_v(1+kC)^2 + \rho_b kb} \; \frac{\partial^2 C}{\partial x^2} \qquad [17]$$

where $1 + \dfrac{\rho_b kb}{\theta_v(1+kC)^2}$ is the retardation factor.

The explicit method of finite differences transforms the partial differential equation, Equation [17], into the difference equation, Equation [18],

$$\begin{aligned} C_i^{j+1} = {} & \frac{D_p \Delta t(1+kC_i^j)^2}{\theta_v(1+kC_i^j)^2(\Delta x)^2 + \rho_b kb(\Delta x)^2} [\, C_{i+1}^j + C_{i-1}^j \,] \\ & + [\, 1 - \frac{2D_p \Delta t(1+kC_i^j)^2}{\theta_v(1+kC_i^j)^2(\Delta x)^2 + \rho_b kb(\Delta x)^2}]\, C_i^j \end{aligned} \qquad [18]$$

for all x < L and

$$C_i^{j+1} = C_i^j + \frac{2D_p \Delta t(1+kC_i^j)^2}{\theta_v(1+kC_i^j)^2(\Delta x)^2 + \rho_b kb(\Delta x)^2} [\, C_{i-1}^j - C_i^j \,] \qquad [19]$$

for x = L. In this model, stability is ensured if for all C_i^j,

$$\frac{D_p \Delta t(1+kC_i^j)^2}{\theta_v(1+kC_i^j)^2(\Delta x)^2 + \rho_b kb(\Delta x)^2} < \frac{1}{2} \quad . \qquad [20]$$

To meet this requirement Δt and Δx were selected to be 0.25 days and 0.5 cm, respectively.

Model 4: Diffusion with Nonsingle-valued Linear, Freundlich or Langmuir Adsorption-desorption

This particular model attempts to account for the hysteresis commonly observed in the desorption of organic chemicals from soils and sediments when using the batch technique to measure desorption. If hysteresis is in fact an occurrence in nature and not an artifact of the batch desorption experimental method, then it is likely that the desorption of a herbicide from a sediment as it diffuses into an overlying waterbody would closely resemble that of batch technique desorption. The reason for this is the fact that in both cases there is no net increase in concentration within the equilibrium solution at any given time which would result in readsorption. Rather, there is a continuous decrease in the herbicide both from the adsorbed and solution phases which is analogous to batch desorption experiments. As a result, the desorption partition coefficients determined in batch desorption experiments for bromacil and diquat should be applicable to the previous three models without any modification to these models. At the very least, the substitution of the desorption partition coefficients for adsorption partition coefficients should provide the other extreme of a range of predictive concentration distributions for the proposed diffusion problem.

The following analytical and numerical solutions are the consequences of the previously mentioned assumptions,

1) Diffusion with nonsingular linear adsorption-desorption

$$\frac{C}{C_o} = \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)} \{\exp[-\frac{D_p}{\theta_v(1+R)}(2n+1)^2\pi^2 t/4L^2]\} \cos \frac{(2n+1)\pi(L-x)}{2L} \qquad [21]$$

where, $R = \frac{\rho_b K_{des}}{\theta_v}$ (i.e., K_{des} is the desorption partition coefficient)

2) Diffusion with nonsingular Freundlich adsorption-desorption

$$C_i^{j+1} = \frac{D_p \Delta t}{\theta_v[(\Delta x)^2 + RN(C_i^j)^{N-1}(\Delta x)^2]}[C_{i+1}^j + C_{i-1}^j] + [1 - \frac{2D_p \Delta t}{\theta_v[(\Delta x)^2 + RN(C_i^j)^{N-1}(\Delta x)^2]}]C_i^j \qquad [22]$$

for $x < L$.

$$C_i^{j+1} = C_i^j + \frac{2D_p \Delta t}{\theta_v[(\Delta x)^2 + RN(C_i^j)^{N-1}(\Delta x)^2]}[C_{i-1}^j - C_i^j] \qquad [23]$$

for x = L, and where for Equation [22] and [23] $R = \frac{\rho_b K_{des}}{\theta_v}$ (i.e., K_{des} is the Freundlich desorption coefficient).

3) Diffusion with nonsingular Langmuir adsorption-desorption

$$C_i^{j+1} = \frac{D_p \Delta t (1+k_{des} C_i^j)^2}{\theta_v (1+k_{des} C_i^j)^2 (\Delta x)^2 + \rho_b k_{des} b_{des} (\Delta x)^2} [C_{i+1}^j + C_{i-1}^j] + \left[1 - \frac{2D_p \Delta t (1+k_{des} C_i^j)^2}{\theta_v (1+k_{des} C_i^j)^2 (\Delta x)^2 + \rho_b k_{des} b_{des} (\Delta x)^2}\right] C_i^j \qquad [24]$$

for x < L.

$$C_i^{j+1} = C_i^j + \frac{2D_p \Delta t (1+k_{des} C_i^j)^2}{\theta_v (1+k_{des} C_i^j)^2 (\Delta x)^2 + \rho_b k_{des} b_{des} (\Delta x)^2} [C_{i-1}^j + C_i^j] \qquad [25]$$

for x = L and where for Equations [24] and [25] k_{des} and b_{des} are the Langmuir desorption affinity constant and desorption maximum, respectively.

In order to obtain the desorption Freundlich coefficients, K_{des} and N, or desorption Langmuir coefficients, k_{des} and b_{des}, for an arbitrarily selected initial equilibrium solution concentration, C_o, the following procedure was used. In the case of Freundlich desorption,

$$\log(K_{des}) = \log(S_o) - N \log(C_o) \qquad [26]$$

where S_o is the initial absorbate concentration (µg/g) from which desorption begins. Corwin and Farmer (1984) found a linear relationship between the S_o of their sediments and N. The relationship for the specific case of bromacil desorption from Clear Lake sediment was

$$N = 0.8158 - (0.0005)\ S_o \qquad [27]$$

and substituting Equation [27] into Equation [26] resulted in,

$$\log(K_{des}) = \log(S_o) - (0.8158 - 0.0005\ S_o) \times \log(C_o) \qquad [28]$$

If we arbitrarily select C_o then we must know the point at which desorption begins (i.e., S_o in relation to C_o) which can be obtained from the Freundlich adsorption isotherm. For the case of Clear Lake, Corwin and Farmer (1984) found the adsorption isotherm to be,

$$\log(S) = 0.92 \log(C) + \log(5.26) \qquad [29]$$

where $S = S_o$ and $C = C_o$ represent the arbitrarily selected point from which desorption begins. Substituting Equation [29] into Equation [28] gives,

$$\log(K_{des}) = 0.92 \log(C_o) + \log(5.26) - [0.8158 - 0.005 \times 10^{0.92\log(C_o)+\log(5.26)}] \times \log(C_o) \qquad [30]$$

Equation [27] can be used to determine N and Equation [30] will determine K_{des}. If it is assumed that C_o = 5 μg/ml then K_{des} and N are 6.338 and 0.8042, respectively. Similarly for C_o = 50 μg/ml, K_{des} = 11.520 and N = 0.7196.

A similar rational can be followed for the case of Langmuir desorption. Using the data represented for the desorption of diquat from Clear Lake sediment presented by Corwin and Farmer (1983), Langmuir desorption coefficients of k_{des} = 0.00417 and b_{des} = 30741 for C_o = 500 μg/ml, and k_{des} = 0.0324 and b_{des} = 42922 for C_o = 5000 μg/ml were obtained.

DISCUSSION OF RESULTS

Representative physical and chemical parameters for what might be considered a typical sediment and adsorbed pesticide, either slightly basic or cationic in nature, were substituted into the appropriate analytical and numerical solutions of Models 1-4. The representative values were from data presented by Corwin and Farmer (1984) for the adsorption of bromacil (Freundlich-type adsorption) and of diquat (Langmuir-type adsorption) upon eight freshwater sediments (see Table 1). In certain cases, specific physical and chemical parameters which were presented by Corwin and Farmer (1984) were also used.

Table 1 - Representative physical and chemical parameters obtained by averaging data presented by Corwin and Farmer (1984).

Parameter	
Molecular diffusion coefficient (D)	0.2160 cm^2/day
Porous molecular diffusion coefficient (D_p)	0.0857 cm^2/day
Volumetric water content (θ_v)	0.5 cm^3/cm^3
Bulk density (ρ_b)	0.8 g/cm3
Freundlich K-bromacil	3
Freundlich n - bromacil	0.9
Langmuir k-diquat	0.0065
Langmuir b-diquat	45000

DIFFUSION MODELS

Model 1: Diffusion with Linear Adsorption-desorption

Figure 2 illustrates the concentration distribution with respect to depth at selected times for a "representative" pesticide which is subject to linear adsorption-desorption. After 600 days approximately 52% of the original pesticide concentration remains in the sediment. In the case of diffusion in the absence of any adsorption-desorption roughly 6% remains in the sediment after the same time period. Obviously, the process of adsorption-desorption retards the diffusion process.

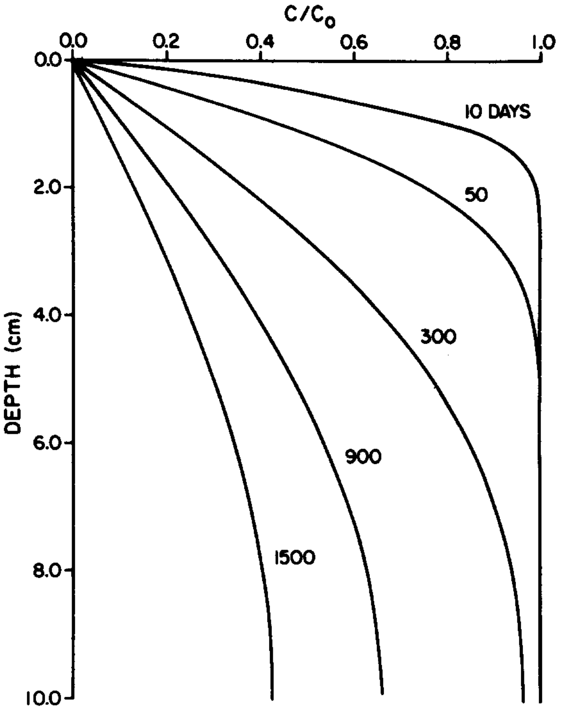

Figure 2: Diffusion of a "representative" linearly-adsorbed pesticide through sediment with an impermeable layer at x = 10 cm ($D_p = 0.0857$ cm^2/day, $\theta_v = 0.5$ cm^3/cm^3, $\rho_b = 0.8$g/cm^3, K = 3).

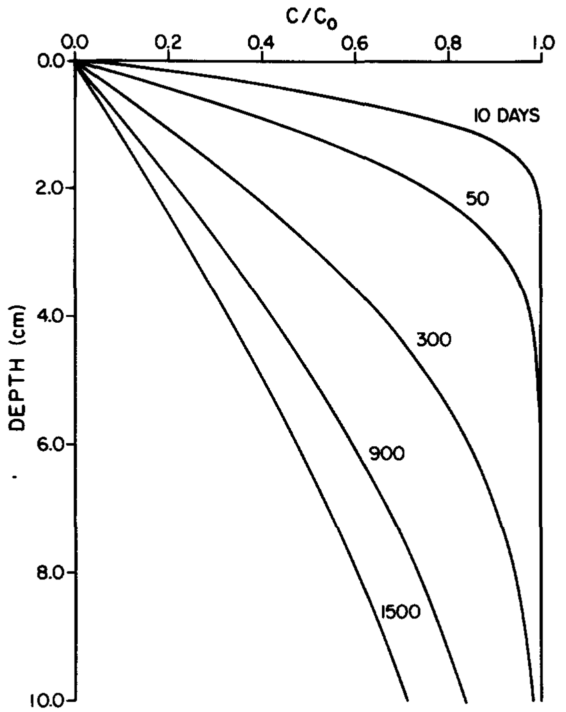

Figure 3: Diffusion of a "representative" linearly-adsorbed pesticide through an infinite sediment layer (D_p = 0.0857 cm^2/day, θ_v = 0.5 cm^3/cm^3, ρ_b = 0.8g/cm^3, K = 3).

The time dependent concentration distributions of Figure 2 are the consequence of restrictions imposed by an impermeable layer as its lower boundary condition, while in Figure 3 the sediment is assumed to be an infinite layer (i.e., $L = \infty$). Because of the presence of an impermeable layer, no upward diffusion can occur below L = 10 cm; consequently, the curves of Figure 2 taper off as they approach L. For an infinite layer there is a continuous upward diffusion from below 10 cm; consequently, the curves are straighter and do not diminish as rapidly as in Figure 2. Whereas 52% of the original pesticide concentration remains in the sediment after 600 days for the case of an impermeable layer as the lower boundary, 56% remains in the top 10 cm for an infinite layer of sediment.

Model 2: Diffusion with Nonlinear Single-valued Freundlich Adsorption-Desorption

Figure 4a shows the effects of nonlinearity of adsorption upon the diffusion process. Figure 4b shows the effect of increasing the partition coefficient, K. An increase in the nonlinearity of adsorption (i.e., 1/n decreases) while maintaining K the same, results in a greater removal of pesticide by diffusion since less pesticide is adsorbed to the sediment

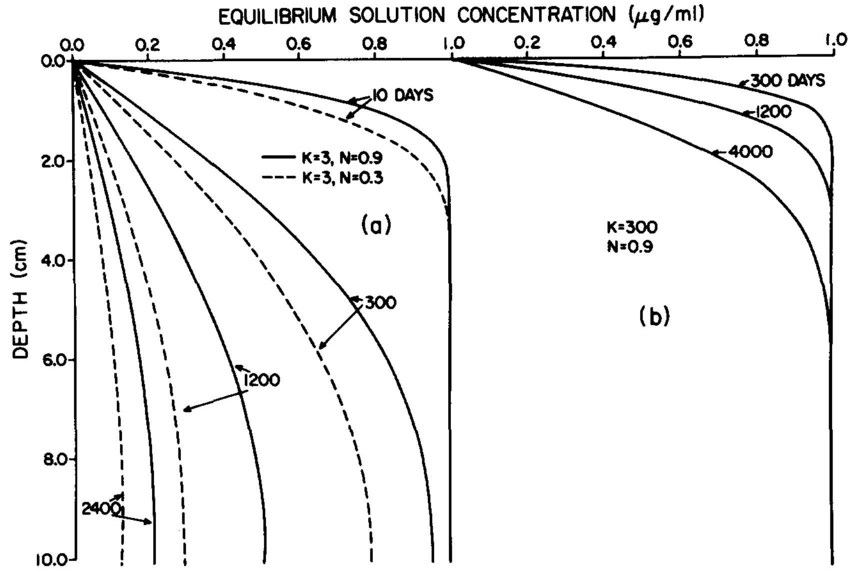

Figure 4: Influence of Freundlich adsorption parameters upon diffusion through sediment (D_p = 0.0857 cm^2/day, θ_v = 0.5 cm^3/cm^3, ρ_b = 0.8g/cm^3, impermeable layer at x = 10 cm)

surface leaving more in solution to undergo diffusion. Nonlinearity is responsible for the diffusion discrepancies which are observed for different initial equilibrium solution concentrations (e.g., C_0 = 5 and C_0 = 50 μg/ml) even though all other physical and chemical parameters may be the same (see Figure 5). This is in contrast to linear adsorption where the amount of herbicide remaining in the sediment relative to the initial solution concentration is independent of the initial equilibrium solution concentration. Due to the nonlinearity of Freundlich-type adsorption, higher initial equilibrium solution concentrations will cause proportionally more of the total amount of pesticide to reside in the solution phase than at lower initial solution concentrations; consequently, more pesticide is available for diffusion.

The effect of the Freundlich adsorption partition coefficient, K, is apparent by comparing Figures 4a and 4b. As would be expected, an increase in K, which is interpreted as an increase in the degree of adsorption, results in less chemical being available for diffusion out of the sediment.

Some of the physical parameters which influence the diffusion process include bulk density, volumetric water content and the molecular diffusion coefficient in aqueous solution. An increase in bulk density decreases diffusion. Since bulk density is determined by the quantity of pore spaces as well as the soil/sediment solids, then sediments that are loose

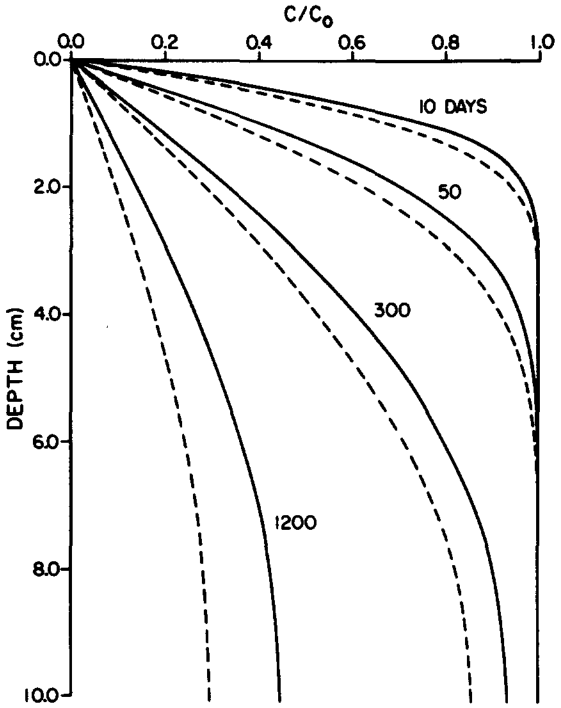

Figure 5: Influence of initial equilibrium solution concentration, C_o, upon diffusion through sediment of a "representative" pesticide undergoing single-valued Freundlich adsorption-desorption (D_p = 0.0857 cm^2/day, θ_v = 0.5 cm^3/cm^3, ρ_b = 0.8g/cm^3, K = 3, N = 0.9, impermeable layer at x = 10 cm). Concentrations illustrated are C_o = 5.0 μg/ml (solid line) and C_o = 500 μg/ml (dashed line).

and porous will have low densities while those that are compact will have higher densities. An increase in compaction results in more material per unit volume which is available as an adsorbent, thereby retarding the diffusion process to a greater extent. Volumetric water content (or total porosity under saturated conditions) influences the tortuosity or path of movement of the diffusing material. It is understandable, therefore, that as the volumetric water content (total porosity) decreases, the pathway becomes longer due to greater tortuosity; thus diffusion decreases.

The molecular diffusion coefficient in aqueous solution is a physical property of the diffusing material which can be influenced by temperature. If it is assumed that the diffusing material is roughly spherical then the diffusion coefficient in a fluid can be defined by the Stokes-Einstein equation,

$$D = \frac{kT}{6\pi\eta r} \qquad [31]$$

where k is Boltzmann's constant, T is the temperature (^oK), η is the coefficient of viscosity and r is the radius of the diffusing material. Since the coefficient of viscosity of a fluid is a function of the temperature as shown below,

$$\eta = \frac{1}{3} \left[\frac{8kmT}{\pi^2 d^2}\right]^{\frac{1}{2}} \qquad [32]$$

where m = molecular mass
d = diameter of molecule

then D is a function of $T^{\frac{1}{2}}$. If this is the case, then by assuming $D = 2.5 \times 10^{-6}$ cm^2/sec = 0.2160 cm^2/day at 25°C will result in D = 0.2087 cm^2/day at 5°C. Quite obviously there is a direct relationship between temperature and the physical process of diffusion.

As well as directly influencing the physical process of diffusion, temperature can also have an influence upon the chemical process of adsorption-desorption which in turn significantly influences the amount of chemical available for diffusion. Since the adsorption of many pesticides (e.g., bromacil) is an exothermic reaction, then temperature increases will result in decreased adsorption. The combined influence of temperature upon the physical process of diffusion and upon the chemical process of adsorption-desorption results in greater retardation of the diffusing herbicide with decreased temperature. This affect is shown in Figure 6 using data from Corwin and Farmer (1984) for the influence of temperature on the adsorption-desorption of bromacil by sediment collected from Castle Lake, a freshwater lake in California. For compounds like bromacil, the effect of temperature upon the adsorption-desorption process is more significant an influence to the overall diffusion process than the direct effect which it has upon the physical diffusion process itself as manifested through changes in the molecular diffusion coefficient. This fact is demonstrated quite dramatically in Figure 6. Figure 6 compares the effect which temperature has upon the physical aspect of diffusion ignoring any influences upon chemical adsorption-desorption processes and upon both the physical process of diffusion and the chemical process of adsorption-desorption. Obviously, the temperature effects upon adsorption-desorption play a more major role in the overall influence of temperature on diffusion. Nevertheless, as can be seen from Figure 6 the effect of temperature on the purely physical aspect of diffusion under these conditions is not negligible for longer periods of diffusion and as such should not be completely ignored.

Model 3: Diffusion with Single-valued Langmuir Adsorption-desorption

Figures 7a-c indicate the influence of the Langmuir adsorption coefficients upon diffusion through a saturated sediment. Increasing the adsorption maximum, b, increases retardation since more pesticide will be adsorbed at a given equilibrium solution concentration (compare Figures 7a and 7b). The adsorption affinity coefficient, k, exhibits the same direct relationship (compare Figures 7a and 7c). Of interest is the fact that Figures 7b and 7c are nearly identical. In addition, at the concentration range of Figures 7a-c, a ten-fold change

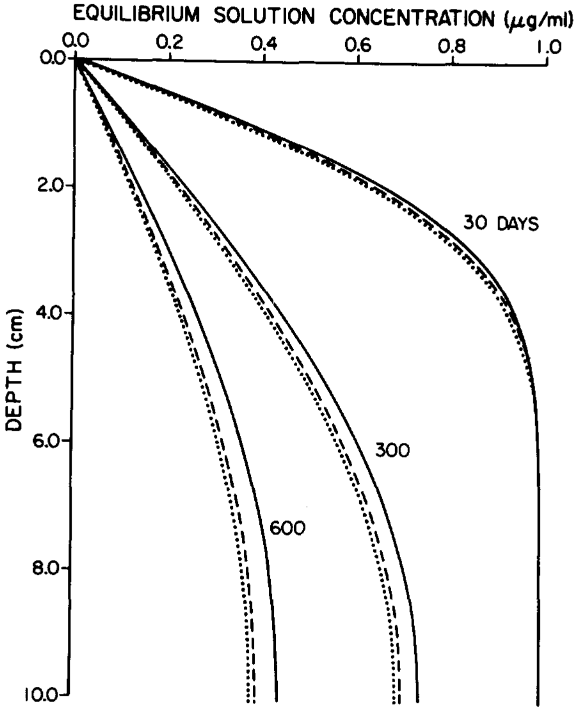

Figure 6: Influence of temperature upon the physical and chemical aspects of the diffusion of bromacil through Castle Lake sediment (data for K, N, and ρ_b obtained from Corwin and Farmer, 1984) - Θ_v = 0.5 cm^3/cm^3, ρ_b = 0.09 g/cm^3, N = 0.93. Experimental conditions shown are T = 5°C, D_p = 0.0828 cm^2/day, K = 7.66 (solid line); T = 5°C, D_p = 0.0828 cm^2/day, K = 6.35 (dashed line); T = 25°C, D_p = 0.0857 cm^2/day, K = 6.35 (dotted line).

in either k or b brings about a ten-fold change in the time scale. This cancelling affect of k and b is not observable at higher concentrations. Rather, the adsorption maximum is found to have a greater influence upon the retardation of the diffusion process than the adsorption affinity for comparable changes in their relative magnitude.

As in the case of Freundlich-type adsorption, Langmuir adsorption is also nonlinear. Since the concentration gradient is the driving force behind the diffusion process, the concentration of herbicide in solution at any given time is critical to the absolute and relative amounts of diffusion which will occur over time. The nonlinearity of Langmuir-type adsorption is such that once the adsorption maximum is reached no additional pesticide is adsorbed; consequently, any further solution concentration increases will remain in solution causing greater diffusion due to an increase in the concentration gradient. Figure 8 indicates the influence which nonlinearity has upon diffusion at different concentrations. The higher the initial solution concentration, the proportionally higher the diffusion of material out of the sediment

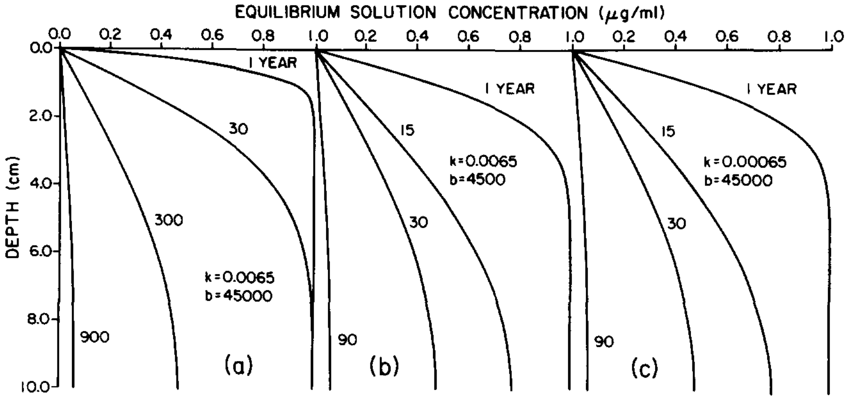

Figure 7: Influence of Langmuir adsorption parameters upon diffusion through sediment (D_p = 0.08757 cm^3/day , θ_v = 0.5 cm^3/cm^3, ρ_b = 0.8 g/cm^3, impermeable layer at x = 10 cm).

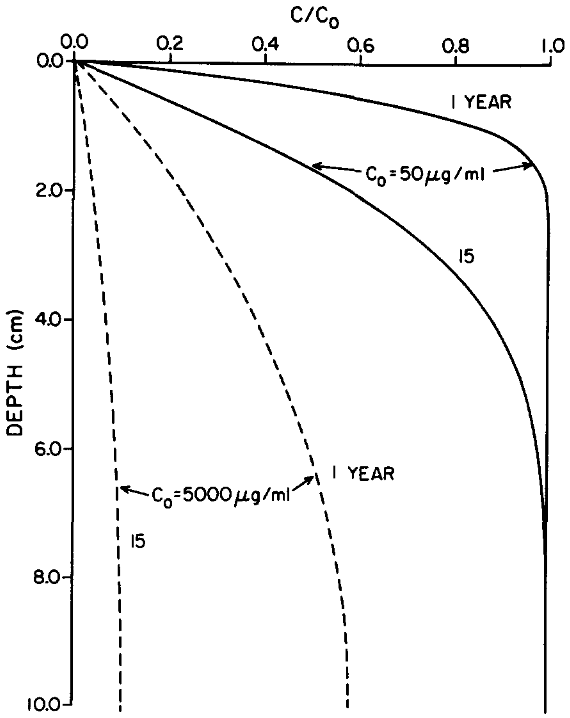

Figure 8: Influence of initial equlibrium solution concentrations, C_o, upon diffusion through sediment of a "representative" pesticide undergoing single-valued Langmuir adsorption-desorption (D_p = 0.08757 cm3/day, θ_v = 0.5 cm3/cm3, ρ_b = 0.8 g/cm3, k = 0.0065, b = 45000, impermeable layer at x = 10 cm).

Qualitatively, bulk density, volumetric water content (i.e., total porosity under saturated conditions) and the molecular diffusion coefficient in aqueous solution have the same influence on the overall diffusion process as in the case of diffusion with Freundlich adsorption-desorption. The effect of temperature upon pesticides which undergo Langmuir-type adsorption has not been well studied on soils and sediments. Corwin and Farmer (1984) found varying results with the cationic pesticide, diquat. In most cases either little change or a decrease in adsorption with increase in temperature over the range of 5° to 25°C was found. The high organic matter content sediments tended to be those in which there was a decrease in adsorption with increased temperature while mineral sediments showed little change. Figures 9 and 10 show quantitatively the difference in the effect of temperature upon diffusion for an organic sediment (i.e., Castle Lakes) and a mineral sediment (i.e., Mockingbird Canyon).

Model 4: Diffusion with Nonsingle-valued Linear/Freundlich or Langmuir Adsorption-desorption

Figures 11 and 12 show the equilibrium solution concentration distributions for the diffusion of bromacil (Freundlich-type adsorption-desorption) and of diquat (Langmuir-type

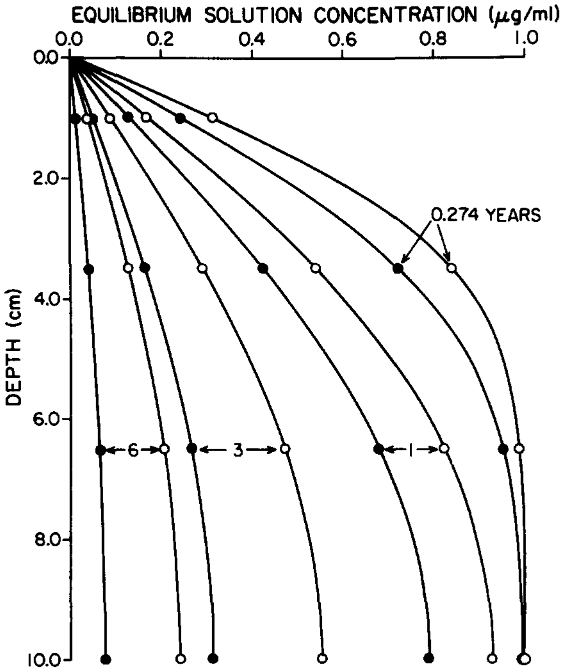

Figure 9: Influence of temperature on the diffusion of diquat through Castle Lake sediment (data for k, b, and ρ_b obtained from Corwin and Farmer, 1984) - θ_v = 0.5, ρ_b = 0.09 g/cm^3. Experimental conditions shown are T = 5°C, D_p = 0.0828 cm^2/day, k = 0.00128, b = 18975 (open circles); T = 25°C, D_p = 0.0857 cm^2/day, k = 0.00052, b = 24390 (closed circles).

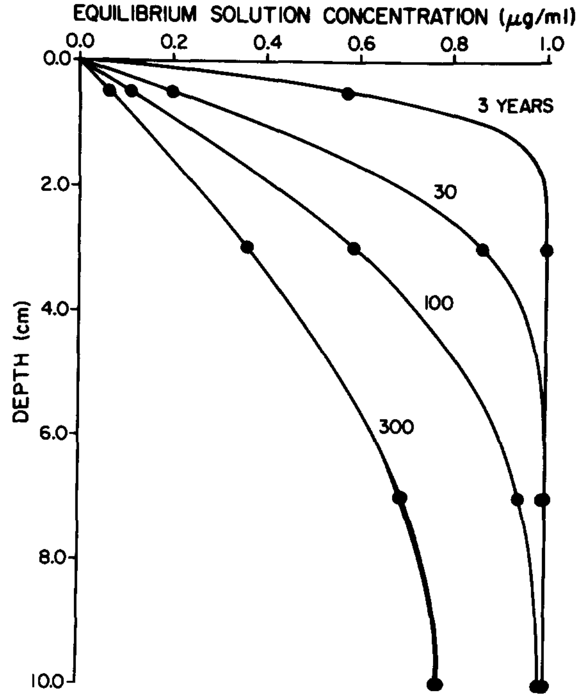

Figure 10: Influence of temperature on the diffusion of diquat through Mockingbird Canyon Reservoir sediment (data for k, b, and ρ_b obtained from Corwin and Farmer, 1984) - $\theta_v = 0.5$, $\rho_b = 0.09$ g/cm^3. Experimental conditions shown are T = 5°C, $D_p = 0.0828$ cm^2/day, k = 0.01040, b = 44248 (open circles); T = 25°C, $D_p = 0.0857$ cm^2/day, k = 0.01070, b = 43860 (closed circles).

adsorption-desorption) from Clear Lake sediment with and without consideration for hysteresis (data obtained from Corwin and Farmer, 1984). In general, hysteresis results in a more rapid removal of pesticide in the equilibrium solution by the diffusion process.

In the Freundlich case, the desorption isotherms are more nonlinear (i.e., 1/n is smaller) and the strengths of adsorption are larger than those of the original adsorption isotherm. The increased nonlinearity and increased strength of adsorption have opposite effects upon the diffusion process. As explained previously, increased nonlinearity will result in more rapid removal of pesticide from the sediment while increasing the strength of adsorption will slow down its removal. The net result is that at the point from which desorption occurs there is a greater concentration of pesticide which is adsorbed to the sediment surface and it is adsorbed with greater strength than would be expected from the original adsorption isotherm; consequently, less pesticide is desorbed as it diffuses from the solution into the overlying water. Because the adsorbed material is more tightly held, the solution concentration diminishes more rapidly than would be expected if the original Freundlich adsorption parameters were used (see Figure 11).

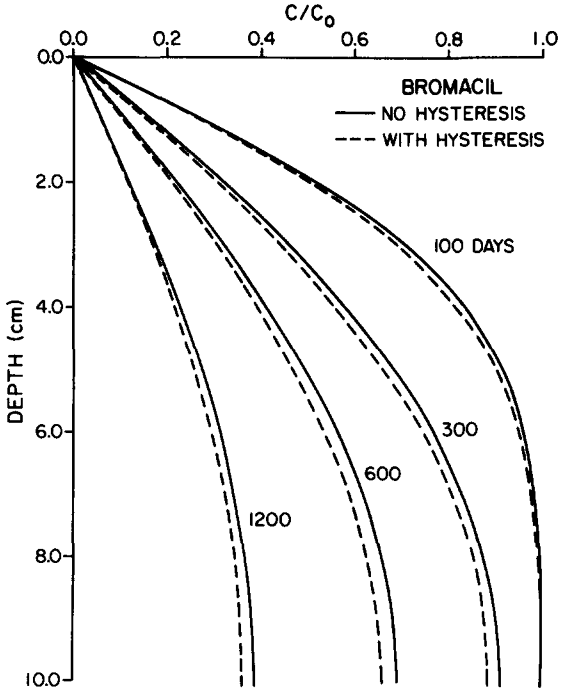

Figure 11: Comparison of the diffusion of bromacil through Clear Lake sediment with hysteresis (K_{des} = 6.34, N_{des} = 0.80) and without hysteresis (K = 5.26, N = 0.92) (data for K, K_{des}, N, N_{des} and ρ_b obtained from Corwin and Farmer, 1984) - D_p = 0.0857 cm^2/day, θ_v = 0.5 cm^3/cm^3, ρ_b = 0.36 g/cm^3.

An analogous explanation can be used to describe the case of diffusion with nonsingle-valued Langmuir adsorption-desorption.

CONCLUSION

Adsorption-desorption reactions are known to play an important role in the transport of solutes. The net effect of adsorption-desorption is to retard solute diffusion through a porous medium. A numerical model of one-dimensional diffusion through saturated sorbing sediments has been presented to quantitatively observe the influence of various physical and chemical parameters as they affect diffusion. Models were developed for the 3 different types of adsorption generally encountered in a sorbing porous medium: linear, Freundlich and Langmuir. An additional model dealing with hysteresis for the above 3 adsorption situations was also presented. The models show that the degree to which a pesticide is retained by a sediment is determined by the sediment's adsorptive capacity, strength of adsorption, porosity and bulk density, as well as the temperature of the aquatic system, the chemical nature of the pesticide and the pesticide's aqueous solution diffusion coefficient. Particular interest was given to the adsorption-desorption reactions. The ability to quantify the changes in

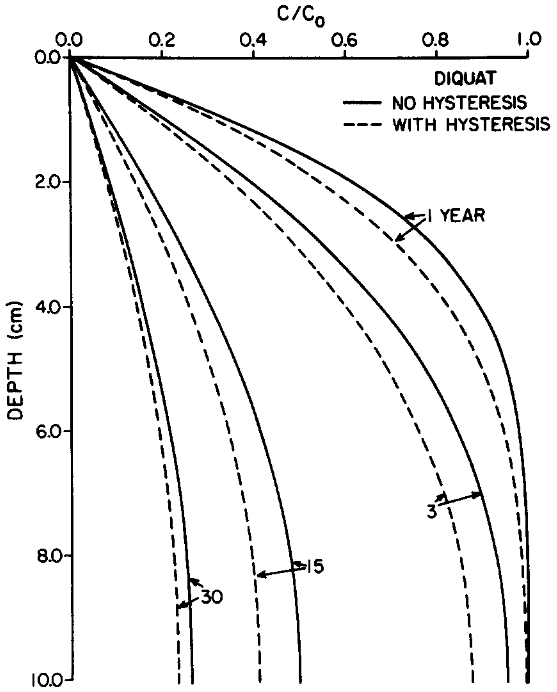

Figure 12: Comparison of the diffusion of diquat through Clear Lake sediment with hysteresis (K_{des} = 0.00417, b_{des} = 30741) and without hysteresis (k = 0.00151, b = 48309) (data for k, k_{des}, b, b_{des} and ρ_b obtained from Corwin and Farmer, 1984) - D_p = 0.0857 cm^2/day, θ_v = 0.5 cm^3/cm^3, ρ_b = 0.36 g/cm^3.

concentration-depth distributions with time resulting from diffusion, as demonstrated in this paper, is not intended as a predictive tool, but rather as a means of assessing the physiochemical interactions which are occurring by varying the magnitude of parameters and comparing their quantitative results.

The adsorption coefficients for Freundlich-type adsorption, K and N, and the analogous coefficients for Langmuir-type adsorption, k and b, reflect the strength and degree of adsorption. The magnitude of these parameters determines the amount of pesticide which is available for diffusion in the solution phase and how readily adsorbed pesticide will desorb from the sediment surface to replenish the pesticide concentration in solution, thereby increasing the concentration gradient.

Hysteresis is a perfect example of the result of the interrelationship of adsorption strength and amount of adsorption. Quantitative results have been given for specific cases which compare the influence of hysteretic and nonhysteretic adsorption-desorption reactions upon diffusion. If hysteresis is an actual phenomenon of nature and not just an artifact of experimental procedure, then it can play a very crucial role in solute transport. The degree to which hysteresis influences the diffusion process for a given pesticide depends on the initial pesticide concentration. Furthermore, the degree of hysteresis will vary considerably for various sediments and pesticides. Because of these significant factors, the existence of hysteresis under natural conditions should be resolved if models of pesticide transport are to have practical value as predictive tools.

As indicated from the lengthy time periods involved in the diffusion of pesticides, particularly cationic pesticides, degradation rates will play a crucial role in determining residual concentrations of pesticides. In the case of strongly adsorbed cationic pesticides, such as the herbicide diquat, the adsorbed phase degradation rate may prove more significant than the degradation rate of pesticide in solution. For application to aquatic systems, further research is needed in the area of anaerobic degradation of pesticides, particularly with respect to the degradation of adsorbed pesticides.

In summary, the pollution of overlying water bodies by the diffusion of pesticides from sediments is a potential problem due to the toxic affect of very low levels of some pesticides to aquatic life forms. From the perspective of water pollution, a sediment with a high adsorptive capacity and a high strength of adsorption would release pesticides to the overlying water at a slower rate and in lower amounts, thereby posing less of a potential hazard to fish. On the other hand, highly organic sediments which could retain high levels of adsorbed pesticide material could pose a threat to filter-feeding organisms which rely upon organic matter at the sediment-water interface as a food source.

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