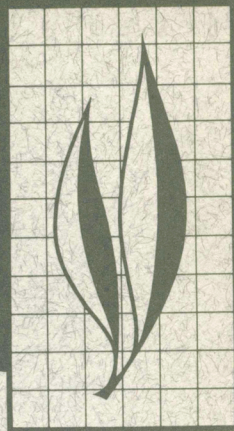


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## A Mathematical Model of Diffusion under Saturated Conditions to Assess the Pollution Potential of Herbicides to Aquatic Systems

D. L. Corwin and W. J. Farmer





## ABSTRACT

The physicochemical dynamics of a pesticide-sediment-water system were studied utilizing a one-dimensional numerical model of diffusion under saturated conditions, with nonlinear Freundlich/Langmuir adsorption-desorption. Specifically, the model was formulated to assess the pollution potential of pesticides to aquatic systems, based upon their ability to migrate within the aquatic environment.

Initial physical and chemical characterization of eight freshwater sediments, and adsorption studies using two chemically dissimilar herbicides—bromacil and diquat—revealed insightful positive relationships between adsorption coefficients and sediment properties. Bromacil showed a high positive correlation between the Freundlich sorption partition coefficient and the organic carbon content. Diquat adsorption, as characterized by a Langmuir-type adsorption, showed a high positive correlation between the Langmuir affinity constant and the surface area, while the Langmuir adsorption maxima correlated highly with the cation exchange capacity of sediments treated for the removal of organic matter. Apparent heats of adsorption for bromacil at 5° and 25°C were low, indicating a predominantly physical type of adsorption. Temperature change was found to have little or no effect upon the adsorption of diquat over the range of observed temperatures, 5° and 25°C. Rates of adsorption for both bromacil and diquat were very rapid, especially on sediments with small organic matter fractions. In general, diquat took slightly longer than bromacil to attain equilibrium. The slower adsorption rate of diquat on high-organic-matter sediments confirms previous findings indicating a possible redistribution of diquat from adsorption sites on the organic fraction to adsorption sites on the clay surface. Varying the initial solution concentration of either bromacil or diquat did not significantly affect the reaction rates. Desorption studies for bromacil and diquat showed that for each sediment, a unique linear relationship existed between the adsorbate concentration at which desorption began and the slope of the desorption isotherm.

*Continued inside back cover.*

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# **A Mathematical Model of Diffusion under Saturated Conditions to Assess the Pollution Potential of Herbicides to Aquatic Systems<sup>1</sup>**

## **INTRODUCTION**

IF THE WORLD'S DEMAND for food is to be met, it is essential that the use of pesticides continue. With the continued use of organic and inorganic chemicals in the environment to control pests, the accumulation of chemical residues becomes significant due to the sensitivity of various plants and animals. As a combined result of the pesticides' toxicity to target and nontarget biological organisms and of worldwide increases in pesticide usage, environmentalists have grown concerned over the effects associated with pesticide migration into various compartments of the environment.

Many freshwater organisms are particularly sensitive to chemical residues and are used as a measure of environmental contamination. As an example, a 96-hour LC<sub>50</sub> for various fish was reported as low as 5  $\mu\text{g/L}$  for an organophosphorus pesticide (Pickering et al. 1962). (LC<sub>50</sub> refers to the aqueous concentration at which a chemical will kill 50 percent of its test subjects.) Many bottom-dwelling filter-feeders such as mollusks are known to accumulate pesticide residues within their tissues. The chemical residues accumulated by aquatic organisms concentrate pesticides beyond levels that occur in sediments and water. Where residues are persistent in bottom sediments, benthic organisms may be damaged even though water concentrations remain low (Wilson and Bond 1969).

Chemical residues in aquatic systems present both real and potential hazards to animals in the higher trophic levels, including humans (Kraybill 1969; Mrak 1969; Pimentel 1971). The transfer of residues from prey to predator along the food chain ultimately results in residue concentrations many thousand times higher than the concentrations present in ambient water. This sort of trophic accumulation has been demonstrated for Clear Lake, California (Hunt and Bischoff 1960).

Birds of prey are particularly susceptible to the effects of trophic accumulation, since they feed on fish and benthic organisms that have been exposed to sediments and water containing pesticides. Birds can generally store high levels of pesticides in their fat deposits without deleterious effects. During a starvation period, however, these chemicals can be released into their systems because of fat utilization. The rapid ensuing buildup of these chemicals in the bloodstream can result in death (Van Velzen, Stiles, and Stickel 1972).

Water and the sediment at the bottoms of water bodies such as rivers, streams, lakes, and ponds are the major compartments of residence in the aquatic system for persistent pesticide residues. The principal sources of pesticides to the aquatic environment include direct applications for the control of water-inhabiting pests; inadvertent applications from aerial spraying, caused by spray drift; "piggyback" migration on eroded soil particles or in runoff waters; accidental spills; residues carried from the atmosphere on rain or dust;

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and discharges of factory or sewage effluents into rivers. Surface runoff, piggyback migration, and aerial transport, however, account for most translocation of pesticides to aquatic ecosystems (Peterle 1970).

Once pesticides have entered the aquatic environment, they may be adsorbed by suspended or bottom sediments. An adsorbed pesticide may be released slowly into the overlying aqueous solution, serving as a source of future contamination even after use of the pesticide has ceased. Ongoing diffusion and adsorption-desorption processes could continue to supply pesticide to the surface waters depending on the persistence of the pesticide. Since very low pesticide concentrations are often toxic to fish and other aquatic life forms, and irrigation waters containing certain pesticide residues are known to produce lower crop yields, it is important to have a means of assessing the pollution potential of pesticides in the aquatic environment.

The object of this paper is to present a simple numerical model of diffusion under saturated conditions, making possible the assessment of the pollution potential of pesticides that can migrate from the sediment to the aqueous phase of the aquatic environment. The model presented in this paper simulates concentration distributions as a function of time, thereby determining the potential for release of pesticide from adsorption sites on the sediment into the aqueous solution.

The solution to this particular problem involves three aspects: a characterization of the physical and chemical properties of sediments selected for their wide-ranging characteristics; an analysis of adsorption-desorption isotherms, including kinetic and thermochemical studies; and finally the development of a diffusion model that accounts for the reversible reactions of adsorption-desorption.

## MATERIALS AND METHODS

Eight sediment samples were collected from sites located throughout California. The sites were chosen for their broad range of physical and chemical properties, particularly with respect to pH, organic matter content, electrical conductivity of the saturated paste, and particle size distribution. The eight sampling sites consisted of five southern California and three northern California water bodies. In southern California, the sites were Mockingbird Canyon Reservoir in Riverside County, San Joaquin Marsh on the University of California's Irvine campus, and three lakes in the San Bernardino Mountains: Baldwin Lake, Big Bear Lake, and Jenks Lake. The northern California water bodies were Clear Lake, a eutrophic lake in Lake County; Castle Lake, a moderately productive cirque lake in Siskiyou County; and Hill Slough, just outside of Fairfield in the Sacramento Delta region of Solano County.

Two sediment samples were taken at each site. First, a 7.5-cm-diameter, 45-cm-long core sample was taken to determine the variation of certain soil properties with depth and provide a cursory indication of heterogeneity. Then, a composite 15-cm-long core sample was taken, along with a water sample from the sediment-water interface.

A sampling device originally devised by Barkley (1971) was used to take the sediment samples. The device consisted of a 7.5-cm (internal diameter) PVC tube that was lowered into the sediment at the end of a galvanized pipe and raised to the surface after the openings were sealed. The vacuum created by sealing all openings was sufficient to hold the sediment sample within the PVC tube. In the case of Castle Lake, however, the sediment was too suspended to be collected with this sampler, so the 45-cm and 15-cm



samples were collected with the aid of scuba equipment. Each sample was sealed and immediately frozen to preserve the chemical and biological state in which it was collected. The samples were taken in waters ranging from 1.5 m to 6 m deep.

Redox potential and pH were measured at 5-cm intervals on thawed core samples. After the 45-cm core samples were freeze-dried for 10 to 14 days, the organic carbon content was determined at 5-cm intervals. In general, each individual sediment was found to vary little across the range selected for composite core samples (the top 15 cm). The water samples from the sediment-water interface were analyzed for pH and electrical conductivity.

After freeze-drying, the 15-cm composite core samples were passed through a 2-mm screen to remove gravel and large organic debris. Initial adsorption studies performed on the screened fraction revealed that reproducibility problems existed due to sample heterogeneity. To rectify this problem a subsample was taken and ground with a rubber-tipped pestle to pass through a 60-mesh (0.25-mm) sieve. The rubber-tipped pestle reduced physical abrasion, preventing the reduction of particles beyond their natural particle size.

To see what effect the grinding had on physical and chemical properties of the 2-mm and 0.25-mm-screened fractions, complete physical and chemical analyses were performed on each. Electrical conductivity and pH of a saturated paste and a 1:5 sediment-to-water paste were measured, as were in situ pH, bulk density, particle size distribution, salt content ( $\text{CaCO}_3$  + soluble salts), organic carbon content, organic matter content, specific surface area, cation exchange capacity, exchange acidity, exchangeable bases, and free iron oxides ( $\text{Fe}_2\text{O}_3$ ).

The physical and chemical methods commonly used to characterize soils were applied to the eight selected sediments. Organic carbon content was determined by the Walkley-Black method outlined by Allison (1965). Organic matter was measured by repeatedly oxidizing the samples with  $\text{H}_2\text{O}_2$  until no further weight loss was observed. Soluble salts and  $\text{CaCO}_3$  were determined gravimetrically after repeated treatment with 1 N  $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$  adjusted to pH 4.5 with  $\text{CH}_3\text{COOH}$ . Mortland and Kemper's (1965) method for determining specific surface area was used. This method provided a means of determining both the internal and external surface area. The pipette method of particle-size analysis was used. Free iron oxides were determined according to Olsen's (1965) technique. A dry ash measurement was obtained by subjecting 30- to 40-g subsamples to  $375^\circ\text{C}$  for 16 hours, after pretreatment at  $110^\circ\text{C}$  for 24 hours had removed any absorbed water. Cation exchange capacity and exchange acidity were derived according to the methods outlined by Chapman and Pratt (1961), and exchangeable bases were determined from the resulting difference.

Adsorption studies for bromacil used the radioassay batch technique with a 1:5 sediment-to-solution ratio. Stock solutions of 1, 5, 10, 25, 50, 75, 100, and 300  $\mu\text{g}/\text{mL}$  bromacil were prepared from carbon-14-labeled and analytical-grade herbicide in 0.01 M  $\text{CaCl}_2$ . Thin-layer chromatography of the radioactive-labeled samples revealed a purity of more than 98 percent for bromacil. Twenty milliliters of stock solution and 4 g of 0.25-mm-screened, air-dried sediment were placed in teflon-coated stainless steel centrifuge tubes and allowed to equilibrate while shaking in a constant temperature environmental chamber for 48 hours. Once equilibrated, the slurry was centrifuged at 15,000 rpm for 15 to 30 minutes. A  $\frac{1}{2}$ -mL aliquot of supernatant was removed and placed in 20 mL of liquid scintillation cocktail (Lavy, Messersmith, and Knoche 1972), which was then measured by liquid scintillation analysis. The pH of the supernatant was also taken at this time. The amount of herbicide adsorbed was determined from the difference between the amount added and the amount remaining in solution after equilibration. Each concentration was replicated three to five times. Adsorption isotherms for bromacil were determined at  $5^\circ$  and  $25^\circ\text{C}$ , and from these data the apparent heats of adsorption could be determined.

Initial kinetic studies for bromacil on three sediments revealed that a 48-hour period was sufficient to attain adsorption equilibrium. The kinetic studies were by a filtration method, using stock solution concentrations of 25 and 300  $\mu\text{g}/\text{mL}$ .

The filtration method involved mixing a 1:5 sediment-to-bromacil stock solution for a specific time (ranging from 30 seconds to 4 days), and quickly terminating the reaction by separating the liquid and solid phases. To achieve this rapid separation, the slurry was filtered through fritted glass. Very rapid separation was critical, especially for short reaction times, so the slurry solution was drawn through the filter by suction. Complete separation was achieved within 2 to 3 seconds. The supernatant was then analyzed by liquid scintillation.

According to desorption equilibrium reaction rates for bromacil on Baldwin Lake sediment, desorption after 48 hours was approximately 90 percent of what it was after 10 days. The potential for degradation effects was considered justification for not proceeding longer than 10 days. Two days was selected as sufficient time for the attainment of desorption equilibrium.

Diquat adsorption studies were similar in technique, except that ultraviolet spectroscopy was the method of measurement. Stock solutions of 1,000, 2,500, 5,000, 25,000, 40,000, 50,000, 100,000, and 125,000  $\mu\text{g}/\text{mL}$  of diquat dibromide monohydrate were prepared from analytical-grade diquat (purity greater than 99 percent). Following equilibration and centrifugation, an aliquot was diluted with a pH 4.5 buffer solution of  $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$  and  $\text{CH}_3\text{COOH}$ . Absorbance measurements at 208 nm on a spectrophotometer determined the concentration remaining in solution. Initial reaction-rate experiments used the same filtration technique outlined for bromacil, and indicated a 48-hour period as sufficient to attain equilibrium. Desorption equilibrium rates for diquat on Baldwin Lake sediment revealed that 95 percent of the desorption that occurred after 10 days had already occurred after 48 hours; consequently, a 48-hour equilibration was chosen for the desorption equilibrium. Thermochemical adsorption isotherm studies were performed at 5° and 25°C.

Adsorption isotherms were also determined on treated samples for bromacil and diquat. Several types of treated sample were used. One treated sample consisted of 0.25-mm-screened sediment that had been treated repeatedly with  $\text{H}_2\text{O}_2$  to remove the organic matter fraction. Another consisted only of the mineral fraction available for adsorption, obtained by treating a 0.25-mm-screened subsample with 1 N  $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$  followed by  $\text{H}_2\text{O}_2$  to obtain the mineral fraction, and then subjecting it to 600°C for 2 hours to collapse the interlayer spacing.

Desorption studies were carried out at 25°C for bromacil and diquat with selected sediments. The desorption experiments used the slurry from previous adsorption experiments, except that 10 mL of supernatant were removed from the centrifuged samples and replaced with 10 mL of 0.01 M  $\text{CaCl}_2$ . The tubes were then shaken in the environmental chamber for 48 hours, centrifuged, and measured as before. This process was repeated for five to six successive desorptions.



## THEORY

The general equation governing the diffusion of a chemical under isothermal, water-saturated conditions within a sorbing porous medium is

$$\theta_v \frac{\delta C}{\delta t} + \rho_b \frac{\delta S}{\delta t} = D_p \frac{\delta^2 C}{\delta x^2} - \mu_l \theta_v C - \mu_s \rho_b S \tag{1}$$

where  $C$  ( $\mu\text{g/mL}$ ) and  $S$  ( $\mu\text{g/g}$ ) are the equilibrium solution and adsorbed concentrations, respectively;  $\theta_v$  ( $\text{cm}^3/\text{cm}^3$ ) is the volumetric water content;  $\rho_b$  ( $\text{g}/\text{cm}^3$ ) is the bulk density;  $D_p$  ( $\text{cm}^2/\text{day}$ ) is the porous diffusion coefficient (assumed constant);  $x$  ( $\text{cm}$ ) is the distance; and  $t$  ( $\text{days}$ ) is the time. The coefficients  $\mu_l$  ( $\text{days}^{-1}$ ) and  $\mu_s$  ( $\text{days}^{-1}$ ) are kinetic coefficients of first-order pesticide degradation for liquid and solid phases, respectively.

Two different types of adsorption isotherm are generally encountered in pesticide-soil-water interactions: Freundlich and Langmuir isotherms. For Freundlich-type adsorption, the relation between  $S$  and  $C$  is given by

$$S = KC^{1/n}, \tag{2}$$

where  $K$  and  $1/n$  are empirical coefficients representing the strength of adsorption and the degree of nonlinearity of adsorption, respectively. Substituting the differentiated form of equation 2 into equation 1 results in equation 3,

$$\frac{\delta C}{\delta t} = \frac{D_p}{\theta_v R_f} \frac{\delta^2 C}{\delta x^2} - \frac{1}{R_f} [\mu_l + n\mu_s(R_f - 1)]C, \tag{3}$$

where the retardation factor  $R_f$  is given by

$$R_f = 1 + \frac{\rho_b K}{\theta_v n} C^{[(1/n)-1]} \tag{4}$$

for Freundlich-type adsorption. In the case of Langmuir-type adsorption we have

$$S = \frac{kbC}{1+kC}, \tag{5}$$

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

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

where

$$R_l = 1 + \frac{\rho_b kb}{\theta_v (1+kC)^2} \tag{7}$$

for Langmuir-type adsorption.

Initial and boundary conditions were imposed to simulate those that might be found in a riverbed or streambed without convective-dispersive flow. Equations 8a, 8b, and 8c outline the initial and boundary conditions.

*initial conditions:*

$$C(x,0) = C_o \qquad 0 < x \leq L \tag{8a}$$

boundary conditions:

$$C(0,t) = 0 \quad t \geq 0 \quad [8b]$$

$$\frac{\delta}{\delta x} C(L,t) = 0 \quad t \geq 0 \quad [8c]$$

These conditions describe an aquatic system in which the sediment has an initial equilibrium solution concentration of  $C_o$  distributed uniformly through the sediment solution, from the sediment-water interface ( $x=0$ ) to some finite depth ( $x=L$ ). The pesticide concentration at the sediment-water interface remains zero at all times, indicating a fast-flowing, well-mixed stream that removes the pesticide as soon as it diffuses from the sediment into the overlying water. An impermeable layer at  $x=L$  restricts any movement of pesticide below depth  $L$  (fig. 1).

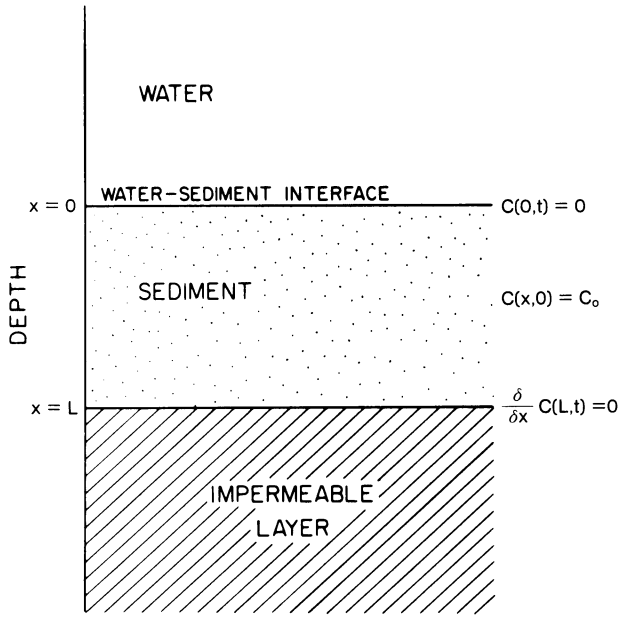


Fig. 1. A schematic illustration showing the initial and boundary conditions for the diffusion of a pesticide through sediment and into an overlying water body with an impermeable layer at the lower boundary.

Using the method of explicit finite-differences on equation 3 we get equation 9 for  $0 < x < L$ ,

$$C_i^{j+1} = \frac{D_p \Delta t}{\theta_v R_f (\Delta x)^2} (C_{i+1}^j + C_{i-1}^j) + \left\{ 1 - \frac{1}{R_f} [\mu_1 + n\mu_s(R_f - 1)] \Delta t - \frac{2D_p \Delta t}{\theta_v R_f (\Delta x)^2} \right\} C_i^j, \quad [9]$$

where  $i$  refers to position,  $j$  refers to time, and where

$$R_f = 1 + \frac{\rho_b K}{\theta_v n} (C_i^j)^{[(1/n)-1]} \quad [10]$$



for Freundlich-type adsorption. For Langmuir-type adsorption, we have

$$C_i^{j+1} = \frac{D_p \Delta t}{\theta_v R_l (\Delta x)^2} (C_{i+1}^j + C_{i-1}^j) + \left\{ 1 - \frac{1}{R_l} [\mu_l + \mu_s(1+kC_i^j)] (R_l - 1) \right\} \Delta t - \frac{2D_p \Delta t}{\theta_v R_l (\Delta x)^2} \left\} C_i^j, \quad [11]$$

where

$$R_l = 1 + \frac{\rho_b k b}{\theta_v (1+kC_i^j)^2}. \quad [12]$$

Imposing the lower boundary condition at  $x=L$ , we get

$$C_i^{j+1} = \frac{2D_p \Delta t}{\theta_v R_l (\Delta x)^2} (C_{i-1}^j) + \left\{ 1 - \frac{1}{R_l} [\mu_l + n\mu_s(R_l - 1)] \right\} \Delta t - \frac{2D_p \Delta t}{\theta_v R_l (\Delta x)^2} \left\} C_i^j \quad [13]$$

for Freundlich adsorption, and

$$C_i^{j+1} = \frac{2D_p \Delta t}{\theta_v R_l (\Delta x)^2} (C_{i-1}^j) + \left\{ 1 - \frac{1}{R_l} [\mu_l + \mu_s(1+kC_i^j)] (R_l - 1) \right\} \Delta t - \frac{2D_p \Delta t}{\theta_v R_l (\Delta x)^2} \left\} C_i^j \quad [14]$$

for Langmuir adsorption.

This explicit method has the advantage of being a simple numerical technique, but it suffers from inherent instability. In order to maintain stability and accuracy,  $\Delta x$  and  $\Delta t$  must be selected so that  $\left\{ \frac{1}{2} - \left[ \frac{1}{2} (B\Delta t) \right] \right\} \geq r$  and  $1 \geq B\Delta t$  (assume  $B \geq 0$  and  $r \geq 0$ ), where for the Freundlich case  $B = (1/R_l) [\mu_l + (\mu_s/N)(R_l - 1)]$  and  $r = (D_p \Delta t) / [\theta_v R_l (\Delta x)^2]$ , and where for the Langmuir case  $B = (1/R_l) [\mu_l + \mu_s (1 + kC_i^j) (R_l - 1)]$  and  $r = (D_p \Delta t) / [\theta_v R_l (\Delta x)^2]$ . The explicit method's accuracy is limited by the truncation error  $E = O(\Delta t) + O[(\Delta x)^2]$ . Consequently,  $\Delta x$  and  $\Delta t$  must be small enough to maintain stability, but not so small that calculations become inefficient. The values of  $\Delta x$  and  $\Delta t$  were selected as 0.5 cm and 0.1 days, respectively. The value for  $D_p$  was derived from the Millington-Quirk (1961) relationship, which, for saturated conditions, is written

$$D_p = (\theta_v)^{4/3} D, \quad [15]$$

where  $D$  (cm<sup>2</sup>/day) is the molecular diffusion coefficient in aqueous solution. This model does not account for solid-liquid phase diffusion of adsorbed molecules, but it was used since under saturated conditions only values of the volumetric water content and the molecular diffusion coefficient in aqueous solution are required.  $D$  at 25°C was selected as  $2.5 \times 10^{-6}$  cm<sup>2</sup>/sec (0.2160 cm<sup>2</sup>/day), which can be used as a representative value for most organic pesticides (Hartley 1964; Jury, Spencer, and Farmer 1983).

Assuming that the diffusing material is roughly spherical, the diffusion coefficient in a fluid should obey the Stokes-Einstein equation,

$$D = \frac{1}{6} \frac{kT}{\pi \eta r}, \quad [16]$$

where  $k$  is Boltzmann's constant,  $T$  is the temperature in kelvins,  $\eta$  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 temperature—

$$\eta = \frac{1}{3} \left( \frac{8kmT}{\pi^2 d^2} \right)^{1/2} \quad [17]$$

(where  $m$  is the molecular mass and  $d$  is the diameter of the molecule)—then  $D$  is a function of  $\sqrt{T}$ . Using equations 16 and 17, and assuming that  $D$  is equal to 0.2160 cm<sup>2</sup>/day at 25°C, one can further assume that  $D$  is equal to 0.2087 cm<sup>2</sup>/day at 5°C.

The accuracy of the explicit numerical solution (eq. 9 and 13) was determined by comparing the finite-difference solution of the diffusion equation for zero and linear adsorption with no degradation to the analytical solutions of the same problems. The analytical solutions to an analogous boundary-value problem for zero and linear adsorption (eq. 1 and 8) were reported by Carslaw and Jaeger (1959). The solution for zero and linear adsorption is

$$\frac{C}{C_0} = \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)} \left\{ \exp \left[ -\frac{D_p}{\theta_v R} \frac{(2n+1)^2 \pi^2}{4L^2} \right] \right\} \cos \frac{(2n+1)\pi(L-x)}{2L}, \quad [18]$$

where  $R = 1$  for zero adsorption, and  $R = 1 + (\rho_b K/v)$  for linear adsorption, with  $K$  representing the linear adsorption coefficient.

A good agreement between the finite-difference and analytical solution for zero adsorption was obtained. After 10 successive time increment iterations using space and time grids of 0.5 cm and 0.1 days, respectively, the maximum difference between the numerical and analytical solution never exceeded 2 percent. Similar results were found for linear adsorption, where the overall error after 10 time increment iterations was also within the limit of 2 percent.

Additional parameters that were needed included half-life values for diquat and bromacil, and initial equilibrium solution concentrations. Under saturated soil conditions, bromacil has been found to have a half-life of 200 days (Wolf and Martin 1974). No quantitative values for the half-life of diquat appear to be available in the literature, probably partly because the chemical nature of diquat complicates the study of its persistence in soils. Diquat adsorbed by montmorillonitic clay minerals at levels below the cation exchange capacity is tightly adsorbed and to a great extent becomes biologically unavailable to microorganisms and plant roots (Coats et al. 1966; Funderburk, Negi, and Lawrence 1966; Knight and Tomlinson 1967; Weber and Coble 1968; Weber, Meek, and Weed 1969; Weber and Scott 1966). In unpublished work, Weber and Weed point out that carbon-14 diquat that had adsorbed onto the internal surfaces of montmorillonite clay in aqueous soil-nutrient suspensions had not been degraded by microorganisms after a 1-year period. The adsorption of cationic herbicides, therefore, results in their persistence in their original form, but in a much reduced biologically active state. Because of this, diquat was assumed to persist indefinitely.

For comparison purposes, two initial equilibrium solution concentrations—5 and 100  $\mu\text{g}/\text{mL}$ —were used for both diquat and bromacil. The 5- $\mu\text{g}/\text{mL}$  solution concentration is a high value in situations where bromacil is used properly, but may be attained if over-application or a minor accident or spill has occurred. An initial equilibrium solution concentration of 100  $\mu\text{g}/\text{mL}$  for bromacil would definitely reflect a major accident or spill. For diquat, either 5  $\mu\text{g}/\text{mL}$  or 100  $\mu\text{g}/\text{mL}$  in the equilibrium solution would be considered very high, since diquat is highly adsorbed by the soil-sediment matrix. Even low levels of diquat in the equilibrium solution represent uncommonly high adsorbed levels.



## DISCUSSION OF RESULTS

Tables 1 and 2 summarize the chemical and physical properties of the 2.0-mm- and 0.25-mm-screened sediment fractions, respectively. As expected, the removal of the medium, coarse, and very coarse sand fractions had very little effect upon the sediment properties, especially when a proportional weight adjustment is made when calculating the properties. It was felt that using the 0.25-mm-screened fraction for the adsorption-desorption studies would ameliorate the problem of reproducibility experienced with the 2.0-mm-screened fraction. Furthermore, because the coarse and medium sand fractions together never constituted more than 5 percent of the total sediment sample for any of the sediments (they constituted less than 2 percent for six of the eight sediments), their removal should not significantly alter the magnitude of adsorption. The data in tables 1 and 2 also show the wide range in properties between the various sediments. The only consistent similarities among the sediments are a relatively high level of fine material and a low percentage of free iron oxides.

Graphs of typical in situ pH and organic carbon content profiles for the 45-cm core samples of Baldwin Lake and San Joaquin Marsh are presented in figure 2. Except for Big Bear Lake, each of the eight sites revealed only a slight variation in pH and organic carbon content over the depth selected for the composite core samples, 0 to 15 cm. The 0- to 15-cm sample was used for all subsequent adsorption-desorption analyses.

To compare the sediments to soils, certain descriptive features including the ratio of organic matter to organic carbon, the specific surface area per gram of organic matter, and the cation exchange capacity (CEC) of the organic matter fraction were calculated for the 2.0-mm-screened fraction. Broadbent (1953) found that the organic-matter-to-organic-carbon ratio (OM:OC) for surface soils was 1.9, and 2.5 for subsoils. This agrees quite well with the 1.8 to 2.2 range found for the eight sediments. The area per gram of organic matter for the sediments ranged from 198 to 478 m<sup>2</sup>/g, which is considerably less than the 558 to 803 m<sup>2</sup>/g for soils that Bower and Gschwend (1952) reported. After excluding San Joaquin Marsh (CEC = 20 meq/100 g), the cation exchange capacity of the organic matter fraction averaged 217 meq/100 g for the remaining sediments. This agrees favorably with the figures Baver (1930) reported for soils, 112 to 252 meq/100 g.

The results of simple and multiple regression analyses made among sediment properties that customarily correlate well in soils are shown in table 3. The relationships of pH to exchange acidity, and charge density to cation exchange capacity and total area showed high positive correlations. The remaining relationships, such as internal surface area to clay percentage; total surface area to clay percentage; total surface area to silt percentage and clay percentage; total surface area to organic matter; and total surface area to organic matter, percent silt, and percent clay, show no correlations.

Analysis of water samples taken from the sediment-water interface (table 4) showed that the pH of the water tended in most cases to be higher than that of the sediment. The electrical conductivity of the water samples tended to be lower than the electrical conductivity of saturated sediment pastes.

TABLE 1. CHEMICAL AND PHYSICAL CHARACTERISTICS  
OF THE 2-MM-SCREENED FRACTION OF FRESHWATER SEDIMENTS

Characteristic* and unit of measure	Big			Mockingbird			San	
	Baldwin Lake	Bear Lake	Castle Lake	Clear Lake	Hill Slough	Jenks Lake	Canyon Reservoir	San Joaquin Marsh
EC <sub>e</sub> dS/m	1.0	1.6	0.5	1.6	6.4	0.5	3.1	9.4
EC <sub>1:5</sub> dS/m	0.6	1.0	0.2	0.8	2.1	0.2	1.2	3.0
pH <sub>SP</sub> (distilled H <sub>2</sub> O)	8.4	6.9	5.2	6.2	6.8	5.6	6.4	6.8
pH <sub>1:5</sub> (distilled H <sub>2</sub> O)	8.5	6.8	5.1	6.5	6.9	5.6	6.5	6.9
pH in situ	8.6	6.4	5.6	6.2	6.7	5.6	6.5	6.8
Bulk density g/m <sup>3</sup>	1.19	0.85	0.09	0.36	0.54	1.68	1.00	1.07
Volumetric water content cm <sup>3</sup> /cm <sup>3</sup>	0.72	0.44	0.17	0.32	0.28	0.53	0.50	0.47
Texture:								
Sand percent	5.0	17.9	23.0	11.2	0.9	2.0	1.2	4.2
Silt percent	25.4	53.7	52.3	48.9	40.0	61.0	49.2	28.9
Clay percent	69.6	28.4	24.7	39.9	59.1	37.0	49.6	66.9
Salt content percent	39.4	17.1	1.1	5.0	6.1	2.6	11.5	10.7
OC content percent	1.2	6.8	13.2	10.2	4.1	3.9	1.9	2.0
OM content percent	2.1	13.4	24.8	21.8	7.9	7.2	3.5	4.3
OM:OC ratio	1.8	2.0	1.9	2.1	1.9	1.9	1.8	2.2
Dry ash content percent	3.04	12.74	25.28	19.67	5.85	6.79	4.14	3.22
CEC meq/100 g	37.0	55.0	40.1	50.9	31.1	21.3	29.3	37.3
EA meq/100 g	0.6	7.3	23.5	21.9	8.0	9.5	9.8	2.5
EB meq/100 g	36.4	47.7	16.6	29.0	23.1	11.8	19.5	34.8
Fe <sub>2</sub> O <sub>3</sub> percent	0.30	0.33	0.45	1.25	0.77	1.81	1.55	0.50
Specific surface area m <sup>2</sup> /g								
Untreated <sup>†</sup> :								
Total <sub>u</sub>	159.1	141.7	55.9	95.6	152.5	71.1	165.0	221.4
Treated <sup>‡</sup> :								
Total <sub>t</sub>	153.0	118.8	3.1	26.0	148.6	39.5	156.3	220.3
External	60.1	18.0	3.6	10.1	54.7	11.3	37.2	80.1
Internal	92.9	100.8	0	15.9	93.9	28.2	119.1	140.2
Area in m <sup>2</sup> /g OM <sup>§</sup>	443	290	216	345	198	478	405	246

\*Key to abbreviations:

EC<sub>e</sub> = electrical conductivity of saturation extract; EC<sub>1:5</sub> = electrical conductivity of 1:5 sediment-to-solution extract; pH<sub>SP</sub> = pH at saturation; pH<sub>1:5</sub> = pH of 1:5 sediment-to-solution suspension; salt = soluble salts and CaCO<sub>3</sub>; OC = organic carbon; OM = organic matter; CEC = cation exchange capacity; EA = exchange acidity; EB = exchangeable bases. Use this key also for table 2.

<sup>†</sup>Untreated (1 N CaCl<sub>2</sub>).

<sup>‡</sup>Treated (H<sub>2</sub>O<sub>2</sub>, 1 N CaCl<sub>2</sub>).

<sup>§</sup>Area in m<sup>2</sup>/g:

$$OM = \frac{\text{total}_u - [\text{total}_t \times (1.00 - \text{residual OM})]}{OM}$$



TABLE 2. CHEMICAL AND PHYSICAL CHARACTERISTICS OF THE 0.25-MM-SCREENED FRACTION OF FRESHWATER SEDIMENTS

Characteristic* and unit of measure	Big						Mockingbird	San
	Baldwin Lake	Bear Lake	Castle Lake	Clear Lake	Hill Slough	Jenks Lake	Canyon Reservoir	Joaquin Marsh
EC <sub>e</sub> dS/m	1.03	2.20	0.52	1.76	7.60	0.54	2.12	9.20
EC <sub>1:5</sub> dS/m	0.54	0.50	0.21	0.72	3.20	0.14	0.60	3.11
pH <sub>SP</sub> (distilled H <sub>2</sub> O)	8.6	7.2	5.7	6.6	7.0	6.1	7.1	7.8
pH <sub>1:5</sub> (distilled H <sub>2</sub> O)	9.0	7.2	5.8	6.8	7.2	6.2	7.4	8.1
pH <sub>SP</sub> (0.01 M CaCl <sub>2</sub> )	8.0	6.7	4.9	5.7	6.6	5.3	6.5	7.3
pH <sub>1:5</sub> (0.01 M CaCl <sub>2</sub> )	8.0	6.7	4.8	6.0	6.6	5.4	6.7	7.1
Silt, fine sand, and very fine sand content percent	26.3	65.4	67.9	55.1	40.3	62.2	49.8	30.2
Clay content percent	73.3	34.6	32.1	44.9	59.6	37.8	50.2	69.8
Salt content percent	37.3	15.6	0.6	3.6	4.5	0.8	11.3	12.3
OC content percent	1.0	7.9	14.5	13.3	4.4	3.0	2.1	2.6
OM content percent	2.0	13.7	22.4	20.8	6.7	4.7	3.4	4.1
OM:OC ratio	2.0	1.7	1.5	1.6	1.5	1.6	1.6	1.6
Dry ash content percent	2.63	12.77	21.74	18.65	6.29	5.42	4.23	3.52
CEC meq/100 g	41.8	62.7	33.8	59.1	41.9	26.5	36.3	48.5
EA meq/100 g	0.2	5.5	19.0	19.1	9.4	11.1	7.1	5.8
Fe <sub>2</sub> O <sub>3</sub> percent	0.29	0.36	0.38	1.50	0.85	1.79	1.56	0.65
Saturation percentage	60	52	185	88	52	32	50	44
Charge density C/m <sup>2</sup>	0.243	0.342	0.470	0.507	0.266	0.348	0.207	0.208
Specific surface area m <sup>2</sup> /g								
Untreated <sup>†</sup> :								
Total	165.7	177.0	69.4	112.4	151.7	73.4	168.8	225.1
Treated <sup>‡</sup> :								
Total	158.2	168.2	27.6	63.2	148.1	58.0	150.9	217.8
External	60.4	27.9	27.3	22.3	54.4	18.6	36.1	78.9
Internal	97.8	140.3	0.3	40.9	93.7	39.4	114.8	138.9
Mineral fraction <sup>§</sup>								
Total specific surface m <sup>2</sup> /g	196.6	100.5	27.6	63.6	130.9	50.9	87.4	251.3
CEC meq/100 g	36.2	44.5	11.2	31.6	33.2	16.1	28.0	49.7
Charge density C/m <sup>2</sup>	0.178	0.427	0.392	0.480	0.245	0.305	0.309	0.91

\*For key to abbreviations, see footnote, table 1.

<sup>†</sup>Untreated (1 N CaCl<sub>2</sub>).<sup>‡</sup>Treated (H<sub>2</sub>O<sub>2</sub>, 1 N CaCl<sub>2</sub>).<sup>§</sup>Treated (1 N NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> · 3H<sub>2</sub>O, H<sub>2</sub>O<sub>2</sub>, 1 N CaCl<sub>2</sub>).

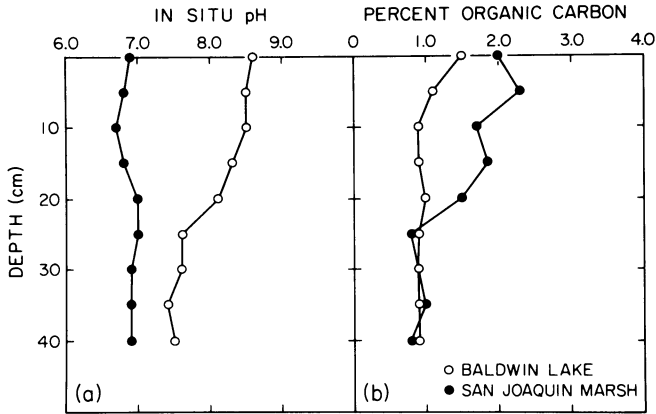


Fig. 2. (a) In situ pH, and (b) percent organic carbon, shown as functions of depth for Baldwin Lake and San Joaquin Marsh sediments.

TABLE 3. CORRELATIONS BETWEEN SEDIMENT PROPERTIES OF THE 0.25-MM-SCREENED FRACTION

Properties correlated	Linear correlation coefficient <i>r</i>	Multiple correlation coefficient <i>r</i>
pH to exchange acidity	0.865*	
Internal surface area to percentage clay	0.512	
Sediment treated with H <sub>2</sub> O <sub>2</sub> and 1 N CaCl <sub>2</sub> :		
Total surface area to percentage clay	0.622	
Total surface area to percentage silt and percentage clay		0.601
Sediment untreated:		
Total surface area to organic matter content	0.393	
Total surface area to organic matter content and percentage clay		0.502
Total surface area to organic matter content, percentage silt, and percentage clay		0.503
Charge density to cation exchange capacity and total surface area:		
Sediment treated with H <sub>2</sub> O <sub>2</sub> and 1 N CaCl <sub>2</sub>		0.954
Sediment treated with 1 N NaC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> · 3H <sub>2</sub> O followed by H <sub>2</sub> O <sub>2</sub>		0.907

\*Significant at the 1 percent level.

TABLE 4. pH AND ELECTRICAL CONDUCTIVITIES OF WATER TAKEN JUST ABOVE THE SEDIMENT-WATER INTERFACE FOR THE EIGHT FRESHWATER SAMPLE SITES

Sample site	pH	Electrical conductivity at 25°C <i>dS/m</i>
Baldwin Lake	8.3	1.2
Big Bear Lake	7.9	0.5
Castle Lake	5.8	0.2
Clear Lake	6.9	0.3
Hill Slough	7.4	3.4
Jenks Lake	6.9	0.2
Mockingbird Canyon Reservoir	6.7	0.6
San Joaquin Marsh	8.2	6.8

### Adsorption-desorption studies

Before any adsorption equilibrium experiments could be undertaken with bromacil, kinetic experiments were necessary to determine the time required to reach equilibrium for a particular concentration. Three of the eight sediments were selected for kinetic experiments: Baldwin Lake, Clear Lake, and Hill Slough. These sediments provided the full range of properties represented by all eight sediments.

Initial kinetic studies with Baldwin Lake sediment revealed some interesting results. Kinetic studies were carried out on samples of Baldwin Lake which were pretreated in different manners: samples dried at 105°C, and samples dried at 105°C then pretreated with 0.01 M CaCl<sub>2</sub> for 24 hours in a shaker. Pretreatment occurred just before the addition of a stock solution of bromacil that brought the initial bromacil concentration to the desired level, 25 or 300 µg/mL. Baldwin Lake sediment reaches an adsorption maximum before coming to equilibrium in the case of no preequilibration with CaCl<sub>2</sub> (fig. 3). The adsorption

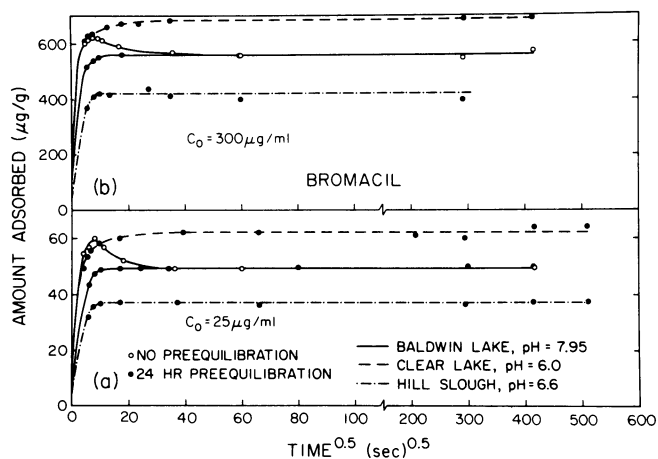


Fig. 3. Bromacil adsorption equilibrium kinetics at 25°C: amount of bromacil adsorbed vs.  $\text{time}^{0.5}$  for three freshwater sediments using initial solution concentrations of (a) 25 µg/mL and (b) 300 µg/mL.

maximum is reached approximately 1 minute after bromacil is added, and equilibration occurs at 20 minutes for 25  $\mu\text{g}/\text{mL}$ , and between 20 and 60 minutes for 300  $\mu\text{g}/\text{mL}$ . This adsorption maximum may be attributable to hydrophobic sites created by drying the samples at 105°C to remove all hygroscopic water adsorbed on the surface. As a result, bromacil is preferentially adsorbed at first. After a short time, however, water begins to compete more favorably for adsorption sites, and gradually equilibrium is reached.

It appears from the data in figure 3 that equilibrium takes longer at higher initial bromacil concentrations if there is no preequilibration with  $\text{CaCl}_2$ . Sixty minutes pass before equilibration of an initial bromacil concentration of 300  $\mu\text{g}/\text{mL}$ , while just 15 minutes are required for an initial concentration of 25  $\mu\text{g}/\text{mL}$ . As a consequence of these results, an equilibration time of 48 hours was selected for bromacil and air-dried sediments. This provided more than adequate time for equilibrium to be reached by all sediments, regardless of the existence of postulated hydrophobic sites due to drying.

Further analysis of the equilibrium-rate graphs for sediments pretreated with  $\text{CaCl}_2$  (fig. 3) reveals that bromacil adsorption is generally very rapid, especially on the sediments with small organic matter fractions. At both concentration levels equilibrium is reached in less than 4 minutes for Baldwin Lake and Hill Slough sediments, which have organic matter contents of 2.0 percent and 6.7 percent, respectively, while Clear Lake (organic matter content 20.8 percent) took approximately 48 hours to reach equilibrium. It would appear that occluded, less-readily available sites become more available with time. The rapid adsorption of bromacil by sediment from Baldwin Lake and Hill Slough, however, indicates a predominantly physical adsorption. The time required to reach equilibrium was not noticeably affected by the initial concentration of bromacil.

The similar rate constants calculated from the kinetic data using the method outlined by Haque et al. (1968) further substantiate the proposition that concentration has no apparent effect on the rate of reaction for either of the two concentrations observed (table 5). These rate constants also confirm quantitatively that sediments with low organic matter contents adsorb bromacil more quickly, since the Baldwin Lake and Hill Slough sediments have higher rate constants.

Adsorption studies for bromacil were performed on each of the eight untreated sediments and a variety of treated sediments in an attempt to understand how bromacil partitions itself among the various fractions found in sediments' organic matter and mineral fractions

TABLE 5. RATE CONSTANTS AND GIBBS FREE ENERGY OF ACTIVATION FOR THE ADSORPTION OF BROMACIL AT TWO CONCENTRATIONS ON THREE SELECTED SEDIMENTS

Sample site	Initial concentration $\mu\text{g}/\text{mL}$	Rate constant $k'$ $\text{sec}^{-1}$	Gibbs free energy of activation $\Delta G \neq^*$ $\text{kcal}/\text{mole}$
Baldwin Lake	25	0.018	19.8
	300	0.018	19.8
Clear Lake	25	0.013	20.0
	300	0.012	20.1
Hill Slough	25	0.019	19.8
	300	0.017	19.9

\* $k' = \frac{kT}{h} \exp \frac{-\Delta G \neq}{RT}$ ;  $\Delta G \neq = -RT \ln \frac{k'h}{kT}$ ;  $k$  = Boltzmann's constant;  $h$  = Planck's constant;  $R$  = Gas constant;  $T$  = Temperature (kelvins).



(including internal and external surfaces of the mineral fraction). In all cases, the data for bromacil adsorption conformed best to the Freundlich adsorption isotherm.

The Freundlich equation is a purely empirical model, expressed as

$$S = K_{ads}C^{1/n}, \quad [19]$$

when dealing solely with adsorption processes. In this case,  $K_{ads}$  represents a measure of the extent of adsorption while  $1/n$  indicates the nonlinear relationship between adsorption and the solution equilibrium concentration.

Equation 19 can be rewritten in a log form that simplifies the determination of the Freundlich adsorption coefficients from experimental data:

$$\log S = \frac{1}{n} \log C + \log K_{ads}. \quad [20]$$

With this equation,  $K_{ads}$  and  $1/n$  can be solved readily by linear regression analysis using a log transformation, or by a log-log plot of the amount of chemical adsorbed per gram of sediment  $S$  and the equilibrium solution concentration  $C$ . In this case,  $1/n$  represents the slope and  $\log K_{ads}$  represents the intercept.

Table 6 summarizes the adsorption coefficients for all eight sediments. The average value of  $1/n$  for the eight untreated sediments at 25°C is slightly less than unity (average  $1/n = 0.92$ ), while the adsorption partition coefficient  $K_{ads}$  ranges from 0.556 to 6.353. A comparison of the adsorption coefficients for untreated sediments at 5° and 25°C shows that as temperature decreases, the degree of nonlinearity  $1/n$  remains essentially unchanged, but the adsorption partition coefficient increases. This is to be expected, since adsorption is an exothermic process; the higher the temperature, the lower the adsorption. The apparent heat of adsorption of each sediment (table 6) is calculated by

$$\Delta H = \frac{R \ln(K_1/K_2)}{1/T_2 - 1/T_1}, \quad [21]$$

where  $K_1$  is the adsorption partition coefficient at temperature  $T_1$ ,  $K_2$  is the adsorption partition coefficient at temperature  $T_2$ , and  $R$  is the gas constant. The apparent heats of adsorption in table 6 are uncorrected for bromacil solubility at 5° and 25°C. The apparent heat of adsorption of bromacil is low for each sediment, further indicating a physical type of adsorption, probably by weak van der Waals forces.

Treatment of the sediments with 1 N  $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$  to remove any  $\text{CaCO}_3$  plus soluble salts, and then with  $\text{H}_2\text{O}_2$  to remove the organic matter, left only the mineral fraction. Adsorption studies on this fraction yielded the results expected, when interpreted qualitatively. In nearly all cases, the isotherms became more closely linear (indicated by  $1/n$  approaching unity). This might be explained in that the mineral fraction contains surfaces that are more chemically homogeneous than organic matter, and therefore less likely to produce nonlinearity in the adsorption isotherm. Except for Baldwin Lake, the adsorption partition coefficient decreased with removal of the organic matter fraction, shown by prior investigators to be the single soil constituent most closely associated with the degree of adsorption (Furmidge and Osgerby 1967; Goring 1962; Graham-Bryce 1967; Lambert 1968; Peck, Corwin, and Farmer 1980). The 1 N  $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$  treatment was probably the most significant factor causing the increase in  $K_{ads}$  for Baldwin Lake, since the removal of  $\text{CaCO}_3$ , an inert adsorptive surface, would have increased the amount of clay per gram of sample, thereby increasing the number of potential adsorption sites for bromacil, and would have reduced any competition with  $\text{Ca}^{+2}$  for adsorption sites.

By heating the mineral fraction to 600°C for 2 hours, the interlayer spacing of the expanding lattice clays was collapsed, removing any internal surface adsorption sites. This

TABLE 6. FREUNDLICH ADSORPTION COEFFICIENTS FOR BROMACIL ON UNTREATED AND TREATED FRESHWATER SEDIMENTS; APPARENT HEATS OF ADSORPTION ARE FOR THE TEMPERATURE RANGE 5° TO 25°C

Sediment sample	Untreated at 5°C				Untreated at 25°C				$\Delta H^*$ kcal/deg mole	Treated samples at 25°C			
	Untreated at 5°C		Untreated at 25°C		Untreated at 5°C		Untreated at 25°C			NaOAC + H <sub>2</sub> O <sub>2</sub> <sup>†</sup>		NaOC + H <sub>2</sub> O <sub>2</sub> + 600°C‡	
	1/n	K <sub>ads</sub>	K <sub>OC</sub>	1/n	K <sub>ads</sub>	K <sub>OC</sub>	1/n	K <sub>ads</sub>		1/n	K <sub>ads</sub>	1/n	K <sub>ads</sub>
Baldwin Lake	0.98	4.52	452	0.98	2.89	289	0.97	5.97	-3.68	0.97	0.74	51.50	
Big Bear Lake	0.87	4.57	57.8	0.86	3.93	49.7	1.01	0.44	-1.24	1.01	0.76	2.57	
Castle Lake	0.93	7.66	52.8	0.93	6.35	43.8	1.05	0.09	-1.54	1.05	no adsorption	no adsorption	
Clear Lake	0.93	7.03	52.9	0.92	5.26	39.5	0.96	0.38	-2.39	0.96	no adsorption	no adsorption	
Hill Slough	0.89	3.69	83.9	0.91	2.72	61.7	0.99	1.02	-2.51	0.99	0.79	6.69	
Jenks Lake	0.90	1.68	56.0	0.89	1.20	39.9	no data	no data	-2.77	no data	0.71	0.55	
Mockingbird Canyon Reservoir	0.92	0.97	46.2	0.95	0.56	26.5	0.97	0.10	-4.52	0.97	0.84	1.08	
San Joaquin Marsh	0.92	1.04	40.0	0.90	0.68	26.3	1.03	0.49	-3.50	1.03	0.78	18.99	

\* Apparent heat of adsorption.

† Sediment treated with 1 N NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> · 3H<sub>2</sub>O followed by treatment with H<sub>2</sub>O<sub>2</sub>, leaving just the mineral fraction; adsorption performed at 25°C.

‡ Sediment treated with 1 N NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> · 3H<sub>2</sub>O, H<sub>2</sub>O<sub>2</sub> and subjected to 600°C for 2 hours, leaving the external surfaces of the mineral fraction; adsorption performed at 25°C.

produced some unexpected results that are probably attributable more to the extreme heating process than to adsorption onto the external surfaces of clays. There is a conspicuous decrease in  $1/n$  in all sediments, indicating increased nonlinearity in the adsorption isotherms. This is unexpected, since a mineral fraction adsorption medium with only external clay surfaces would seem likely to yield linear isotherms because of the homogeneity of the adsorption surface. The removal of internal adsorptive surfaces would also be expected to produce less drastic increases in the adsorption partition coefficient than were found.  $K_{ads}$  increased from 5 to 40 times in magnitude. These combined factors suggest that the heating process substantially altered the adsorptive surfaces of the mineral fraction.

Interpreting the results from these treated samples obviously requires extreme caution because of possible changes in the sediments caused by such drastic pretreatment. Nevertheless, the results certainly indicate the presence of possible adsorption sites other than those provided by the organic matter.

Earlier investigators (Goring 1967; Hamaker and Thompson 1972; Karickhoff 1981; Lambert 1968; Lambert, Porter, and Schieferstein 1965) have found that when the adsorption partition coefficient is normalized to organic carbon (OC) by the equation

$$K_{OC} = \frac{K_{ads}}{\%OC} \times 100, \quad [22]$$

$K_{OC}$  is generally less variable than when  $K$  is expressed solely on a total sediment basis (table 6). Baldwin Lake (organic carbon content 1.0 percent) had a higher  $K_{OC}$  than the other sediments. This is commonly the case for low organic matter soils or sediments. Hamaker and Thompson (1972) proposed that this was because the mineral phase may make a significant contribution to the total adsorption. In contrast, San Joaquin Marsh sediment (organic carbon content 2.6 percent, clay content 69.8 percent) showed a  $K_{OC}$  similar to those of the other sediments even though its organic carbon content and clay content were roughly equal to those of Baldwin Lake (organic carbon content 1.0 percent, clay content 73.3 percent). Just why the clay provided sites for adsorption of bromacil on Baldwin Lake sediment but not on San Joaquin Marsh sediment remains unknown.

Linear regression analysis of the adsorption partition coefficient and individual sediment properties (table 7) confirms previous findings for soils that show high positive correlations between the organic fraction (as reflected by percentage organic matter, percentage organic carbon, or percentage dry ash) and the degree of adsorption represented quantitatively by  $K_{ads}$  (Furmidge and Osgerby 1967; Goring 1962; Graham-Bryce 1967; Lambert 1968; Peck, Corwin, and Farmer 1980). A positive correlation also exists between charge density and degree of bromacil adsorption, both for untreated sediments and for sediments treated for the removal of organic matter.

Multiple regression analyses of the Freundlich adsorption coefficient for bromacil and sediment properties indicate that  $K_{ads}$  is best predicted from the combined properties of organic matter (% OM), exchange acidity (EA), free iron oxides (%  $Fe_2O_3$ ), and clay (% clay), when used as the independent variables of a linear multiple regression equation:

$$K_{ads} = 0.800 + 0.248(\% OM) - 0.007(EA) + 0.011(\% \text{clay}) - 0.810(\% Fe_2O_3) \\ r^2 = 0.986. \quad [23]$$

The results of bromacil desorption studies performed on Big Bear Lake, Castle Lake, and Clear Lake are summarized in table 8. The desorption isotherms conformed well to the Freundlich equation,

$$S_{des} = K_{des} C^{1/n} \quad [24]$$

where  $S_{des}$  is the amount of chemical (per mass of adsorbent) remaining adsorbed to the

adsorbent's surface after a desorption,  $C$  is the equilibrium concentration in solution, and  $K_{des}$  and  $1/n$  are the Freundlich desorption coefficients.  $K_{des}$  reflects the degree of adsorption after desorption has occurred. For the organic sediments of Castle Lake and Clear Lake,  $K_{des}$  increases and  $1/n$  decreases with an increase in the concentration of

TABLE 7. LINEAR REGRESSION ANALYSIS OF FREUNDLICH SORPTION PARTITION COEFFICIENT,  $k_{ads}$ , AND INDIVIDUAL SEDIMENT PROPERTIES FOR BROMACIL AT 25°C

Soil property	Correlation coefficient $r$	Regression equation $k_{ads} =$		$r^2$
Exchange acidity	0.632	0.982 + 0.204	exchange acidity	0.400
pH <sub>1:5</sub> (0.01 M CaCl <sub>2</sub> )	-0.459	9.292 - 0.990	pH <sub>1:5</sub>	0.210
Organic matter	0.908	0.637 + 0.238	percentage organic matter	0.824
Organic carbon	0.902	0.709 + 0.367	percentage organic carbon	0.813
Dry ash	0.911	0.473 + 0.263	percentage dry ash	0.829
Clay	-0.487	6.242 - 0.066	percentage clay	0.237
Fe <sub>2</sub> O <sub>3</sub>	-0.379	4.175 - 1.331	percentage Fe <sub>2</sub> O <sub>3</sub>	0.144
Exchangeable bases	-0.021	3.055 - 0.003	exchangeable bases	0.000
Untreated sediment sample:				
Total area	-0.518	5.878 - 0.021	total area	0.268
Total cation exchange capacity	-0.313	0.589 + 0.054	total cation exchange capacity	0.098
Charge density	0.846	-2.136 + 15.698	charge density	0.716
Sediment sample treated with H <sub>2</sub> O <sub>2</sub> to remove organic matter:				
Total area	-0.602	5.358 - 0.019	total area	0.363
Total cation exchange capacity	-0.322	4.603 - 0.053	total cation exchange capacity	0.104
Charge density	0.800	-1.641 + 15.852	charge density	0.639

TABLE 8. LINEAR REGRESSION ANALYSIS OF FREUNDLICH DESORPTION ISOTHERMS FOR BROMACIL ON SELECTED SEDIMENTS AT 25°C

Sediment sample	$S_o^*$	$K_{des}^\dagger$	$1/n$	Regression equations	$r^2$
				$1/n =$	
Big Bear Lake ( $K_{ads}^\ddagger = 3.93$ )	10.02	4.77	0.71	0.7348 + 0.0003 $S_o$	0.88
	43.78	5.36	0.76		
	116.25	4.85	0.80		
	407.09	3.93	0.86		
Castle Lake ( $K_{ads}^\ddagger = 6.35$ )	13.27	6.72	0.85	0.8425 - 0.00003 $S_o$	0.96
	64.34	8.13	0.84		
	184.04	9.56	0.83		
	674.71	10.56	0.82		
Clear Lake ( $K_{ads}^\ddagger = 5.26$ )	12.27	6.71	0.81	0.8158 - 0.0005 $S_o$	0.99
	58.37	7.71	0.79		
	161.50	11.00	0.74		

\*Initial adsorbate concentration at which desorption began.

†Freundlich desorption partition coefficient.

‡Freundlich adsorption partition coefficient.



bromacil adsorbed onto the sediment surface before desorption. This suggests that at higher adsorbate concentrations the desorption isotherm becomes more nonlinear and the strength of adsorption increases. For a more mineral-type sediment, Big Bear Lake, the opposite was true. From the linear regression analysis of  $1/n$  and the initial adsorbate concentration of Big Bear Lake sediment, an empirical relationship was found (table 8). Regression equations with  $r^2$  ranging from 0.88 to 0.99 indicate that it is possible to predict with reasonable certainty the desorption values of  $1/n$  for the three sediments from any acceptable initial adsorbate concentration of bromacil. By knowing both the desorption  $1/n$ , as determined from the regression equation, and the initial adsorbate concentration at which desorption commences, the desorption isotherm can be determined. This means of modeling the adsorption-desorption process is effective as long as desorption is a continuous process uninterrupted by re-adsorption. This would be the expected case for the diffusion of an adsorbed chemical from a sediment into an overlying water body.

Initial kinetic studies were also performed with diquat to determine the time required to attain equilibrium, as well as to obtain further insight into the intermolecular interactions involved in adsorption. Figure 4 shows that diquat took a slightly longer time to attain equilibrium than did bromacil. This is also apparent from the lower reaction rate constants for diquat (compare tables 5 and 9). Once again, the lowest rate constants are associated with Clear Lake, which is most notably different from Baldwin Lake and Hill Slough in the high organic matter content of its sediment. From the reaction-time graphs, especially those of Clear Lake and Hill Slough, diquat's behavior appears to begin with a rapid adsorption period, followed by a slow increase in adsorption. This is quite evident in figure 4*b*, where Clear Lake sediment continues slowly to adsorb diquat. Even after 3 days, equilibrium is not reached. Since only slight increases were seen beyond 2 days for any of the three sediments, a 48-hour period was adopted as an acceptable equilibrium time for adsorption equilibrium work. The continued slow, steady increase in the adsorption of diquat by the sediments agrees with that of diquat adsorption by soils as indicated in a review by Knight and Tomlinson (1970). They concluded that the chemical was redistributed in soils, particularly in peat or muck soils. Ostensibly, diquat is initially

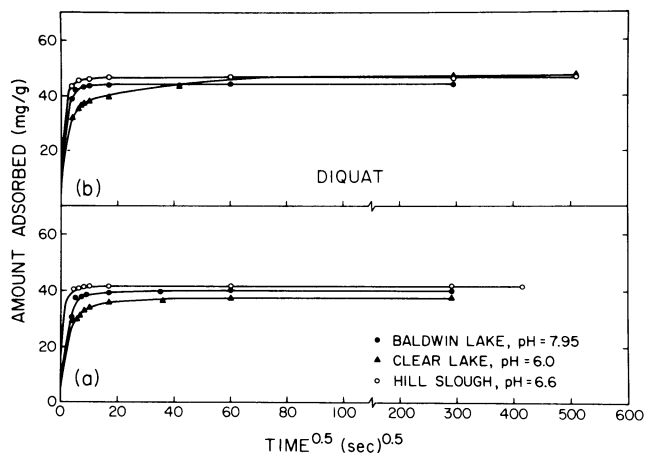


Fig. 4. Diquat adsorption equilibrium kinetics at 25°C: amount of diquat adsorbed vs.  $\text{time}^{0.5}$  for three freshwater sediments using initial solution concentrations of (a) 10,000  $\mu\text{g/mL}$ , and (b) 20,000  $\mu\text{g/mL}$ .

TABLE 9. RATE CONSTANTS AND GIBBS FREE ENERGY OF ACTIVATION FOR THE ADSORPTION OF DIQUAT AT TWO CONCENTRATIONS ON THREE SELECTED SEDIMENTS

Sediment sample	Initial concentration $\mu\text{g/mL}$	Rate constant $k'$ $\text{sec}^{-1}$	Gibbs free energy of activation $\Delta G^\ddagger$ $\text{kcal/mole}$
Baldwin Lake	10,000	0.012	20.1
	20,000	0.014	20.0
Clear Lake	10,000	$2.78 \times 10^{-3}$	20.9
	20,000	$2.60 \times 10^{-3}$	21.0
Hill Slough	10,000	0.014	20.0
	20,000	0.016	19.9

reversibly adsorbed onto the organic matter of soil, but with time there is a migration to clay surfaces. Adsorption in soils and in sediments seems to follow the general pattern of an initially rapid physical adsorption followed by the slow establishment of stronger chemisorption bonds.

The adsorption equilibrium data for diquat on treated and untreated sediment samples conformed quite well to the linear form of the Langmuir equation,

$$\frac{C}{S} = \frac{1}{kb} + \frac{C}{b}, \quad [25]$$

where  $S$  is the amount of chemical adsorbed per unit weight of adsorbent ( $\mu\text{g/g}$ ),  $C$  is the equilibrium solution concentration ( $\mu\text{g/mL}$ ),  $b$  is the adsorption maximum, and  $k$  is an affinity constant related to the bonding energy of adsorbent to adsorbate. Linear regression lines were calculated and the Langmuir constants  $b$  and  $k$  were found for each of the eight sediments (table 10). The  $r^2$  values for the regression lines ranged from 0.993 to 1.000, indicating that the adsorption data conformed extremely well to the Langmuir linear equation over the selected range of concentrations.

As expected for a cationic herbicide, the adsorption maxima for diquat were relatively high. Like previous studies on montmorillonite (Weber, Perry, and Upchurch 1965), this study showed temperature to have for the most part little or no effect upon the adsorption of diquat over the relatively narrow range of observed temperatures,  $5^\circ$  and  $25^\circ\text{C}$ . Though this is not readily apparent from the calculated Langmuir adsorption constants of table 10, it becomes much more obvious when the adsorption isotherms at  $5^\circ$  and  $25^\circ\text{C}$  for each sediment are plotted (fig. 5). Castle Lake and Hill Slough sediments are notable exceptions—increased temperatures resulted in a conspicuous increase of their adsorption maxima. This direct relationship of temperature to adsorption maximum was also observed by Weber, Perry, and Upchurch, but on charcoal.

A qualitative comparison of diquat adsorption isotherms and their corresponding Langmuir adsorption constants at  $25^\circ\text{C}$  for the treated and untreated sediments revealed expected results (table 10). The removal of the organic matter fraction with  $\text{H}_2\text{O}_2$  resulted only in a slight decrease of the adsorption maximum for Baldwin Lake, Mockingbird Canyon Reservoir, and San Joaquin Marsh sediments, since their organic matter fractions were very low (below 4.1 percent). In all other cases, removal of the organic matter produced a significant reduction in the adsorption, indicating the importance of organic matter as a supplier of adsorption sites. The removal of  $\text{CaCO}_3$  from the mineral fraction after the

TABLE 10. LANGMUIR ADSORPTION MAXIMA AND AFFINITY CONSTANTS FOR DIQUAT ON UNTREATED AND TREATED FRESHWATER SEDIMENTS (0.25-MM-SCREENED FRACTION)

Sample site	Untreated samples						Treated samples at 25°C					
	Untreated at 5°C			Untreated at 25°C			H <sub>2</sub> O <sub>2</sub>		NaOAc + H <sub>2</sub> O <sub>2</sub> <sup>†</sup>		NaOAc + H <sub>2</sub> O <sub>2</sub> + 600°C <sup>‡</sup>	
	b μg/g	k × 10 <sup>-3</sup> mL/μg	b μg/g	k × 10 <sup>-3</sup> mL/μg	b μg/g	k × 10 <sup>-3</sup> mL/μg	b μg/g	k × 10 <sup>-3</sup> mL/μg	b μg/g	k × 10 <sup>-3</sup> mL/μg	b μg/g	k × 10 <sup>-3</sup> mL/μg
Baldwin Lake	42,553	14.3	44,053	8.66	42,918	12.6	74,074	8.57	54,645	11.9		
Big Bear Lake	53,476	5.43	52,356	8.95	40,650	10.6	42,918	13.2	27,993	23.8		
Castle Lake	18,975	1.28	24,390	0.52	5,510	1.41	4,950	2.27	4,636	13.6		
Clear Lake	46,948	2.15	48,309	1.51	28,736	2.01	29,940	3.91	22,026	4.46		
Hill Slough	46,296	4.59	53,191	6.19	43,668	3.34	39,526	20.4	25,253	1.60		
Jenks Lake	24,038	2.06	24,311	2.54	18,727	4.25	16,750	0	7,675	6.94		
Mockingbird Canyon Reservoir	44,248	10.4	43,860	10.7	42,373	12.2	38,314	16.8	13,495	0		
San Joaquin Marsh	65,359	8.03	69,930	11.7	68,966	21.6	80,000	17.2	50,505	10.2		

\*Treated with H<sub>2</sub>O<sub>2</sub> for the removal of the organic matter fraction.

<sup>†</sup>Treated with in sodium acetate followed by H<sub>2</sub>O<sub>2</sub> to remove soluble salts, CaCO<sub>3</sub> and organic matter.

<sup>‡</sup>Treated with in 1 N NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> · 3H<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub>, and heated to 600°C for 2 hours to leave a mineral fraction with only external surfaces.

organic matter had been removed (1 N  $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O} + \text{H}_2\text{O}_2$  treatment) resulted in increased adsorption for Baldwin Lake, Big Bear Lake, and San Joaquin Marsh sediments. This result was expected, since the removal of  $\text{CaCO}_3$  is known to reduce the competition of  $\text{Ca}^{+2}$  for exchange sites. In addition, each sediment had a sizable amount of  $\text{CaCO}_3$  present, and  $\text{CaCO}_3$  would not be expected to offer any adsorption sites. The fact that Mockingbird Canyon Reservoir actually decreased when its sizable  $\text{CaCO}_3$  fraction was removed is not readily explained. A comparison of the adsorption of diquat on the external surfaces of each sediment's mineral fraction (1 N  $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O} + \text{H}_2\text{O}_2 + 600^\circ\text{C}$  treatment) and on the entire mineral fraction (1 N  $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O} + \text{H}_2\text{O}_2$  treatment) indicated that in most cases the majority of adsorption occurred on the external surfaces even though the internal surface area was greater. Steric hindrance and charge density differences between external and internal surfaces seem to be possible causes. Mockingbird Canyon Reservoir sediment is the only obvious exception to the predominance of external surface adsorption.

Correlations between individual sediment properties and the Langmuir affinity constant  $k$  are shown in table 11. Surface area was the only property that correlated highly to the affinity constant, with a correlation coefficient of 0.937. Even though only a moderate negative correlation existed between charge density  $\sigma$  and  $k$ , a plot of  $\sigma$  and  $k$  revealed a particularly interesting exponential relationship (fig. 6). The affinity constant  $k$  increases exponentially as a function of decreasing charge density. This means that the charge separation of diquat is such that a charge density on the adsorbent surface of approximately 0.2 coulombs/m<sup>2</sup> ( $6 \times 10^4$  esu/cm<sup>2</sup>) results in the greatest bonding energy of adsorbent for diquat over the range of observed charge densities. Knowledge of the charge density of an adsorbent permits a means of approximating the affinity constant from the "best fit" equation,

$$k = 0.0508 (0.001)^\sigma - 0.0012, \quad [26]$$

where  $\sigma$  is the charge density in coulombs/m<sup>2</sup>.

Table 12 provides a similar linear regression analysis for the Langmuir adsorption maxima  $b$ . On the basis of individual sediment properties,  $b$  also correlates well with surface area ( $r = 0.904$ ). Previous work with diquat has demonstrated that diquat adsorption on

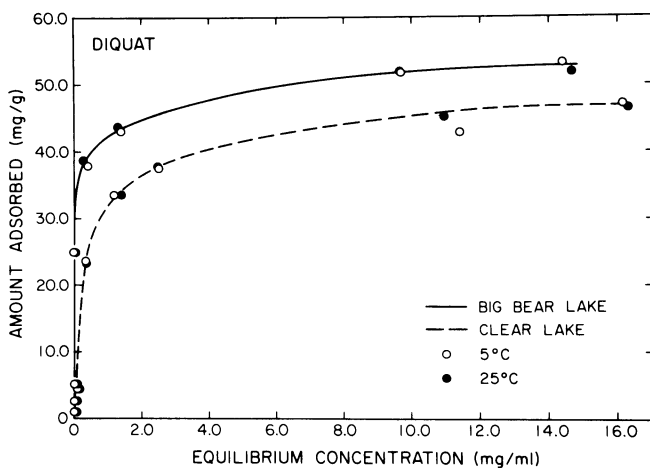


Fig. 5. Representative adsorption equilibrium isotherms at 5°C and 25°C, for Big Bear Lake and Clear Lake sediments.



clays was related directly to the clays' cation exchange capacity, and as such involved an ion-exchange mechanism of adsorption (Dixon et al. 1970; Gamar and Mustafa 1975; Philen, Weed, and Weber 1970; Weber, Ward, and Weed 1968; Weber and Weed 1968). This is also the case for the eight sediments after they were treated to remove organic

TABLE 11. LINEAR REGRESSION ANALYSIS OF LANGMUIR AFFINITY CONSTANTS,  $k$ , AND INDIVIDUAL SEDIMENT PROPERTIES FOR DIQUAT AT 25°C

Soil property	Correlation coefficient $r$	Regression equation $k \times 10^{-3} =$	$r^2$
Exchange acidity	-0.846	11.695 - 0.554 exchange acidity	0.716
pH <sub>1.5</sub> (0.01 M CaCl <sub>2</sub> )	0.816	-16.586 + 3.580 pH <sub>1.5</sub>	0.665
Organic matter	-0.699	9.963 - 0.372 percentage organic matter	0.489
Organic carbon	-0.722	9.989 - 0.597 percentage organic carbon	0.522
Dry ash	-0.722	10.332 - 0.424 percentage dry ash	0.521
Clay	0.612	-2.070 + 0.167 percentage clay	0.375
Fe <sub>2</sub> O <sub>3</sub>	-0.246	7.966 - 1.757 percentage Fe <sub>2</sub> O <sub>3</sub>	0.061
Exchangeable bases	0.590	0.262 + 0.178 exchangeable bases	0.349
Untreated sediment sample:			
Total area	0.937	-4.425 + 0.075 total area	0.878
Total cation exchange capacity	0.233	2.778 + 0.081 exchange capacity	0.054
Charge density	-0.884	17.113 - 33.295 charge density	0.782
Sediment sample treated with H <sub>2</sub> O <sub>2</sub> to remove organic matter:			
Total area	0.836	0.209 + 0.077 total area	0.699
Total cation exchange capacity	0.739	3.956 + 0.398 exchange capacity	0.547
Charge density	-0.590	20.359 - 37.541 charge density	0.348

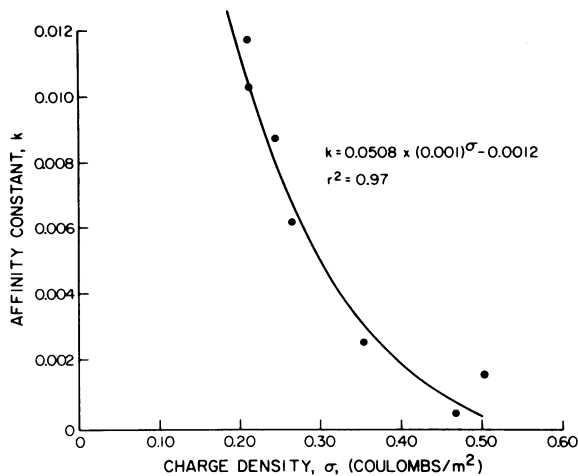


Fig. 6. Langmuir affinity constant,  $k$ , for diquat, as related to the charge density,  $\sigma$ , of seven freshwater sediments.

matter ( $r = 0.904$ ). Untreated sediments showed little correlation between total cation exchange capacity and  $b$  ( $r = 0.658$ ). Apparently, the organic matter fraction influences the ion exchange process through its effects on the structure of solvating water of the macromolecular organic matter, since water structure is important in determining the extent of adsorption (Hamaker and Thompson 1972).

TABLE 12. LINEAR REGRESSION ANALYSIS OF LANGMUIR ADSORPTION MAXIMA,  $b$ , AND INDIVIDUAL SEDIMENT PROPERTIES FOR DIQUAT AT 25°C

Soil property	Correlation coefficient $r$	Regression equation $b \times 10^3 =$		$r^2$
Exchange acidity	-0.389	48.490 - 0.685	exchange acidity	0.151
pH <sub>1:5</sub> (0.01 M CaCl <sub>2</sub> )	0.677	20.786 + 10.267	pH <sub>1:5</sub>	0.458
Organic matter	-0.280	50.115 - 0.521	percentage organic matter	0.078
Organic carbon	-0.294	50.245 - 0.851	percentage organic carbon	0.087
Dry ash	-0.353	51.862 - 0.724	percentage dry ash	0.125
Clay	0.619	15.297 + 0.592	percentage clay	0.383
Fe <sub>2</sub> O <sub>3</sub>	-0.256	50.943 - 6.385	percentage Fe <sub>2</sub> O <sub>3</sub>	0.066
Exchangeable bases	0.769	17.344 + 0.811	exchangeable bases	0.592
Untreated sediment sample:				
Total area	0.904	8.729 + 0.254	total area	0.817
Total cation exchange capacity	0.658	9.824 + 0.804	total cation exchange capacity	0.433
Charge density	-0.485	65.733 - 63.853	charge density	0.235
Sediment sample treated with H <sub>2</sub> O <sub>2</sub> to remove organic matter:				
Total area	0.893	11.165 + 0.223	total area	0.798
Total cation exchange capacity	0.904	-4.954 + 1.322	total cation exchange capacity	0.818
Charge density	-0.577	67.953 - 99.754	charge density	0.333

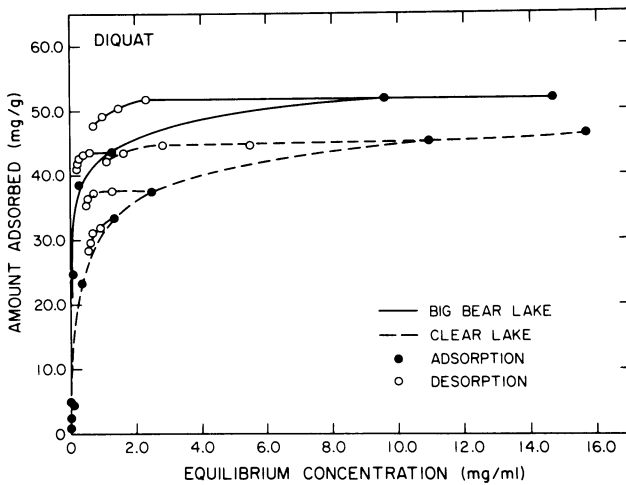


Fig. 7. Representative diquat adsorption-desorption equilibrium isotherms at 25°C, for Big Bear Lake and Clear Lake.

Diquat desorption studies were performed on each sediment at four initial adsorbate concentrations. Typical adsorption-desorption isotherm curves for diquat are plotted in figure 7. The desorption curves were described with the linear form of the Langmuir equation. Table 13 summarizes the adsorption maxima  $b$  and affinity constants  $k$  calculated for each desorption curve, using linear regression analysis. For all eight sediments, diquat was adsorbed so tightly to the sediment surface for an initial adsorbate concentration of 2,500  $\mu\text{g/g}$  that no desorption occurred. Presumably, at very high adsorbate concentrations, sorption includes both ion exchange and partitioning into the organic carbon fraction. At the lower adsorbate concentrations, sorption is essentially the result of ion exchange alone. The strong bond of ion exchange holds diquat so tightly that no desorption can occur for any of the eight sediments at initial adsorbate concentrations below 2,500  $\mu\text{g/g}$ . A linear relationship was found to exist for diquat as for bromacil, between the slope ( $1/b$ )

TABLE 13. LINEAR REGRESSION ANALYSIS OF LANGMUIR DESORPTION ISOTHERMS FOR DIQUAT ON EIGHT FRESHWATER SEDIMENTS AT 25°C

Sediment sample	$S_o^*$ $\mu\text{g/g}$	Adsorption maxima $b$	Affinity constants $k$	Regression equations $1/b$	$r^2$
Baldwin Lake	2,500	—†	—†	$4.95 \times 10^{-5}$	0.99
	37,240	37,453	0.350	$-(6.13 \times 10^{-10}) S_o$	
	40,400	40,650	0.053		
	43,125	43,290	0.011		
Big Bear Lake	2,500	—†	—†	$3.66 \times 10^{-5}$	0.95
	38,600	42,735	0.034	$-(3.32 \times 10^{-10}) S_o$	
	43,535	44,053	0.075		
	52,000	52,356	0.019		
Castle Lake	2,500	—†	—†	$1.009 \times 10^{-4}$	0.99
	16,250	16,722	0.0087	$-(2.57 \times 10^{-9}) S_o$	
	18,125	18,657	0.0063		
	22,250	22,676	0.0042		
Clear Lake	2,500	—†	—†	$4.13 \times 10^{-5}$	0.91
	33,500	37,594	0.0063	$-(4.22 \times 10^{-10}) S_o$	
	37,700	38,023	0.050		
	45,250	45,662	0.014		
Hill Slough	2,500	—†	—†	$4.48 \times 10^{-5}$	0.99
	38,030	38,168	0.755	$-(4.94 \times 10^{-10}) S_o$	
	43,060	43,290	0.130		
	52,375	52,632	0.012		
Jenks Lake	2,500	—†	—†	$8.35 \times 10^{-5}$	1.00
	21,100	21,552	0.013	$-(1.76 \times 10^{-9}) S_o$	
	22,200	22,472	0.015		
	24,463	24,691	0.007		
Mockingbird Canyon Reservoir	2,500	—†	—†	$4.94 \times 10^{-5}$	1.00
	37,500	37,594	0.573	$-(6.09 \times 10^{-10}) S_o$	
	40,850	40,984	0.285		
	43,750	43,860	0.382		
San Joaquin Marsh	2,500	—†	—†	$3.83 \times 10^{-5}$	0.98
	39,880	40,000	1.53	$-(3.48 \times 10^{-9}) S_o$	
	49,530	49,505	1.35		
	69,500	69,444	1.22		

\*Initial adsorbate concentration at which desorption began.

†No desorption was detected at  $S_o = 2,500 \mu\text{g/g}$ .

of the desorption isotherm and the initial adsorbate concentration from which desorption occurred. In table 13,  $r^2$  values close to unity confirm the close relationship between the slope of the desorption isotherms for each sediment and the initial adsorbate concentration on the adsorbent surface.

### Diffusion model simulations

Figure 8 illustrates the diffusion of bromacil through each of the eight freshwater sediments, as influenced by temperature, assuming that degradation proceeds at a constant rate irrespective of temperature changes. Degradation, however, is usually temperature-dependent, and lowering the temperature could reduce the degradation rate. The lack of data on the degradation rate of bromacil necessitated the assumption of a constant degradation rate with temperature change. For the same reason, it was also assumed that  $\mu_s$  for bromacil was equal to zero (see eq. 1). Baldwin Lake sediment shows the smallest effect of temperature on the diffusion process (fig. 8a); consequently, only a small change in the rate of diffusion would be detectable between winter and summer at a given site. The opposite is true of Clear Lake sediment, which would demonstrate a rather wide range of diffusion rates as temperature changed (fig. 8d).

Temperature can significantly influence both the physical and chemical aspects of the diffusion process. Since the adsorption of bromacil is an exothermic reaction, adsorption decreases at higher temperatures, thereby lowering the retardation effect of adsorption. Diffusion is more rapid, since more chemical remains in solution. The temperature effect

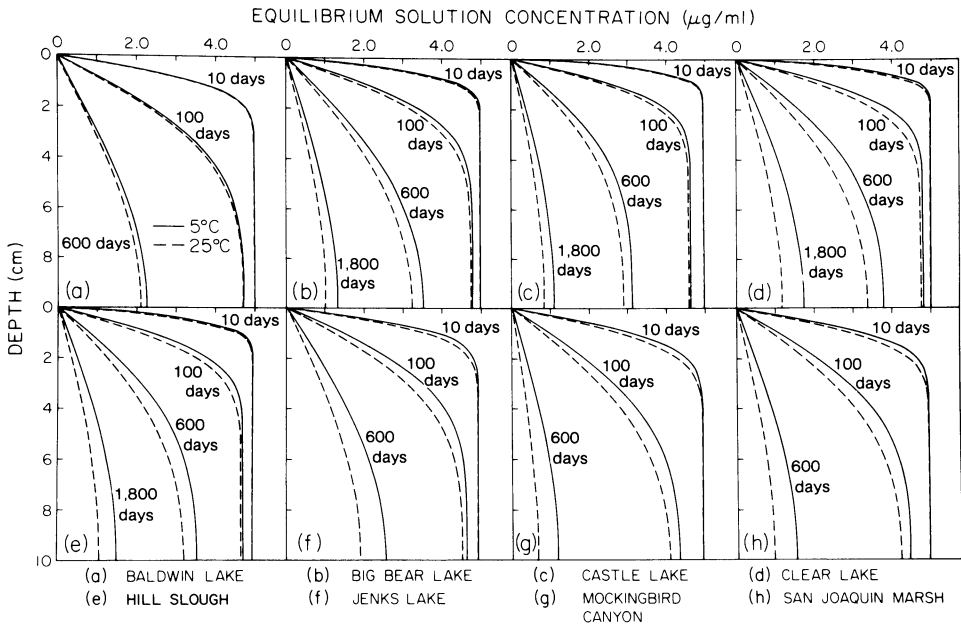


Fig. 8. Influence of temperature, 5° and 25°C, on the simulated diffusion of bromacil through eight freshwater sediments. Initial equilibrium solution concentration is 5 µg/mL; degradation rate is assumed constant with temperature, at  $\mu_l$  0.00347/day; aqueous diffusion coefficient,  $D$ , at 5°C is 0.2087 cm<sup>2</sup>/day; and  $D$  at 25°C is 0.2160 cm<sup>2</sup>/day.



is complicated further when bromacil's solubility is considered. In addition, lower temperatures decrease the molecular diffusion coefficient. The net result is a concentration range within which the potential equilibrium solution concentration distributions for bromacil will most likely occur after a given time at sediment temperatures between 5°C and 25°C, disregarding any hysteretic effects.

A comparison of figures 8a through b shows that the fastest diffusion occurs in Mockingbird Canyon Reservoir sediment at 25°C, while the slowest occurs in Clear Lake sediment at 5°C. After 600 days, only 8.4 percent of the initial bromacil equilibrium solution concentration remains in Mockingbird Canyon Reservoir sediment at 25°C, while 53.2 percent remains in Clear Lake sediment at 5°C. Mockingbird Canyon Reservoir sediment is characterized by a high bulk density, high volumetric water content, low strength of adsorption, and nearly linear adsorption isotherm. In contrast, Clear Lake sediment has a low bulk density, low volumetric water content, high strength of adsorption, and nearly linear adsorption isotherm. Since Clear Lake and Mockingbird Canyon Reservoir are representative cases of low and high diffusion, respectively, further references and comparisons will be restricted primarily to these two sediments.

Figure 9 shows the adsorbed phase distribution of bromacil for Clear Lake and Mockingbird Canyon Reservoir sediments for the same time periods as figure 8. As expected, the sediment that displays less adsorption (Mockingbird Canyon Reservoir) will have a greater proportion of bromacil removed by diffusion and degradation processes. For example, less than 10 percent of the initial adsorbate concentration of bromacil remains on Mockingbird Canyon Reservoir sediment after 600 days, but approximately 50 percent remains on the Clear Lake sediment. The net release of pesticide from the adsorbed and solution phases into the overlying water, however, is of greater environmental concern.

Generally, the net contribution of a pesticide from the adsorbed and solution phases of a high-organic-matter sediment is great because that sediment adsorbs more pesticide, and ends up with more accumulated pesticide to release. This generality applies when comparing two sediments with the same bulk density, but with variations in pesticide adsorptive capacity caused primarily by organic matter content. For instance, assuming similar bulk densities, after 600 days the combined solution and adsorbed phases of Clear

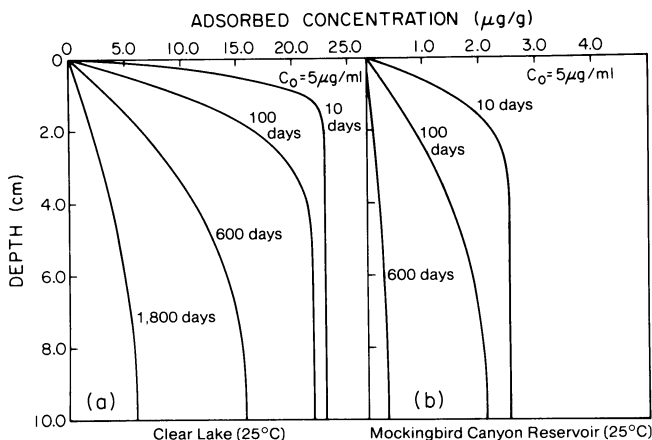


Fig. 9. Adsorbed phase concentration for the simulated diffusion of bromacil through two freshwater sediments, (a) Clear Lake and (b) Mockingbird Canyon Reservoir.  $C_0$  refers to the initial equilibrium solution concentration.

Lake sediment would release nearly twice as much pesticide into the overlying water as would Mockingbird Canyon Reservoir sediment. Taking the true bulk densities into account, however, the net releases of the two sediments are approximately equal. If pollution of the overlying aqueous solution is the primary concern, due to a concern for the sensitivity of fish to organic pollutants, then at an equivalent initial equilibrium solution concentration Clear Lake and Mockingbird Canyon Reservoir will have similar pollution hazard potentials. On the other hand, filter-feeding organisms that graze for organic matter within the top few centimeters of sediment will encounter high pesticide concentrations on particles that have high adsorptive capacities, as in Clear Lake. Either for fish or for benthic organisms, the pollution level of Clear Lake appears to pose a potential threat.

Using the diffusion model, the effect of degradation can be separated from the physical process of diffusion in the overall removal of bromacil from the equilibrium solution (fig. 10). The adsorption process complicates degradation, since it determines the amount of pesticide that will remain in the solution and adsorbed phases. This partitioning can affect the degradation rate since solution and adsorbed phase degradation rates may differ significantly. In Clear Lake sediment approximately 85.7 percent of the initial equilibrium solution concentration remains after 100 days without allowance for degradation, while 80.9 percent remains with allowance for degradation. After 600 days, 65.7 percent and 46.4 percent remain, respectively. Mockingbird Canyon Reservoir sediment does not display as much increasing difference with time: approximately 66.9 percent of the initial bromacil solution concentration remains after 100 days without degradation, and 56.1 percent remains with degradation; while after 600 days, 23.3 percent and 8.5 percent remain, respectively. Because of the greater adsorption of bromacil by Clear Lake sediment than by Mockingbird Canyon Reservoir sediment, the degradation process plays a more significant role in the removal of Clear Lake's bromacil, since bromacil persists there for a greater length of time. The small initial influence of degradation on the removal of bromacil from the equilibrium solution for Clear Lake sediment is caused by the small amount that remains in solution due to the high degree of adsorption. The greater retardation of movement of bromacil in Clear Lake sediment causes more bromacil to be removed by degradation with increased time, since it is slowly released into solution where it can undergo degradation. In the case of Mockingbird Canyon Reservoir there is comparatively

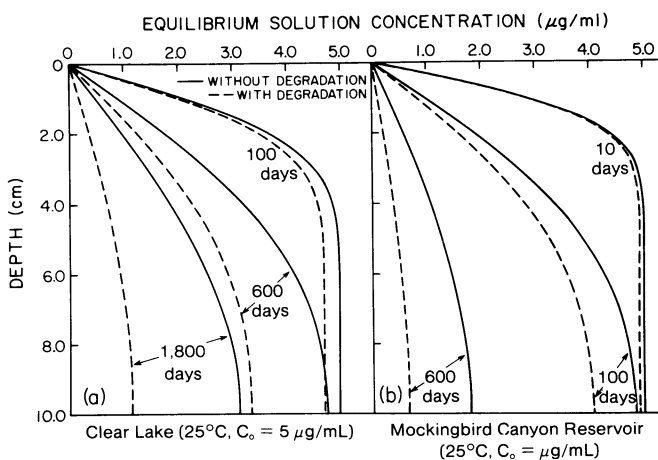


Fig. 10. Effect of degradation on the equilibrium solution concentration,  $C_0$ , for simulated diffusion of bromacil in (a) Clear Lake and (b) Mockingbird Canyon Reservoir.

less degradation, since bromacil is removed more by diffusion than degradation. Degradation plays an extremely crucial role in the removal of bromacil both from solution and, directly or indirectly, from the adsorbed phase. Even if degradation does not occur in the adsorbed phase, as assumed in our model, it most certainly will decrease the equilibrium solution concentration, and in turn cause desorption of the pesticide from the adsorbed phase.

Because bromacil adsorption is nonlinear, higher initial concentrations will leave greater proportions of bromacil in the equilibrium solution, relative to the initial solution concentration (fig. 11). Higher initial solution concentrations diffuse more rapidly because proportionally lower amounts of bromacil are adsorbed. Since Big Bear Lake exhibits the greatest nonlinearity of adsorption ( $1/n = 0.86$ ), the difference in diffusion rates for low and high initial solution concentrations are greater for this sediment than for the others.

Figure 12 compares the equilibrium solution concentration distributions for bromacil diffusion with hysteretic and nonhysteretic treatment of the adsorption-desorption reactions at two initial concentrations and for three sediments (Big Bear Lake, Castle Lake, and Clear Lake). In the diffusion problem outlined by equations 3 and 8a through c, the sediments continually desorb pesticide material because of the constant decrease in solution concentration that results from the diffusion and degradation processes, so the use of desorption isotherms as in table 8 seems appropriate. The use of the batch-technique Freundlich coefficients for desorption isotherms,  $K_{des}$  and  $1/n$ , produces slight but important differences between the equilibrium solution concentrations of hysteretic and nonhysteretic curves (fig. 12). Hysteresis is most significant for Big Bear Lake (fig. 12a and b). The data

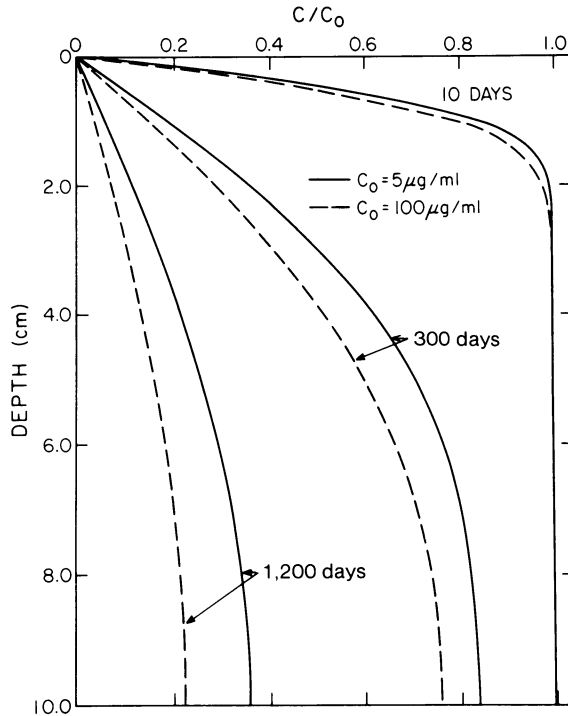


Fig. 11. Effect of the initial equilibrium solution concentration,  $C_0$ , on the simulated diffusion of bromacil through Big Bear Lake sediment.

in figures 12a, b, c, and f imply that, because of increased adsorption, hysteresis reduces the amount of bromacil available for diffusion in the solution phase. This is confirmed by the determination of the total amount of bromacil remaining in the sediment profile, which is greater for hysteresis than for no hysteresis. Figures 12d and e demonstrate a retardation of the diffusion process for the solution phase as well. Determination of the total amount of bromacil remaining in the sediment profile for figures 12d and e, similarly, shows the retardation of the diffusion process under hysteresis. But although hysteresis slows diffusion out of the sediment, the equilibrium solution concentration for hysteresis may be either greater or less than for no hysteresis, depending on time and individual sediment characteristics.

The diffusion of diquat is shown in figure 13 for each of the eight freshwater sediments, at 5° and 25°C. Unlike bromacil, diquat at 5°C did not always diffuse slower than at 25°C. The dominant factor determining the net effect of temperature on diquat's diffusion is the specific effect temperature has upon the adsorption-desorption process of each individual sediment (table 10). Baldwin Lake, Castle Lake, and Clear Lake demonstrate an increased retardation of diquat with decrease in temperature (like bromacil), while Big Bear Lake, Hill Slough, Jenks Lake, and San Joaquin Marsh show an increased diffusion rate brought about by a decrease in adsorption. Mockingbird Canyon Reservoir sediment seemed unaffected by temperature over the narrow range of observation. Diquat diffusion was the most rapid for Castle Lake, 25°C. The slowest diffusion was for San Joaquin Marsh, 5°C.

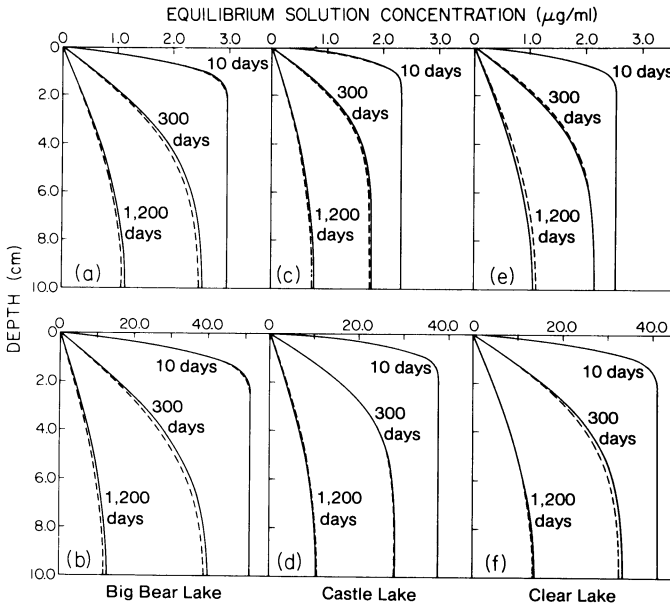


Fig. 12. Comparisons of hysteretic (*broken line*) and nonhysteretic (*solid line*) adsorption as they influence the simulated diffusion of bromacil through three freshwater sediments at two initial equilibrium solution concentrations: Big Bear Lake at  $C_o$  (a)  $3.0 \mu\text{g/mL}$  and (b)  $51.75 \mu\text{g/mL}$ , Castle Lake at  $C_o$  (c)  $2.35 \mu\text{g/mL}$  and (d)  $38.19 \mu\text{g/mL}$ , and Clear Lake at  $C_o$  (e)  $2.55 \mu\text{g/mL}$  and (f)  $41.35 \mu\text{g/mL}$ .

A number of properties and conditions influence the diffusion of diquat: hysteresis, adsorption capacity, nonlinearity of adsorption, porosity, bulk density, temperature, concentration gradient, and diffusion coefficient. Aside from temperature and adsorption interactions, these properties influence the diffusion of diquat in a similar manner. The greatest contrasting feature between bromacil and diquat is the extremely high and tenacious adsorption of diquat by the sediments. This is to be expected, since bromacil's adsorption is by nonpolar partitioning, while diquat is adsorbed by ion exchange. The strong adsorption of diquat makes the degradation rate of the adsorbed phase an extremely important factor in judging its pollution potential. Filter-feeding organisms are, presumably, threatened by the ingestion of organic materials containing high levels of adsorbed diquat. Since diquat is held so strongly, the only means of removing it as a threat to benthic organisms is by degradation. There is little data available concerning the degradation of adsorbed diquat, but diquat appears to persist in the adsorbed phase for a very long time (Weed Science Society of America 1974). It is essential, therefore, to have some understanding of the physiological effects that strongly adsorbed pesticides have upon benthic organisms when they are ingested. It must be known whether or not diquat is totally biologically inactive and nontoxic in the adsorbed state.

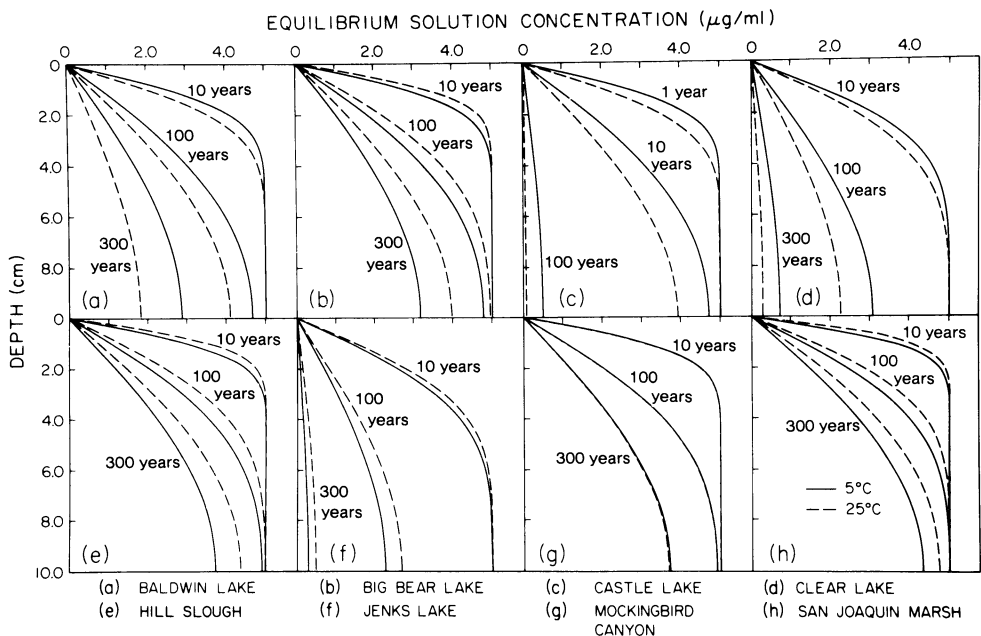


Fig. 13. Influence of temperature, 5° and 25°C, on the simulated diffusion of diquat through eight freshwater sediments. Initial equilibrium solution concentration is 5 µg/mL; degradation rate is assumed negligible ( $\mu_l = \mu_s = 0$ ); aqueous diffusion coefficient,  $D$ , at 5°C is 0.2087 cm<sup>2</sup>/day; and  $D$  at 25°C is 0.2160 cm<sup>2</sup>/day.

## CONCLUSIONS

A mathematical model has been developed to provide quantitative information for assessing the pollution potential of a pesticide diffusing from a bottom sediment into an overlying water body. An explicit finite-difference solution to the general diffusion equation for a sorbing porous medium under saturated conditions is given. The finite-difference solution satisfies boundary conditions descriptive of a stream or well-mixed lake. By entering descriptive physical and chemical parameters, the solution generates equilibrium-solution and adsorbed-phase concentration distributions through the sediment at selected time intervals.

Before determining whether a pesticide can pose a threat to the aquatic environment, it is necessary to consider which compartment of the aquatic environment will prove most sensitive to the pesticide's presence. This can be accomplished by determining in which compartment of the aquatic environment the most sensitive organism resides or interacts. Since many fish are especially sensitive to low pesticide concentrations, the overlying water body is often viewed as the critical portion of the aquatic environment. Organic sediments, however, can adsorb high pesticide concentrations. When ingested by filter-feeding benthic organisms, these sediments can in turn concentrate the pesticide to many times the ambient concentration, and then pass it further up the food chain. If the pesticide does not degrade to any great extent in the adsorbed phase, it can remain adsorbed in a biologically inactive state for a considerable period, and then desorb into the solution phase. This could extend the expected persistence of the pesticide within the sediment. All these factors must be considered before a pesticide can be assessed for its potential as a pollutant hazard.

A number of interacting physical, chemical, and biological factors influence the diffusion process. These include temperature, the chemical nature of the pesticide, adsorption-desorption processes, the presence or absence of adsorption hysteresis, initial pesticide concentration levels, degradation, and the physical and chemical properties of the sediment.

Bromacil is a modestly adsorbed herbicide that diffuses less in sediments of cooler climates than in those of warmer climates. A broad range of diffusion rates would be expected for sediments that vary widely in their physical and chemical properties (organic matter content, pH, volumetric water content, and bulk density). Properties such as organic matter content, exchange acidity, free iron oxides, and clay content all influence the adsorption of bromacil, and in turn retard diffusion. Bulk density and volumetric water content are physical properties that influence the extent of adsorption and the diffusion path, respectively. Because the diffusion of bromacil through mineral and organic sediments is slow, degradation plays a significant role in the removal of bromacil from the aquatic environment. Hysteresis can also potentially influence the degree to which a pesticide is available for migration via diffusion.

An analysis of the eight sediments at the same initial equilibrium solution concentration shows that Clear Lake sediment retains bromacil to the greatest degree, while Mockingbird Canyon Reservoir sediment releases proportionally more bromacil into the overlying water. In general, the sediments with higher adsorptive capacities do not release bromacil as quickly in proportion to the initial equilibrium concentration as do those with lower capacities, but the greater amount of bromacil adsorbed to the higher adsorption capacity sediments acts as a continued source of the pesticide. The result of the high adsorptive capacity is that the net release of pesticide to the overlying water is greater for these sediments.

In contrast to bromacil, diquat is very strongly adsorbed, and as such persists for a very long period in a biologically inactive state. Whether or not diquat poses an actual threat



to any of the benthic organisms that ingest contaminated sediment particles remains to be experimentally explored. Nevertheless, potentially high concentrations of diquat could accumulate in these organisms and move up the food chain. Diquat's greatest threat to aquatic organisms and their predators is not through diffusion, but through ingested organic sediment material carrying adsorbed diquat. Of the eight freshwater sediments, San Joaquin Marsh poses a greater potential threat than any of the other sediments because of its greater adsorptive capacity.

Further research in pesticide persistence and the kinetics of biological and chemical degradation is necessary for accurate evaluation of the threat of these chemicals to the aquatic environment. No real confidence can be given to assessments such as the one proposed in this model unless half-lives for the specific set of conditions are available. Widely varying half-lives can be found in the literature for a single pesticide, depending upon the conditions under which degradation was observed. A more complete study of pesticide half-lives under aerobic and anaerobic conditions, on adsorbed surfaces and in solution, must be conducted before assessment models can have practical value for a broad range of pesticides and sediments.

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