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Nonsingle-Valued Adsorption–Desorption of Bromacil and Diquat by Freshwater Sediments

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■ The adsorption and desorption of bromacil and diquat on eight freshwater sediments were studied. Nonsingle-valued adsorption–desorption isotherms of bromacil conformed to a set of Freundlich equations, while diquat nonsingular adsorption–desorption isotherms were best described by a set of Langmuir equations. A high degree of positive correlation was found to exist between the degree of bromacil adsorption and the sediment properties of organic carbon content and of charge density. Calculated Freundlich adsorption coefficients for bromacil ranged from 0.891 to 0.984 for $1/n$ and from 0.556 to 6.353 for K. The Langmuir affinity constant, k, for diquat adsorption on untreated sediments correlated well with the surface area while the adsorption maxima, b, correlated highly with the CEC for sediments treated for the removal of organic matter. For untreated sediments the Langmuir adsorption affinity constants ranged from 0.52×10^{-3} to 11.7×10^{-3} and the adsorption maxima ranged from 24 331 to 69 930. In general, the adsorption maxima for treated sediments decreased while the affinity constants increased when compared to the Langmuir coefficients of the untreated sediments. A surface charge density of approximately $0.2\ \mathrm{C/m^2}$ ($6 \times 10^4\ \mathrm{esu/cm^2}$) was found to result in the greatest bonding energy of the sediments for diquat. Desorption studies for both bromacil and diquat revealed that a linear relationship existed between the slope of the desorption isotherms and the initial adsorbate concentration from which desorption started.

Introduction

Recently, particular interest has been given to pesticide–sediment–water interactions (*1–8*) since the aquatic environment constitutes a potential sink for many pesticides as a result of direct application, accidental spills, and/or "piggyback" transport upon eroded soil particles or in runoff waters.

Pesticides are known to be toxic to aquatic life over wide ranges of concentrations. Substantial differences in susceptibility to different compounds exist between and within species. For example, 96-h LC50 values of from 5 to 610 000 μg/L were reported for various species of fish exposed to organophosphate pesticides (*9*). Since very low concentrations of certain pesticides can be potentially toxic to fish and other forms of aquatic life, it is important to have a knowledge of the chemical dynamics of pesticide–sediment–water interactions. As a result, one of the areas of prime consideration in pesticide–sediment–water interactions has been that of the adsorption and desorption of pesticides by sediments.

Adsorption–desorption pesticide studies have revealed that, in many instances, the desorption process is not completely reversible. This is not to say that there is true irreversibility of the desorption process but rather that the kinetics of desorption may be such that the desorption and adsorption paths are nonsingular. The observed hysteries of the desorption of pesticides by soils (*10–15*) and sediments (*16, 17*) is of importance due to the fact that it results in a release of pesticide to the soil solution which is impossible to predict from adsorption isotherm data alone. Even when desorption isotherm data are available, it is difficult to predict the partitioning of the pesticide between the liquid and solid phases over long periods of time due to the continuous gradual change of pesticide concentration in the soil solution. Past models that have accounted for nonsingle-valued adsorption–desorption have been kinetic (*18, 19*) and empirically based models (*20*).

It will be the primary purpose of this paper to develop simple and multiple regression models from a compre-

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hensive adsorption–desorption study of two chemically dissimilar herbicides on a variety of freshwater sediments. These models will make it possible to predict various pesticide sorption parameters from sediment properties. Similarly, the problem of hysteresis will be addressed by using linear regression analysis of adsorption and desorption isotherms. This approach is presented as an alternate empirical approach to account for nonsingular adsorption–desorption. An additional intention of the paper is to provide some insight into the interrelationship between some of the physical and chemical properties of sediments which in turn may influence the adsorption–desorption process.

Materials and Methods

Sediment samples were collected from eight water bodies located throughout California. These sites were selected to provide sediment samples with a wide range of physical and chemical properties. Five of the sites were from southern California and included Mockingbird Canyon Reservoir in the Riverside vicinity which receives runoff from citrus groves, San Joaquin Marsh, which is a freshwater marsh reserve located on the UC Irvine campus, and three lakes located in the San Bernardino Mountains: Baldwin Lake, Big Bear Lake, and Jenks Lake. Baldwin Lake receives secondary effluent from Big Bear City sewage treatment facility while Big Bear Lake and Jenks Lake receive water from runoff, horizontal groundwater flow, and precipitation. The three northern California water bodies included Clear Lake, which is a eutrophic lake located in Lake County, Castle Lake, which is a moderately productive cirque lake located in Siskiyou County, and the Hill Slough just outside of Fairfield in the Sacramento Delta region of Solano County.

Samples collected at each of the eight water bodies consisted of 45-cm core and 15-cm composite core sediment samples and water samples from the sediment–water interface. The samples were collected in 7.5-cm (3-in.) diameter PVC tubes at water depths ranging from 1.5 to 6 m (*21*). All samples were immediately sealed and frozen.

Prior to use the sediment samples were freeze-dried and passed through a 2-mm screen to remove large organic debris and gravel. Initial adsorption studies with the less than 2-mm-size fraction revealed that reproducibility problems existed due to sample heterogeneity. This problem was rectified by preparing a subsample which had been ground by using a rubber-tipped pestle to pass a 60-mesh (0.25 mm) sieve. The use of the rubber-tipped pestle reduced physical abrasion, thereby helping to prevent the reduction of particles beyond their natural particle size.

The techniques commonly used in the characterization of soils were used for the characterization of both the less than 2-mm and the less than 0.25-mm fractions of the sediments. The organic carbon content was determined by the Walkley–Black method, while organic matter was determined by treatment with H_2O_2 following the removal of salts with 1 N sodium acetate adjusted to a pH of 4.5 with acetic acid. The specific surface area was determined according to the method outlined by Mortland and Kemper (*22*) which provided a means of determining the external and internal surface area. Particle size analysis was carried out by means of the pipet method, and the free iron oxides (percent Fe_2O_3) were determined by the method outlined by Olson (*23*). Dry ash was obtained by subjecting 30–40-g subsamples to 375 °C for 16 h after pretreatment at 110 °C for 24 h to remove any adsorbed water. Cation exchange capacity (CEC) and exchange acidity (EA) were determined through the use of methods outlined by Chapman and Pratt (*24*). Exchangeable bases (EB) were determined by difference.

Adsorption studies for bromacil were undertaken by using the radioassay batch technique and a 1 to 5 sediment to solution ratio. The 15-cm composite core sediment samples were used throughout the adsorption studies. Stock solutions of 1, 5, 10, 25, 50, 75, 100, and 300 μg/mL bromacil were prepared from ^{14}C-labeled and analytical grade herbicide in 0.01 M $CaCl_2$. Thin-layer chromatography performed on the radioactve-labeled samples revealed a purity of >98% for bromacil. Twenty milliliters of stock solution and 4 g of less than 0.25-mm sediment were placed in a Teflon-coated stainless steel tube and allowed to equilibrate by shaking in a constant temperature environmental chamber for 48 h. Initial kinetic studies had revealed that 48 h was sufficient time for the attainment of adsorption equilibrium. Once equilibrated, the slurry was centrifuged at 15 000 rpm for 15–30 min and a $^1/_2$-mL aliquot of supernatant placed into 20 mL of liquid scintillation cocktail (*25*) for radioassay. The pH of the supernatant was measured at this time. The amount of herbicide adsorbed was taken to be the difference between the amount added and the amount remaining in solution after equilibration. Each concentration was replicated 3–5 times.

Similarly, diquat adsorption studies were performed by using the batch technique, except that UV spectroscopy was used as the method of measurement. Stock solutions of 1000, 2500, 5000, 25 000, 40 000, 50 000, 100 000, and 125 000 μg/mL diquat dibromide monohydrate were prepared from analytical grade diquat (>99% pure). Following equilibration and centrifugation as previously described, an aliquot was taken and diluted with a buffer solution (pH 4.5) of sodium acetate and glacial acetic acid. Absorbance measurements were taken at 308 nm on a Beckman DU spectrophotometer to determine the concentration remaining in solution.

Adsorption isotherms were also determined with diquat on subsamples of the less than 0.25-mm sediment which had been repeatedly treated with H_2O_2 to remove the organic matter fraction.

Desorption studies were carried out with bromacil and diquat on selected sediments. The desorption experiments utilized the slurry from previous adsorption experiments except 10 mL of supernatant was removed from the centrifuged sample and replaced with 10 mL of 0.01 M $CaCl_2$. The tube was then shaken in the environment chamber for 48 h, centrifuged, and measured as before. This stepwise desorption process was repeated for five to six successive desorptions. Desorption kinetic studies conducted over an 8-day period revealed that after 48 h over 93% of the total 8-day desorbed material had been desorbed for both bromacil and diquat; consequently, for convenience 48 h was also selected as the equilibrium time for the desorption studies.

Results and Discussion

Tables I and II summarize the physical and chemical properties of the eight freshwater sediments for both the less than 2-mm- and the less than 0.25-mm-size fractions, respectively. The tables show a wide range in properties among the selected sediments. Similarity exists amongst the sediments, however, in their high level of fine material (i.e., silt and clay). As can be seen in comparing Tables I and II, the removal of the coarse and medium sands (0.25–2 mm) had little effect on cation-exchange capacity, exchange acidity, organic carbon and organic matter content, dry ash, specific surface area, and free iron oxides. The pH of the less than 0.25-mm fraction, however, was

Table I. Chemical and Physical Characteristics of the Less Than 2-mm-Size Fraction of Freshwater Sediments[a]

	Baldwin Lake	Big Bear Lake	Castle Lake	Clear Lake	Delta (Hill Slough)	Jenks Lake	Mockingbird Canyon	San Joaquin Marsh
EC_e, dS/m	1.0	1.6	0.5	1.6	6.4	0.2	3.1	9.4
$EC_{1:5}$, dS/m	0.6	1.0	0.2	0.8	2.1	0.2	1.2	3.0
pH_{SP} (distilled H_2O)	8.4	6.9	5.2	6.2	6.8	5.6	6.4	6.8
$pH_{1:5}$ (distilled H_2O)	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/cm^3	1.19	0.85	0.09	0.36	0.54	1.68	1.00	1.07
texture								
% sand	5.0	17.9	23.0	11.2	0.9	2.0	1.2	4.2
% silt	25.4	53.7	52.3	48.9	40.0	61.0	49.2	28.9
% clay	69.6	28.4	24.7	39.9	59.1	37.0	49.6	66.9
% salt (soluble + $CaCO_3$)	39.4	17.1	1.1	5.0	6.1	2.6	11.5	10.7
% organic carbon (OC)	1.2	6.8	13.2	10.2	4.1	3.9	1.9	2.0
% organic matter (OM)	2.1	13.4	24.8	21.8	7.9	7.2	3.5	4.3
OM/OC	1.8	2.0	1.9	2.1	1.9	1.9	1.8	2.2
% dry ash	3.04	12.74	25.28	19.67	5.85	6.79	4.14	3.22
CEC, mequiv/100 g	37.0	55.0	40.1	50.9	31.1	21.3	29.3	37.3
EA, mequiv/100 g	0.6	7.3	23.5	21.9	8.0	9.5	9.8	2.5
EB, mequiv/100 g	36.4	47.7	16.6	29.0	23.1	11.8	19.5	34.8
% Fe_2O_3	0.30	0.33	0.45	1.25	0.77	1.81	1.55	0.50
specific surface area, m^2/g								
total–untreated[b]	159.1	141.7	55.9	95.6	152.5	71.1	165.0	221.4
total–treated[c]	153.0	118.8	3.1	26.0	148.6	39.5	156.3	220.3
external–treated[c]	60.1	18.0	3.6	10.1	54.7	11.3	37.2	80.1
internal-treated[c]	9.29	100.8	0	15.9	93.9	28.2	119.1	140.2
OM basis[d]	353	177	213	320	56	440	280	61
CEC of OM, mequiv/100 g[e]	315	177	112	164	219	238	273	20
CEC of mineral fraction, mequiv/100 g	51.9	45.0	16.6	20.7	16.0	4.6	23.2	42.9

[a] Electrical conductivities were determined on the saturation extract (EC_e) and for a 1 to 5 sediment to distilled water pastes ($EC_{1:5}$). The pH measurements were for the saturated paste (pH_{SP}) and a 1 to 5 sediment to distilled water paste ($pH_{1:5}$). [b] Untreated (1 N $CaCl_2$). [c] Treated (H_2O_2, 1 N $CaCl_2$). [d] Area m^2/g of OM = [total[b] − [total[c] × (1.00 − fraction of residual OM)]]/(g of OM/g of soil). [e] CEC mequiv/100 g of OM = [total CEC − CEC of mineral fraction × [1 − (fraction of OM and salt)]]/(g of OM/100 g) × 100.

Table II. Chemical and Physical Characteristics of the Less Than 0.25-mm-Size Fraction of Freshwater Sediments[a]

	Baldwin Lake	Big Bear Lake	Castle Lake	Clear Lake	Delta (Hill Slough)	Jenks Lake	Mockingbird Canyon	San Joaquin Marsh
EC_e, dS/m	1.03	2.20	0.52	1.76	7.60	0.54	2.12	9.20
$EC_{1:5}$, dS/m	0.54	0.50	0.21	0.72	3.20	0.14	0.60	3.11
pH_{SP} (distilled H_2O)	8.6	7.2	5.7	6.6	7.0	6.1	7.1	7.8
$pH_{1:5}$ (distilled H_2O)	9.0	7.2	5.8	6.8	7.2	6.2	7.4	8.1
pH_{SP} (0.01 M $CaCl_2$)	8.0	6.7	4.9	5.7	6.6	5.3	6.5	7.3
$pH_{1:5}$ (0.01 M $CaCl_2$)	8.0	6.7	4.8	6.0	6.6	5.4	6.7	7.1
% silt and sand	26.3	65.4	67.9	55.1	40.3	62.2	49.8	30.2
% clay	73.3	34.6	32.1	44.9	59.6	37.8	50.2	69.8
% salt (soluble + $CaCO_3$)	37.3	15.6	0.6	3.6	4.5	0.8	11.3	12.3
% organic carbon (OC)	1.0	7.9	14.5	13.3	4.4	3.0	2.1	2.6
% organic matter (OM)	2.0	13.7	22.4	20.8	6.7	4.7	3.4	4.1
OM/OC	2.0	1.7	1.5	1.6	1.5	1.6	1.6	1.6
% dry ash	2.63	12.77	21.74	18.65	6.29	5.42	4.23	3.52
CEC (mequiv/100 g)	41.8	62.7	33.8	59.1	41.9	26.5	36.3	48.5
EA (mequiv/100 g)	0.2	5.5	19.0	19.1	9.4	11.1	7.1	5.8
% Fe_2O_3	0.29	0.36	0.38	1.50	0.85	1.79	1.56	0.65
saturation percentage	60.0	51.5	184.5	87.5	52.0	63.5	50.0	44.0
charge density, C/m^2	0.243	0.342	0.470	0.507	0.266	0.348	0.207	0.208
specific surface area, m^2/g								
total–untreated[b]	165.7	177.0	69.4	112.4	151.7	73.4	168.8	225.1
total–treated[c]	158.2	168.2	27.6	63.2	148.1	58.0	150.9	217.8
external–treated[c]	60.4	27.9	27.3	22.3	54.4	18.6	36.1	78.9
internal–treated[c]	97.8	140.3	0.3	40.9	93.7	39.4	114.8	138.9
mineral fraction[d]								
total specific surface, m^2/g	196.6	100.5	27.6	63.6	130.9	50.9	87.4	251.3
CEC, mequiv/100 g	36.2	44.5	11.2	31.6	33.2	16.1	28.0	49.7
charge density, C/m^2	0.178	0.427	0.392	0.480	0.245	0.305	0.309	0.191

[a] Electrical conductivities were determined on the saturation extract (EC_e) and for a 1 to 5 sediment to distilled water pastes ($EC_{1:5}$). The pH measurements were for the saturated paste (pH_{SP}) and a 1 to 5 sediment to distilled water paste ($pH_{1:5}$). [b] Untreated (1 N $CaCl_2$). [c] Treated (H_2O_2, 1 N $CaCl_2$). [d] Treated (1 N $NaC_2H_3O_2 \cdot 3H_2O$, H_2O_2, 1 N $CaCl_2$).

Table III. Correlations between Sediment Properties of the Less Than 0.25-mm-Size Fraction

properties correlated	linear correlation coefficient (r)	multiple correlation coefficient (r)
pH to exchange acidity	0.865[e]	
internal surface area to % clay	0.512	
total surface area[a] to % clay	0.622	
total surface area[a] to % silt and % clay		0.601
total surface area[b] to OM	0.393	
total surface area[b] to OM and % clay		0.502
total surface area[b] to OM, % silt, and % clay		0.503
charge density[d] to CEC[d] and total area[d]		0.954[e]
charge density[c] to CEC[c] and total area[c]		0.907[e]

[a] Treated: sediment treated with hydrogen peroxide and 1 N $CaCl_2$. [b] Untreated: sediment untreated. [c] Treated: sediment treated with 1 N sodium acetate followed by hydrogen peroxide. [d] Statistically significant at the 5% level. [e] Statistically significant at the 1% level.

noticeably greater than the pH of the less than 2-mm fraction. The use of the less than 0.25-mm fraction for the adsorption–desorption studies not only would ameliorate the problem of reproducibility experienced with the less than 2-mm-size fraction but also would better accentuate the process of adsorption because of its close relation to the amount of organic matter and the amount of fine material, thus, enhancing any correlations which may be made.

Certain descriptive features were calculated for the less than 2-mm fraction of the sediments and compared with values normally reported for soils. The organic matter to organic carbon ratio (OM/OC) ranged from 1.8 to 2.2 with an average of 2.0 which is slightly higher than the 1.9 ratio for surface soils and less than 2.5 for subsoils cited in the literature (*26*). The area per gram of organic matter ranged from 56 to 440 m^2/g which is lower than the range 558–803 m^2/g cited by Bower and Gschwend (*27*). The cation-exchange capacity of the organic matter fraction fraction averaged 214 mequiv/100 g when the unexplainably low organic matter cation-exchange capacity of San Joaquin Marsh (20 mequiv/100 g) was omitted. This compares favorably with soils which range from 112 to 252 mequiv/100 g of organic matter as cited by Baver (*28*).

Table III compares correlation coefficients of both simple and multiple correlations made between sediment properties of the less than 0.25-mm-size fraction. As can be seen, there is a high correlation between pH and exchange acidity, as would be expected, as well as a high correlation between charge density and the properties of cation-exchange capacity and total surface area. Total surface area, however, does not correlate well with organic matter and/or finer particles (i.e., silt and clay), nor does internal surface area correlate with the percent of clay material. With the possible exception of the low correlation obtained between the total surface area and the finer particle fraction, the sediment properties were generally consistent with similar properties measured on soils by other investigators.

Table IV. Water Properties of the Eight Freshwater Sample Sites

sample site	pH	electrical conductivity, dS/m
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
Delta (Hill Slough)	7.4	3.4
Jenks Lake	6.9	0.2
Mockingbird Canyon	6.7	0.6
San Joaquin Marsh	8.2	6.8

Redox potential, pH, and organic carbon content determined at 5-cm increments for the 45-cm core samples revealed that, in general, the sediments varied only slightly over the depth increment selected for the composite core samples, 0–15 cm. Because of this general uniformity in properties within the top 0–15 cm, a composite of this depth increment was used for all adsorption–desorption analysis. Analysis of water samples taken from the sediment–water interface (Table IV) showed that the pH of the water in most cases tended to be higher than that of the sediment while the electrical conductivity of the water tended to be lower than the EC_e of the freeze-dried sediment, with the high electrical conductivities being high in both the water and sediment and with the low ones low.

The adsorption data for bromacil, a weakly basic herbicide, best fit a Freundlich isotherm for the range of concentrations used. That is

$$S_{\text{ads}} = K_{\text{ads}} C^{1/n} \quad (1)$$

where S_{ads} is the amount of chemical adsorbed (μg) per mass of soil or sediment (g), C is the equilibrium concentration of chemical in solution (μg/mL), and K_{ads} and $1/n$ are coefficients of adsorption. K_{ads} is a measure of the degree or strength of adsorption while $1/n$ indicates the degree of nonlinearity between solution equilibrium concentration and adsorption.

In the log form, eq 1 becomes

$$\log S_{\text{ads}} = (1/n) \log C + \log K_{\text{ads}} \quad (2)$$

Thus, K_{ads} and $1/n$ in eq 2 can be readily solved by linear regression analysis by using a log transformation or graphically by a log–log plot of the amount of herbicide adsorbed per gram of sediment (S_{ads}) and the equilibrium solution herbicide concentration (C). K_{ads} is the intercept and $1/n$ is the slope of the line. Figure 1 illustrates a typical set of bromacil adsorption–desorption isotherms for one of the sediments.

The values of K_{ads} and $1/n$ for bromacil adsorption on the untreated sediments are given in Table V. The value of $1/n$ for the eight sediments is slightly less than unity (i.e., average $1/n = 0.917$) while the adsorption partition coefficient, K_{ads}, ranges from 0.556 to 6.353. Linear regression analysis of the adsorption partition coefficient and individual sediment properties confirm previous findings with soils which show a high degree of positive correlation ($r = 0.902$) between organic carbon and the degree of adsorption represented quantitatively by K_{ads} (*29–32*). The following regression equation relating K_{ads} to percent organic carbon was obtained:

$$K_{\text{ads}} = 0.709 + 0.367(\%\ \text{organic carbon}) \quad (3)$$

As shown by numerous previous investigators (*7*, *33–35*, *31*), when the adsorption partition coefficient is normalized to organic carbon by the following equation

$$K_{\text{OC}} = \frac{K_{\text{ads}}}{\%\ \text{organic carbon}} \times 100 \quad (4)$$

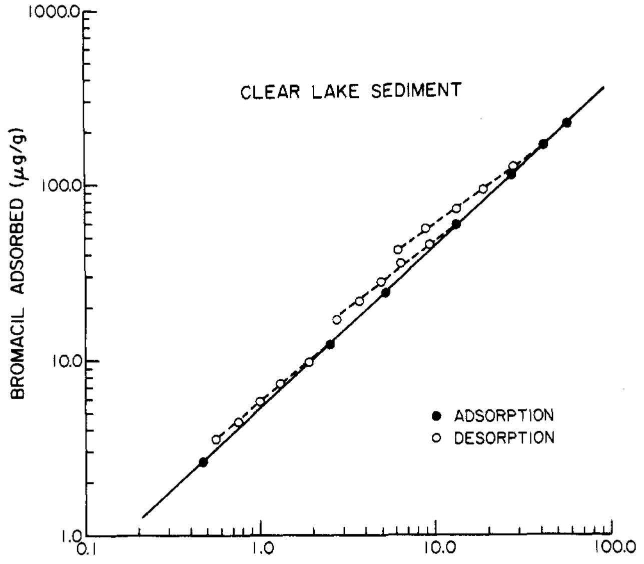

Figure 1. Representative adsorption–desorption isotherms showing the adsorption–desorption of bromacil upon Clear Lake sediment at 25 °C.

Table V. Freundlich Adsorption Partition Coefficients and K_{OC}'s for Bromacil on the Less Than 0.25-mm-Size Fraction of Untreated Sediments at 25 °C

	Freundlich adsorption partition coefficients		
site	$1/n$	K_{ads}	K_{OC}
Baldwin Lake	0.984	2.891	289.1
Big Bear Lake	0.860	3.926	49.7
Castle Lake	0.930	6.353	43.8
Clear Lake	0.917	5.260	39.5
Delta (Hill Slough)	0.905	2.716	61.7
Jenks Lake	0.891	1.197	39.9
Mockingbird Canyon	0.951	0.556	26.5
San Joaquin Marsh	0.900	0.684	26.3
average	0.917	2.948	41.1[a]
standard deviation	0.038	2.134	12.5

[a] The K_{OC} value for Baldwin Lake was excluded from the calculation of the average K_{OC}.

Table VI. Linear Regression Analysis of Freundlich Desorption Isotherms for Bromacil on Selected Sediments

sediment sample	S_0,[a] μg/g	K_{des}	$1/n$	regression equations	R^2
Big Bear Lake	10.02	4.773	0.712	$1/n = 0.734 + 0.0003S_0$	0.88
	43.78	5.363	0.758		
	116.25	4.851	0.797		
	407.09	3.931	0.860		
Castle Lake	13.27	6.724	0.845	$1/n = 0.8424 - 0.00003S_0$	0.96
	64.34	8.130	0.840		
	184.04	9.556	0.834		
	674.71	10.556	0.820		
Clear Lake	12.27	5.709	0.809	$1/n = 0.8158 - 0.0005S_0$	0.99
	58.37	7.709	0.791		
	161.50	11.001	0.740		

[a] Initial adsorbate concentration at which desorption began.

K_{OC} is found to be generally less variable than when expressed solely on a total sediment basis (Table V). Baldwin Lake (organic carbon content = 1.0%) had higher K_{OC} than the other sediments which is commonly the case for low organic matter soils or sediments. Hamaker and Thompson (*33*) propose that this tendency is due to the fact that the mineral phases may be responsible for making a significant contribution to the total adsorption. Since the ratio of clay to organic carbon is very high in the case of Baldwin Lake, it is not reasonable to expect carbon to govern the sorptive response; consequently, the Baldwin Lake K_{OC} was excluded from the average K_{OC} calculation.

A positive correlation also exists between charge density and the degree of bromacil adsorption for both untreated sediments ($r = 0.846$) and sediments treated for the removal of organic matter ($r = 0.800$). Because of possible changes in the soil from such drastic treatments as wet oxidation (e.g., H_2O_2), caution should be taken in the interpretation of these data. However, the results do indicate the presence of possible adsorption sites other than those provided by organic matter.

Multiple regression analysis of the Freundlich adsorption coefficient for bromacil and sediment properties indicate that K_{ads} could be best predicted from the combined properties of organic matter, exchange acidity, percent Fe_2O_3, and percent clay when used as the independent variables of a linear multiple regression equation.

$$K_{ads} = 0.800 + 0.248(\%\text{ organic matter}) - 0.007(\text{exchange acidity}) + 0.011(\%\text{ clay}) - 0.810(\%\ Fe_2O_3) \quad (5)$$

$$R^2 = 0.986$$

The results of bromacil desorption studies performed on sediments from Big Bear Lake, Castle Lake, and Clear Lake are summarized in Table VI. The Freudlich equation is used to describe the desorption isotherm data:

$$S_{des} = K_{des}C^{1/n} \quad (6)$$

where S_{des} is the amount of chemical remaining adsorbed to the surface of the adsorbent after a desorption event per mass of the adsorbent, C is the equilibrium concentration in solution, and K_{des} and $1/n$ are constants. In this case, K_{des} reflects the degree of adsorption after desorption has occurred.

Analysis of the desorption data in Table VI for each of the three sediments using linear regression analysis on the initial surface concentration of the adsorbate and the slope ($1/n$) reveals a high correlation. The high R^2 values for the regression equations of Table VI show that it is possible to predict the desorption isotherms of bromacil for each of the three selected sediments with only the knowledge of the initial adsorbate concentration prior to any desorption. This provides a means of modeling the adsorption–desorption process as long as desorption is a continuous process uninterrupted by readsorption.

The adsorption isotherms for diquat showed it to be a very strongly adsorbed herbicide. Figure 2 illustrates a typical set of adsorption–desorption isotherms. The adsorption data for diquat, a strongly basic herbicide, was described by the following linear form of the Langmuir equation:

$$C/S = 1/(kb) + C/b \quad (7)$$

where S is the amount adsorbed per unit weight of adsorbent (μg/g), C is the equilibrium concentration (μg/mL), b is the adsorption maximum, and k is an affinity constant related to the bonding energy of adsorbent for adsorbate. Linear regression lines were calculated, and the Langmuir constants, b and k, were found for each of the eight sediments (see Table VII). The R^2 values for the

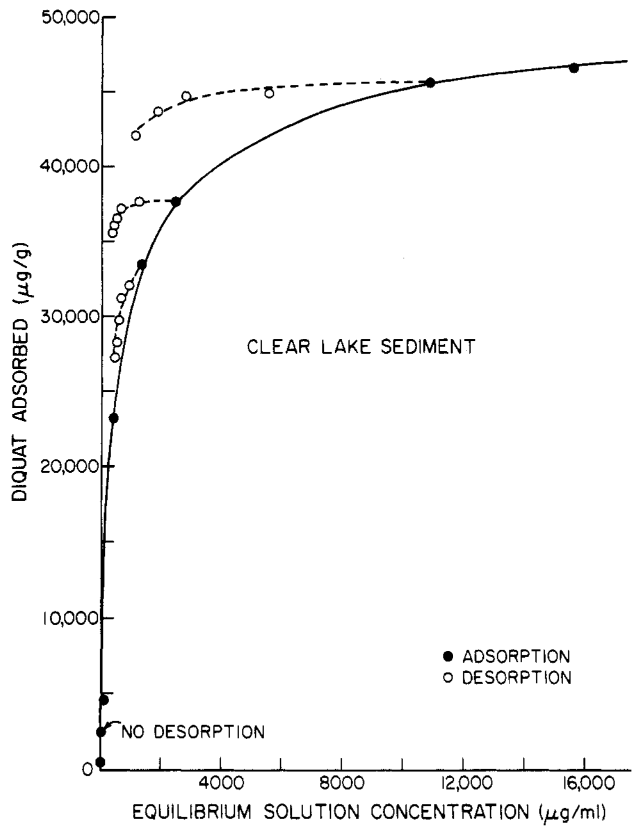

Figure 2. Representative adsorption–desorption isotherms showing the adsorption–desorption of diquat upon Clear Lake sediment at 25 °C.

Table VII. Langmuir Adsorption Maxima and Affinity Constants for Diquat on Untreated and Treated Sediments at 25 °C

	untreated sediment		treated sediments[a]	
site	adsorption maxima, b	affinity constants, k ($\times 10^{-3}$)	adsorption maxima, b	affinity constants, k ($\times 10^{-3}$)
Baldwin Lake	44053	8.66	42918	12.6
Big Bear Lake	52356	8.95	40650	10.6
Castle Lake	24390	0.52	5510	1.41
Clear Lake	48309	1.51	28736	2.01
Delta (Hill Slough)	53191	6.19	43668	3.34
Jenks Lake	24331	2.54	18727	4.25
Mockingbird Canyon	43860	10.1	42373	12.2
San Joaquin Marsh	69930	11.7	68966	21.6

[a] Treated for removal of organic matter with hydrogen peroxide.

regression lines ranged from 0.997 to 1.000, indicating that the adsorption data conformed extremely well to the Langmuir linear equation over the range of selected concentrations. As expected for a cationic herbicide, the adsorption maxima for diquat were relatively high ranging from 24331 to 69930 μg/g.

Correlations between individual soil properties and the Langmuir affinity constant, k were performed. Surface area was the only property which was highly correlated to the affinity constant ($r = 0.937$). Of particular interest, however, was the relationship between surface charge density of the sediments and k. A moderate negative correlation ($r = -0.884$) between charge density and k was found by the linear regression analysis, but a plot of charge density and k revealed an interesting exponential function. Figure 3 illustrates that the affinity constants increase exponentially as a function of decreasing charge density excluding Big Bear Lake. This indicates that the charge separation of diquat is such that a charge density on the adsorbent surface of approximately 0.2 C/m^2 (6×10^4 esu/cm^2) results in the greatest bonding energy of adsorbent for diquat over the range of observed charge densities. Furthermore, knowledge of the charge density of an adsorbent permits a means of approximating the affinity constant from the "best fit" equation

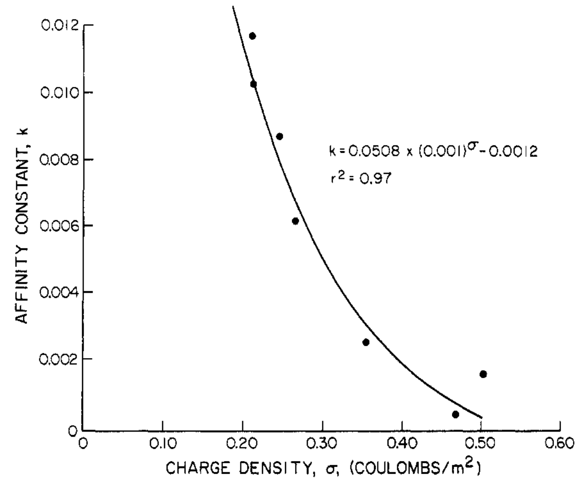

Figure 3. Langmuir affinity constant, K, for diquat as related to the charge density, σ, of seven freshwater sediments.

$$k = 0.0508(0.001)^{\sigma} - 0.0012 \qquad (8)$$

where σ is the charge density.

A similar linear regression analysis between individual soil properties and the Langmuir adsorption maxima, b, was performed. On an individual soil property basis, b also correlated well with surface area ($r = 0.904$).

$$b = 8.729 + 0.254(\text{total area}) \qquad (9)$$

Previous work with diquat by other investigators demonstrated that the adsorption of diquat on clays was directly related to the cation-exchange capacity and as such involved an ion-exchange mechanism of adsorption (*36–40*). This was also the case for the eight sediments after they were treated for the removal of organic matter. Correlations between CEC and b of the sediments treated for the removal of organic matter showed a high positive correlation ($r = 0.904$). Untreated sediments, however, showed little correlation between CEC and b ($r = 0.658$). Ostensibly, the organic matter fraction influences the process of ion exchange possibly through its varying effect upon the structure of solvating water of the macromolecular organic matter since water structure is important in determining the extent of adsorption (*33*).

Desorption studies were performed on each sediment at four different initial adsorbate concentrations. The desorption curves were described with the linear form of the Langmuir equation. Table VIII summarizes the adsorption maxima, b, and affinity constants, k, calculated for each desorption curve. For all eight sediments, diquat was adsorbed so tightly to the sediment surface for an initial adsorbate concentration of 2500 μg/g that no desorption occurred. As in the case of bromacil, a linear relationship was found to exist for diquat between the slope ($1/b$) of the desorption isotherm and the initial adsorbate concentration from which desorption occurred. Table VIII displays the linear regression equation for each sediment

Table VIII. Linear Regression Analysis of Langmuir Desorption Isotherms for Diquat on Eight Freshwater Sediments

sediment sample	S_0,[a] μg/g	b	k	regression equations	R^2
Baldwin Lake	2 500			$1/b = (4.95 \times 10^{-5}) - (6.13 \times 10^{-10})S^0$	0.99
	37 240	37 453	0.350		
	40 400	40 650	0.053		
	43 125	43 290	0.011		
Big Bear Lake	2 500			$1/b = (3.66 \times 10^{-5}) - (3.32 \times 10^{-10})S^0$	0.95
	38 600	42 735	0.034		
	43 535	44 053	0.075		
	52 000	52 356	0.019		
Castle Lake	2 500			$1/b = (1.009 \times 10^{-4}) - (2.57 \times 10^{-9})S^0$	0.99
	16 250	16 722	0.0087		
	18 125	18 657	0.0063		
	22 250	22 676	0.0042		
Clear Lake	2 500			$1/b = (4.13 \times 10^{-5}) - (4.22 \times 10^{-10})S^0$	0.91
	33 500	37 594	0.0063		
	37 700	38 023	0.050		
	45 250	45 662	0.014		
Delta (Hills Slough)	2 500			$1/b = (4.48 \times 10^{-5}) - (4.94 \times 10^{-10})S^0$	0.99
	38 030	38 168	0.755		
	43 060	43 290	0.130		
	52 375	52 632	0.012		
Jenks Lake	2 500			$1/b = (8.35 \times 10^{-5}) - (1.76 \times 10^{-9})S^0$	1.00
	21 100	21 552	0.013		
	22 200	22 472	0.015		
	24 463	24 691	0.007		
Mockingbird Canyon	2 500			$1/b = (4.94 \times 10^{-5}) - (6.09 \times 10^{-10})S^0$	1.00
	37 500	37 594	0.573		
	40 850	40 984	0.285		
	43 750	43 860	0.382		
San Joaquin Marsh	2 500			$1/b = (3.83 \times 10^{-5}) - (0.348 \times 10^{-9})S^0$	0.98
	39 880	40 000	1.53		
	49 530	49 505	1.35		
	69 500	69 444	1.22		

[a] Initial adsorbate concentration at which desorption began.

as well as the corresponding R^2 values. 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.

Summary

Adsorption and desorption are key chemical processes in determining the amount of herbicide which is available for movement in soils and sediments. In order to attain a predictive level of knowledge of the fate of herbicides in aquatic systems, it is crucial that both the adsorption and desorption of herbicides by sediments be quantitatively characterized. The complexity of sediment as an adsorptive media makes a statistical approach to modeling adsorption and desorption a favorable one.

The calculated adsorption–desorption isotherm parameters for bromacil and diquat shown in Tables V–VIII indicate that the processes of adsorption and desorption are obviously not single valued for the predetermined equilibrium time. This hysteretic effect indicates that no single equation will describe both processes. Certain questions still remain as to whether kinetic limitations are the principal cause for the observed nonsingularity. Since desorption kinetic experiments were only carried out up to 8 days, further desorption kinetic studies on sterilized sediments for much longer periods of time (8–30 days) need to be carried out to confirm whether or not significant solute–surface interactions are still occurring.

The Freundlich equation was used to describe both the adsorption and desorption data for bromacil, while the Langmuir equation best fit the adsorption–desorption isotherms obtained for diquat. Though a single Freundlich or Langmuir equation could be used to describe the adsorption isotherm for a given sediment, this was not the case for desorption which required a different set of desorption parameters for each initial adsorbate concentration at which desorption was initiated. It was found, however, that the slope of each desorption curve, whether for bromacil or diquat, was a function of the initial adsorbate concentration on the adsorbent surface. As such, linear regression equations were derived for each sediment and herbicide concentration which made it possible to predict the desorption isotherm at any point along the adsorption isotherm.

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Registry No. Bromacil, 314-40-9; diquat, 2764-72-9.

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Persistence of Pesticides in Surface Soil and Relation to Sublimation

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■ To help explain low concentrations of DDT found in some birds of Kenya, a field test of the rate of disappearance of DDT from soil near Lake Nakuru, Kenya, was conducted and gave a half-life of 110 days. The data suggest that the DDT sublimed directly without prior degradation to DDE. Calculated sublimation rates based on mass transfer through the boundary layer are sufficient to account for the rapid disappearance. The model gives a sublimation rate proportional to the vapor pressure of DDT, the $^2/_3$ power of its diffusivity in air, and the 0.60 power of the wind speed. The results show that sublimation alone can account for the disappearance of pesticides of low volatility even if they are strongly adsorbed on soils and that the uncontrolled use of DDT in Kenya may affect wildlife to a lesser extent than had been feared.

A field test of the rate of disappearance of DDT from a tropical soil is reported. Kenya was chosen for the test because it places no restrictions on the use of DDT and other insecticides, and so these chemicals form a potential threat to both the human population and the spectacular wildlife for which Kenya is renowned. Because DDT is cheap and useful for control of malaria and agricultural pests, reduction of its use might cause significant economic and health problems.

The threat posed to wildlife by uncontrolled use of DDT is particularly severe at Lake Nakuru, a small lake (42 km^2) at an elevation of 1758 m in the Great Rift Valley 35 km south of the equator. Over 400 species of birds have been identified there, and the lake is a principal feeding ground of the lesser flamingo (*Phoeniconiais minor*), more than a million of which can sometimes be seen. The lake was declared a National Park in 1968—the first national park in Africa to be set aside on account of its bird life, though it is also a refuge for over 50 species of mammals.

Lake Nakuru is unusually vulnerable to pollution. Its average depth is about 2 m, it has no outlet, and it is the low point in a basin of about 1940 km^2 largely devoted to agriculture. The lake also receives storm sewers and sewage outfall from the city of Nakuru, which is adjacent to the Park boundary, has a population of 100 000, and is the fastest growing major city in Kenya.

Ecologically Lake Nakuru is simple and, therefore, probably vulnerable to perturbations. The lake is so alkaline (pH 10.5) that few forms of life can survive there. The abundant blue-green alga (*Spirulina platensis*) is the basis of its food chain. The principal herbivores are the lesser flamingo, a single species of fish (*Tilapia grahami*), and a small copepod (*Lovelulu sp.*), all of which feed on algae. The fish and copepods in turn are the principal foods of an estimated 27 000 other aquatic birds. Rainfall averages 8 cm/month from March through November and about 3 cm/month from December through February. The daily average maximum, mean, and minimum tempera-

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