EXPERIMENTAL AND SIMULATED P TRANSPORT IN SOIL USING A MULTIREACTION MODEL

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A miscible displacement technique was used to investigate the mobility of P in columns of Bh soil materials from two dairies in the Lake Okeechobee Basin. Phosphorus-laden solutions with four (5, 10, 50, and 100 g m^{-3}) initial concentrations (C_0) were applied to soil columns. An increase in the value of C_0 increased P mobility as determined by BTCs. Shapes of BTCs were characteristic of kinetically-controlled nonlinear sorption reactions, i.e., early breakthrough, clockwise rotation, and tailing.

A 2-site sorption/transport model with fast and slow sorption kinetics was calibrated from the BTC for one of the four C_0 values for each of two soils and then used to simulate BTCs for the other three C_0 values. Simulations based on the two highest C_0 values compared favorably to observed BTCs for all but the lowest C_0 value. Simulations based on the two lowest C_0 values compared favorably only to the BTCs at that C_0 value. Thus the sorption rate coefficients were not independent of influent C_0 for these two soils. Phosphorus retardation was underestimated for simulations of $C_0 = 11, 51$, and 97 g m^{-3} using k_1, k_2, and f input parameters obtained by calibration using the BTC for $C_0 = 5$ g m^{-3} and it was overestimated for simulation of $C_0 = 5$ g m^{-3} when input parameters for the model were obtained by calibrating using the BTCs for the three highest C_0 values.

Experimental enhancement of early P breakthrough in effluent from columns that received $C_0 = 5$ g m^{-3} was attributed to the initial presence of residual soil P that was either partially irreversible or very slowly desorbable in water.

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Excessive applications of fertilizer, animal wastes, or treated municipal wastewater to sandy soils are well known to contaminate local groundwater and surface water supplies with P (Mansell et al. 1991). Downward seepage of P-laden water to groundwater, subsequent lateral subsurface flow to streams, and overland flow during periods of shallow water tables can increase P levels in nearby lakes or estuaries and thus promote eutrophication. Eutrophication of the Peel-Harvey Estuary in Western Australia was attributed to excessive use of phosphatic fertilizer on Bassendean sands in the surrounding watershed (Hodgkin et al. 1980); and eutrophication of Lake Okeechobee in Florida was attributed to excessive accumulation of P from dairy waste/wastewater in the Taylor Creek/Nubbin Slough (TCNS) watershed (Allen et al. 1982).

Soils in the TCNS watershed are typically Spodosols with acid, sandy surface A1 and subsurface E1 (albic) horizons and Bh spodic horizons. Soil materials in the Bh horizon tend to sorb P from solution because of the presence of Al oxides, whereas albic soil material is essentially inert with respect to P sorption (Burgoa 1989). Water flow in the profile occurs predominantly through the A1 and E1 horizons with highly variable permeability in the partially consolidated Bh horizons (Burgoa 1989). During summer rainy periods, limited permeability in the underlying Bh horizon and relatively flat topography contribute to shallow water tables and subsequent lateral flow through the E1 horizon. During renovation of animal wastewater in acid, sandy soils, mobility of P is influenced primarily by inorganic (orthophosphate) forms, although high molecular weight organic forms migrate through soil under conditions of high dose rates (Gerritse 1981). Application of wastewater with high concentrations of P greatly enhances the mobility of inorganic P in sandy soils compared to applications of influent with low P concentrations. The convex nonlinearity for sorption isotherms for such soils results in P retardation during transport that tends to decrease with increasing concentration in solution.

Relatively high pore water velocities (i.e., small residence times) combined with slow sorption reactions in sandy soils requires that P transport models consider sorption kinetics (Mansell et al. 1991). Mobility of applied P can be inhibited by the occurrence of either very slow desorption or partially-irreversible sorption by soil components.

The objective of this investigation was to evaluate a nonlinear, kinetic, multireaction sorption/transport model for describing observed mobility of P applied to columns of Spodosols. Soil material from spodic horizons (Bh) from two dairies in the TCNS watershed of the Lake Okeechobee Basin were used. Soil material from Bh horizons in Spodosols is particularly important to P sorption due to the accumulation of organic matter and Al-Fe oxides in a quartz sand matrix.

CONCEPTUAL TRANSPORT MODELS

Reaction of P with acid, sandy soils such as Spodosols generally involves local nonequilibrium sorption during water flow and partially irreversible sorption processes (Mansell et al. 1991). The latter primarily occur due to reactions with Fe and Al oxides present in the soil. The term sorption is used in a general sense here to include P retention, adsorption, and chelation with humic acids (Al and Fe may form bridges between organic ligands and P ions). Irreversible sorption is considered to involve fixation and chemisorption. Scientists generally agree that many types of P retention can take place simultaneously. Less is known as to whether these reactions operate in series or in parallel. Experimental techniques are available in the literature to monitor retention, sorption, and fixation reactions. Although a mathematical model to describe P reactions in soil completely does not actually exist, models which approximate these reactions do. Multireaction-type sorption models constitute a class of such approximations and offer practical means to approximate P mobility during water flow in soils.

Most sorption-type models for describing P transport assume that P compounds move and react with the soil as a single component (i.e., species or chemical form), ignoring other components (such as organic anions) which can compete with P for soil sorption sites. Multi-site and multi-reaction, single-component transport models that assume reversible, kinetic, non-

linear mechanisms (with and without irreversible reactions) have been used with some success in describing P transport in acid, sandy soils. Multi-reaction models have in general provided improved results over the use of single-reaction models (Selim et al. 1990). Miscible displacement of aqueous P solutions through soil columns provides BTCs which are characteristically retarded due to sorption reactions and asymmetric with considerable tailing due to sorption nonlinearity and kinetics. Because of slow and fast kinetic sorption reactions, large numbers of pore volumes of effluent must generally be collected from soil columns in order for P concentrations to reach the influent concentrations C_0.

A general multireaction model for describing P sorption and transport in soils is available (Mansell et al. 1991). Orthophosphate transport was coupled with plant uptake, mineralization of organic P, reversible sorption-desorption reactions, and irreversible sorption or precipitation sinks for conditions of unsteady, saturated/unsaturated flow in soil. For steady, saturated flow in soil, convective-dispersive transport coupled with reversible sorption is described by

$$\theta \frac{\partial C}{\partial t} + \rho \frac{\partial [\Sigma S_j]}{\partial t} = \theta D \frac{\partial^2 C}{\partial z^2} - q \frac{\partial C}{\partial z} \qquad (1)$$

where C is the P concentration in the soil solution [g m^{-3}], S_j represents concentrations of any of two reversibly sorbed forms (S_1 and S_2) of inorganic P [g Mg^{-1}], D is the hydrodynamic dispersion coefficient [m^2 s^{-1}], q is the Darcy water flux [m s^{-1}], ρ is dry soil bulk density [Mg m^{-3}], and θ is volumetric water content [m^3 m^{-3}].

Rates of P sorption for reversible forms of P can be expressed as follows for S_1:

$$\frac{\partial S_1}{\partial t} = \frac{\theta}{\rho} k_1 C^m - k_2 S_1 \qquad (2)$$

where k_1 and k_2 are forward and backward rate coefficients (Units of s^{-1} when $m = 1$; See Fig. 1) and m is a dimensionless constant which corresponds to the exponent of C in the Freundlich equation; and for S_2:

$$\frac{\partial S_2}{\partial t} = \frac{\theta}{\rho} k_3 C^m - k_4 S_2 \qquad (3)$$

where k_3 and k_4 are forward and backward rate coefficients (Units of s^{-1} when $m = 1$; See Fig.
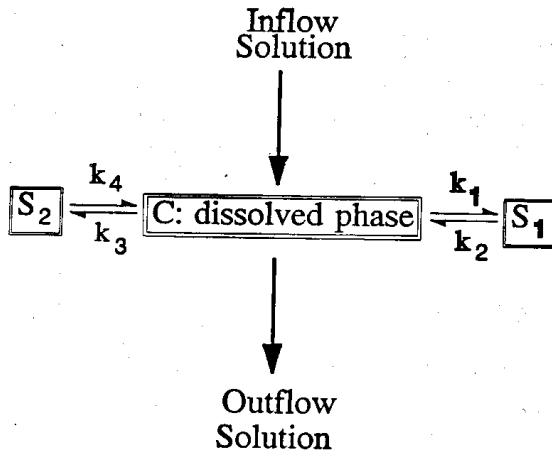
Inflow
Solution

FIG. 1. Schematic diagram of 2-site (fast and slow reactions) kinetic model for P sorption and transport with water flow in soil.

1). For P sorption reactions in most soils the exponent in the Freundlich equation (Nelson and Logan 1983) typically has values of $m \leq 0.8$, providing convex nonlinear isotherms (Lai and Jurinak 1972) which favor adsorption of P. Under conditions of local equilibrium, equations (2) and (3) reduce to the isotherm

$$S = S_1 + S_2 = K_{eq}C^m; \qquad (4)$$

where $K_{eq} = K_1 + K_2$ is the overall equilibrium distribution coefficient and distribution coefficients K_1 and K_2 are described by

$$K_1 = [\theta/\rho] \, k_1/k_2 \qquad (5)$$

and

$$K_2 = [\theta/\rho] \, k_3/k_4. \qquad (6)$$

The derivative for equation (4) provides the sorption buffering capacity $B(C)$ of a soil under equilibrium conditions (Mansell and Selim 1981)

$$B(C) = \partial S/\partial C = m \, K_{eq}C^{m-1}. \qquad (7)$$

For hypothetical conditions where local equilibrium occurs between S_1, S_2 and C compartments and no irreversible sorption occurs, then the equation for P transport simplifies to

$$\frac{\partial C}{\partial t} = \left[\frac{D}{R(C)}\right] \frac{\partial^2 C}{\partial z^2} - \left[\frac{v}{R(C)}\right] \frac{\partial C}{\partial z} \qquad (8)$$

where

$$R(C) = 1 + [\rho/\theta]B(C) \qquad (9)$$

is a dimensionless retardation function $R(C)$ resulting from reversible sorption and $v = q/\theta$ is the average pore water velocity. Substitution of equation (7) into (9) clearly reveals that for convex sorption isotherms $(m < 1)$, P mobility for a given C in applied influent solution is inhibited by large values for K_{eq} for a soil in question; but for a soil with a given value of K_{eq}, P mobility tends to increase in a nonlinear manner as C in the influent increases. The nonlinearity of R(C) thus requires the use of a numerical mathematical solution for equation (8).

An iterative Crank-Nicholson finite-differencing technique (Selim et al. 1976) can be used to solve the convective-dispersive transport and sorption equations with the appropriate initial and boundary conditions to obtain values of concentration $C(z, t)$ for given soil depth z and time t. Because preliminary investigations did not reveal perceptive desorption of residual P when water was infiltrated into columns of air-dry spodic soil materials from these soils, all simulations assumed initial conditions of $C_i = 0$ and $S_i = 0$ in the soil. For assumptions of kinetic sorption, equation (1) is appropriate for P transport, but for instantaneous sorption equation (8) should be used.

A parallel 2-site kinetic model for P sorption and transport (Fig. 1) is a special case for the general multireaction model where rapid and slow kinetic reactions control the distributions of P between S_1 and S_2 sorbed compartments, respectively, and the solution compartment C. The equilibrium distribution coefficients for the rapid and slow reactions are defined as $K_1 \equiv fK_{eq}$ and $K_2 \equiv (1 - f)K_{eq}$, respectively, where f is the fraction of sorption sites associated with rapid kinetic reactions that result in the S_1 sorbed P.

Three other sorption models—1-site instantaneous involving equilibrium P transfer between S_1 and C compartments, 1-site kinetic with time-dependent transfer of P between S_1 and C compartments, and 2-site kinetic/instantaneous with kinetic sorption for S_1 sites and instantaneous for S_2 sites—were also used.

MATERIALS AND METHODS

Bulk samples of subsurface spodic horizons (Bh horizon) were collected from profiles of Immokalee (Arenic Haplaquod) and Myakka (Aeric Haplaquod) soil series located at Dry

Lake #1 and W. F. Rucks dairies, respectively, from Okeechobee county in southern Florida.

Soil samples were air-dried and sieved prior to use in the experiments. Mehlich I extractable P (MIP) was determined on duplicate 5-g air-dry soil samples, sieved through a 2-mm screen, and mixed with 20 ml of Mehlich I extracting solution (i.e., 0.05 M HCl + 0.025 M H_2SO_4) in 50-ml glass tubes. The suspensions were tumbled for 5 min in an end-over-end shaker and filtered through Whatman filter paper (No. 42). The filtrate was analyzed for P colorimetrically by the ascorbic-acid method (John 1970). Total extractable phosphorus (TEP) was determined by the alkaline-oxidation method following the procedure of Dick and Tabatabai (1977).

Soil columns used in the miscible-displacement experiments were prepared by hand-packing air-dry soil into acrylic plastic cylinders with 3.78-cm inside diameter and length of 2 cm. Short columns were used in order to permit the displacement of large numbers of pore volumes of influent within relatively short time periods. No attempt was made to remove residual P present in the soils. Solutions with given P concentrations (C_0) were applied vertically with constant flux uniformly applied to the surface of short soil columns until a desired number of pore volumes of effluent were collected for each. Initially, a brief period of unsteady, unsaturated water flow occurred during infiltration of the first pore volume of influent solution. Saturated steady flow was established rapidly during the end of the first effluent pore volume, and continued for the duration of infiltration. A designated volume (or pulse) of aqueous electrolyte

solutions containing concentration C_0 of P (as KH_2PO_4 in KCl) was displaced through the soil columns. The ionic strength of all four influent P solutions was maintained constant at 10 mol m^{-3} using KCl. Input flux was maintained constant with a peristaltic pump. Effluent fractions were collected with an automatic fraction collector. After application of each P influent solution, a 10 mol m^{-3} KCl solution without P was displaced through each column until the P concentration in the effluent solution became $\leq 0.05\ C_0$.

Aqueous KCl solutions with a range of P concentrations (C_0: 5, 10, 50, and 100 g m^{-3}) were miscibly displaced through the soil columns during steady, saturated flow (Table 1). Depending upon the value of C_0, flow was terminated after 120 to 290 pore volumes of influent had been applied. Breakthrough curves (BTCs) of P dimensionless concentration (C/C_0) in column effluent versus pore volumes (Ω) of effluent were prepared for each soil column.

After completing each column run, the wet-soil columns were weighed to calculate the pore volume for each column. Concentrations of P in the effluent were determined by the ascorbic acid-molybdenum blue colorimetric method (John 1970).

Pertinent physical parameters for the soil columns are summarized in Tables 1 and 2 for soils from the Rucks Dairy and the Dry Lake Dairy, respectively.

Pulses of nonreactive electrolyte solution as described above containing tritiated water (^3H_2O) were used to obtain breakthrough curves (step function) on selected soil columns. Radioactivity of applied pulses of ^3H_2O was 7.4 × 10⁸

TABLE 1

Descriptive parameters used to simulate P transport during miscible displacement of solutions through columns of Myakka soil from the Rucks dairy under conditions of steady flow

Parameter	Column 1	Column 2	Column 3	Column 4
C_0 (g m^{-3})	97	51	11	5
Pulse duration (s)	75,559	63,665	218,298	217,542
Total duration (s)	136,602	166,412	321,692	415,867
Darcy flux (m s^{-1})	7.083 × 10^{-6}	7.139 × 10^{-6}	7.194 × 10^{-6}	6.694 × 10^{-6}
C_{init} (g m^{-3})[a]	1.0 × 10^{-9}	1.0 × 10^{-9}	1.0 × 10^{-9}	1.0 × 10^{-9}
θ_{sat} ($m^3\ m^{-3}$)	0.41	0.45	0.44	0.48
ρ (Mg m^{-3})	1.55	1.50	1.51	1.45
Δx (m)	2.0 × 10^{-4}	2.0 × 10^{-4}	2.0 × 10^{-4}	2.0 × 10^{-4}
Δt_{max} (s)	100	100	100	100
Column length (m)	0.02	0.02	0.02	0.02

[a] The parameter C_{init} is the initial P concentration in the soil solution.

TABLE 2

Descriptive parameters used to simulate P transport during miscible displacement of solutions through columns of Immokalee soil from the Dry Lake dairy under conditions of steady flow

Parameter	Column 5	Column 6	Column 7	Column 8
C_0 (g m^{-3})	102	51	11	5
Pulse duration (s)	72,327	82,772	143,272	223,119
Total duration (s)	179,723	165,971	417,131	415,867
Darcy flux (m s^{-1})	7.083×10^{-6}	7.472×10^{-6}	7.333×10^{-6}	7.528×10^{-6}
C_{init} (g m^{-3})	1.0×10^{-9}	1.0×10^{-9}	1.0×10^{-9}	1.0×10^{-9}
θ_{sat} (m^3 m^{-3})	0.40	0.42	0.43	0.47
ρ (Mg m^{-3})	1.61	1.61	1.62	1.55
Δx (m)	2.0×10^{-4}	2.0×10^{-4}	2.0×10^{-4}	2.0×10^{-4}
Δt_{max} (s)	100	100	100	100
Column length (m)	0.02	0.02	0.02	0.02

Bq m^{-3} in aqueous solution. The tritiated water was applied to columns after the P desorption BTCs were terminated, under the same water flow condition (saturated water content, steady flow, and pore water velocity). Dispersion coefficients were calculated using the Parker and van Genuchten model (1984) fitted to observed BTCs for ^{3}H$_2$O. Data are presented in Burgoa (1989).

PARAMETER ESTIMATION

An iterative search procedure was used to obtain "best-fit" estimates for a given parameter. For each parameter to be fitted, a minimum value (P_{min}), a maximum value (P_{max}), the number of divisions (N_p) into which the range is to be divided, and an iteration tolerance (T_p; see Tables 1 and 2) are specified. A value of the parameter is determined by:

$$P_i = P_{min} + i \ \Gamma/N_p \qquad (10)$$

where

$$\Gamma = P_{max} - P_{min} \qquad (11)$$

for $i = 0$ to N_p. For each value of P_i, a simulation is performed, and the results are compared to the observed results to generate an estimate of the "goodness-of-fit", G_i, where

$$G_i = \sum_{j=1}^{N_{obs}} \left[\frac{V_{s,j} - V_{o,j}}{V_{o,j}} \right]^2 \qquad (12)$$

N_{obs} is the number of observed values, $V_{o,j}$ is the jth observed value, and $V_{s,j}$ is the corresponding simulated value. When all simulations have been completed, the minimum G_i is determined.

There are three possibilities:

$$P_{min} = P_{min} - \Gamma/2 \text{ and}$$

$$P_{max} = P_{max} - \Gamma/2 \text{ for } P_i = P_{min}; \qquad (13)$$

$$P_{min} = P_{min} + \Gamma/2 \text{ and}$$

$$P_{max} = P_{max} + \Gamma/2 \text{ for } P_i = P_{max}; \qquad (14)$$

or

$$P_{min} = P_i - \Gamma/8 \text{ and}$$
$$P_{max} = P_i + \Gamma/8 \text{ for } P_{min} < P_i < P_{max}. \qquad (15)$$

The first two alternatives shift the search range without altering its magnitude, whereas the last alternative contracts the search range to 25% of the original magnitude around P_i. If $\Gamma \le T_p$, then the search stops, and P_i is taken as the "best-fit" estimate. Otherwise, the search is repeated over the new range. The number of simulations required per search is a product of the number of divisions across all parameters being fitted, i.e., if there are three parameters with four divisions, each cycle would require 4^3 simulations. In this paper, three parameters—k_1, k_3, and f—were fitted, two parameters—the distribution coefficient K_{eq} and the Freundlich exponent m—were obtained by separate experiment, and two parameters—k_2 and k_4—were calculated using the fitted and experimental parameters and equations (5) and (6).

RESULTS AND DISCUSSION

Values for Freundlich equation parameters (Figs. 2 to 6 and Table 3) indicate convex P sorption isotherms for both soils and higher

FIG. 2. Experimental and simulated P BTC's for displacement of P solutions with concentrations (C_0) of 51, 11, and 5 g m^{-3} to columns of Myakka soil from the Rucks dairy using rate coefficients obtained by fitting (calibrating) the 2-site model to the data for 97 g m^{-3} (* indicates the C_0 used for calibration).
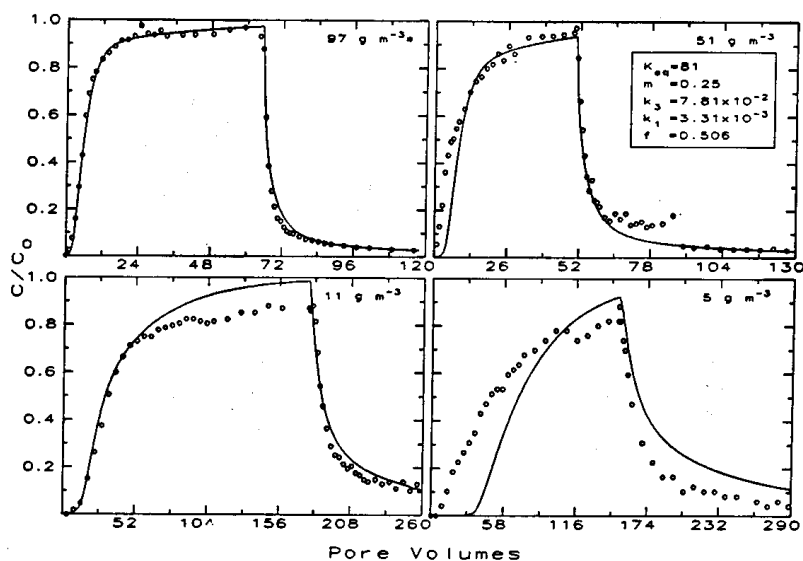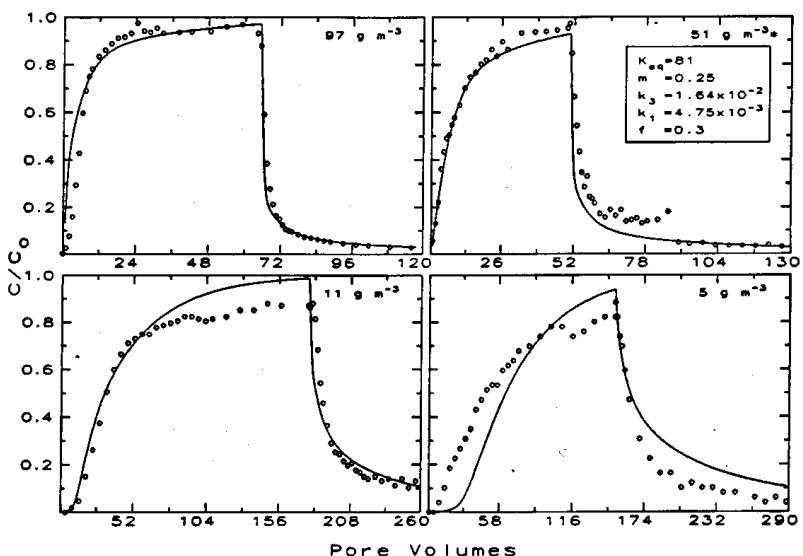

FIG. 3. Experimental and simulated P BTC's for displacement of P solutions with concentrations of 97, 11, and 5 g m^{-3} to columns of soil from the Rucks dairy using rate coefficients obtained by fitting (calibrating) the 2-site model to the data for 51 g m^{-3}.

potential for P sorption for Myakka soil (K_{eq} = 81 m^3 Mg^{-1} and m = 0.25) than for Immokalee soil (K_{eq} = 49 m^3 Mg^{-1} and m = 0.29). Under hypothetical conditions of very slow water flow so that sorption equilibrium is a valid assumption, retardation values for a given local P concentration C in solution can be calculated for Myakka and Immokalee soils using K_{eq} and m values (See equations 7 and 9) from the functions $R = 1 + 20.3\ (\rho/\theta)\ C^{-0.75}$ and $R = 1 + 14.2$ $(\rho/\theta)\ C^{-0.71}$, respectively. For assumed conditions of sorption equilibrium for either soil, these functions imply that retardation of phosphorus BTCs should decrease with increasing C_0 for applied solutions. Using experimental values for

ρ and θ in these expressions shows that retardation values corresponding to C_0 = 5 g m^{-3} ($R \sim 18$) were approximately 6 times larger than values for C_0 = 100 g m^{-3} ($R \sim 3$) for Immokalee soil and 7 times ($R \sim 21$ for C_0 = 5 g m^{-3}) for the Myakka soil. A dependency of retardation upon C_0 for influent solutions was in fact observed in BTCs (Fig. 2) even under medium-flow conditions where effects of sorption kinetics were observed. Tailing and clockwise rotation observed in experimental BTCs (Fig. 2) were attributed to kinetic and nonlinear aspects of P sorption (Mansell et al. 1991). For a given C_0 in column influent, the retardation functions also imply that greater retardation should occur

FIG. 4. Experimental and simulated P BTC's for displacement of P solutions with concentrations of 97, 51, and 5 g m⁻³ to columns of soil from the Rucks dairy using rate coefficients obtained by fitting (calibrating) the 2-site model to the data for 11 g m⁻³.
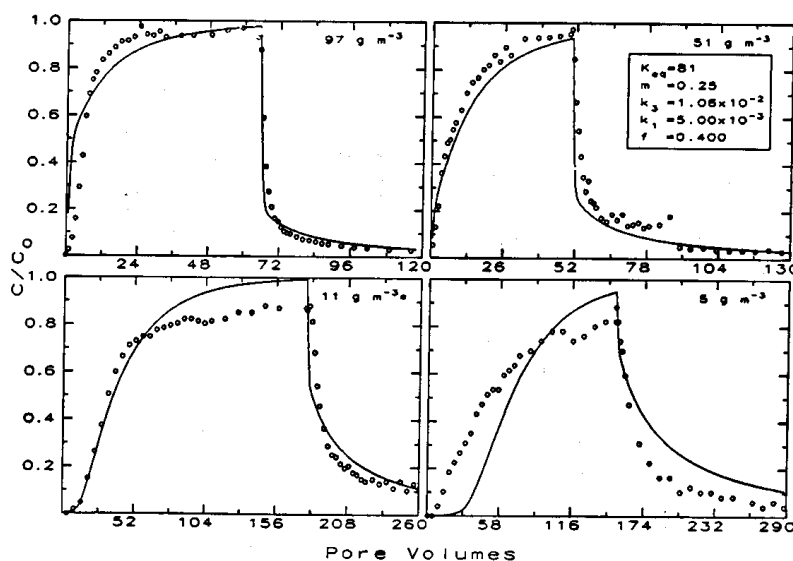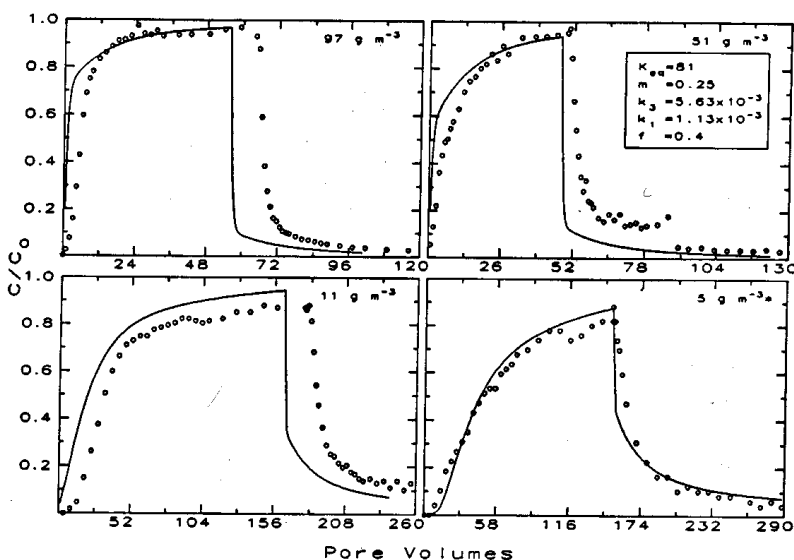

FIG. 5. Experimental and simulated P BTC's for displacement of P solutions with concentrations of 97, 51, and 11 g m⁻³ to columns of soil from the Rucks dairy using rate coefficients obtained by fitting (calibrating) the 2-site model to the data for 5 g m⁻³.

for Myakka soil than for Immokalee under conditions of local equilibrium. This dependency of retardation upon soil type was also observed (Fig. 3 and 6) experimentally during miscible displacement of P-laden solutions through soil columns.

Using equation (7), the values of equilibrium sorption buffering capacities B(C) for Myakka soil are 1.34 and 1.19 times larger than for the Immokalee soil for C values of 5 and 100 g m⁻³, respectively. For the P BTCs for soil columns shown in Figs. 3 and 6, earlier experimental breakthrough of P in column effluent and steeper curves for $C_0 = 5$ g m⁻³ also reflect a larger influence of kinetic sorption upon P re-

tardation in the Myakka soil than for the Immokalee soil. When $C_0 = 100$ g m⁻³, the effect of kinetic sorption resulted in a much smaller retardation influence for P movement in Myakka soil than for Immokalee soil.

Initial residual levels of P for the Myakka soil were larger than for the Immokalee soil. Mehlich I (MIP) and total extractable phosphorus (TEP) in the Immokalee soil from the Dry Lake Dairy were 6.2 and 12.6 mg kg⁻¹, respectively. Mehlich I (MIP) and total extractable phosphorus (TEP) in the Myakka soil from the Rucks Dairy were 24.1 and 38.2 mg kg⁻¹, respectively. Initial levels of MIP and TEP for Myakka soil were thus approximately 3.9 and 3.0 times larger than for

FIG. 6. Experimental and simulated P BTC's for displacement of P solutions with concentrations of 101, 11, and 5 g m^{-3} to columns of Immokalee soil from the Dry Lake dairy using rate coefficients obtained by fitting (calibrating) the 2-site model to the data for 51 g m^{-3}.
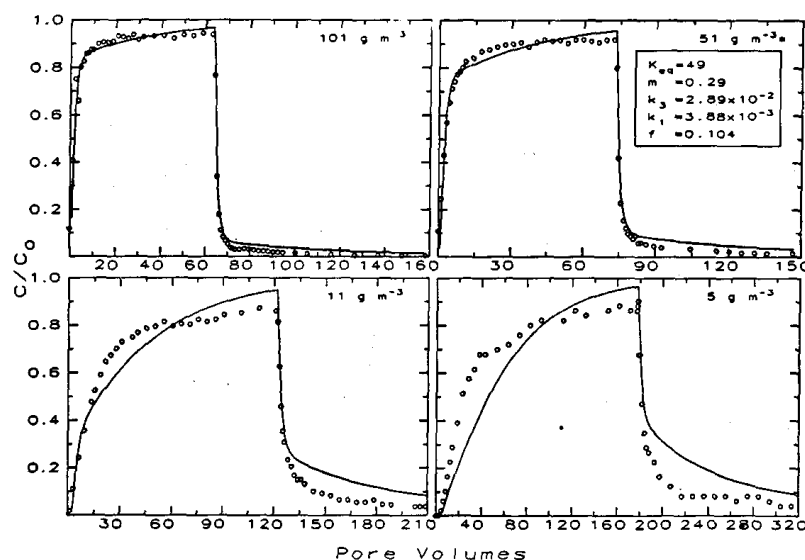
TABLE 3

Optimal kinetic rate coefficients and related parameters obtained for spodic Immokalee soil from the Dry Lake dairy and for Myakka soil from the Rucks dairy

Parameter Model Description	Immokalee soil 2 Kinetic Sites (Model #1)	Myakka soil		
		1 Instantaneous Site (Model #2)	1 Kinetic Site (Model #3)	1 Kinetic + 1 Instantaneous (Model #4)
C_0 (g m^{-3})	51	51	51	51
	(Column 6)	(Column 2)	(Column 2)	(Column 2)
k_1 (s^{-1})	3.875 × 10^{-3}	NA	NA	1.963 × 10^{-2}
k_2 (s^{-1})	2.302 × 10^{-5}	NA	NA	9.898 × 10^{-5}
k_3 (s^{-1})	2.891 × 10^{-2}	NA	1.851 × 10^{-2}	NA
k_4 (s^{-1})	1.481 × 10^{-3}	NA	6.855 × 10^{-5}	NA
k_3/k_4	NA	35.858	NA	4.688 × 10^{-2}
K_{eq} (m^3 Mg^{-1})	49	81	81	81
m	0.29	0.25	0.25	0.25
f	0.104	1.000	1.000	0.266

the Immokalee soil, respectively. Unfortunately, the use of MIP and TEP data provides no information as to the reversibility of the residual P present in these soils.

A 2-site kinetic sorption/transport model was calibrated for one of the input solution C_0 values using experimental values for K_{eq} and m parameters (See Figs. 2 to 6 and Table 3) from the Freundlich sorption equation reported earlier (Burgoa 1989) for soils used in this work and using best-fit estimates for f, k_1, and k_3 parameters. These parameter values were then used to simulate phosphorus BTCs for the other three C_0 values. Simulations of phosphorus BTCs for columns of Myakka soil (Rucks Dairy) when calibrations were based upon C_0 values of 5 (Fig. 5), 11 (Fig. 4), 51 (Fig. 3), and 97 (Fig. 2) g m^{-3}

did not provide a unique set of estimates for f, k_1, and k_3 parameters over the entire range of P concentration in the influent solutions. Estimates for the forward rate coefficient k_1 based upon the lowest C_0 tended to be smaller than those obtained with calibrations based upon the three higher values of C_0. Simulations based upon calibrations for the two highest values of C_0 described experimental BTCs reasonably well for all but the lowest influent concentration. Also, simulations based upon a calibration using $C_0 = 5$ g m^{-3} underestimated retardation for experimental BTCs associated with 11, 51, and 97 g m^{-3} concentrations in the influent.

Obviously, the net behavior of P sorption was somewhat different when the influent solution contained $C_0 = 5$ and 11 g m^{-3} relative to influent

solutions with higher P concentrations. This difference was attributed to an influence of initial sorbed-phase P in the soil columns that was essentially ignored utilizing initial conditions of $C_i = 0$ and $S_i = 0$ in all simulations. For the larger values of C_0, these initial conditions adequately approximated reality but did not do so for the smallest value of C_0. Apparently, P present initially in the soil was either irreversibly sorbed or desorbed sufficiently slowly as to provide C_i essentially near zero during flow through soil columns. For $C_0 = 5$ g m^{-3}, P breakthrough did not occur in column effluent in Myakka (Fig. 3) and Immokalee (Fig. 6) soils, respectively, until approximately 6 and 8 pore volumes of effluent supporting the use of $C_i = 0$. However, utilization of $S_i = 0$ does not appear to be consistent with experimental BTCs. This hypothesis appears to be supported (Fig. 3) by observed underestimation of P retardation for simulations of $C_0 = 11$, 51 and 97 g m^{-3} using k_1, k_2, and f input parameters obtained by calibration using the BTC for $C_0 = 5$ g m^{-3}; and by observed overestimation of P retardation for simulation of $C_0 = 5$ g m^{-3} when input parameters for the model were obtained by calibrating using the BTC for $C_0 = 97$ g m^{-3}. Experimental determination of convex sorption isotherms for soils with residual P present may possibly provide parameters that are sufficiently adequate to simulate BTCs with large C_0 but not for cases with small values of C_0. Further research is needed to thoroughly determine the influence of residual soil P upon sorption-desorption during miscible displacement of P-laden solutions through columns of these soils.

Simulations (2-site kinetic model) of P BTCs for columns of Immokalee soil from the Dry Lake Dairy when calibration was based upon $C_0 = 51$ g m^{-3} described (Fig. 7) observed BTC's for $C_0 = 101$ g m^{-3} but generally underestimated tailing and rotation for $C_0 = 11$ and 5 g m^{-3} data. Estimates obtained for f, k_1, and k_3 parameters are presented in Table 3.

Phosphorus BTC's (Fig. 7) for Myakka soil (Rucks Dairy) were described reasonably well by the 2-site kinetic and 2-site kinetic/instantaneous models. A 1-site kinetic generally described BTCs. A 1-site instantaneous model overestimated retardation, underestimated tailing of P BTC's, and is not recommended for describing P mobility for the conditions of relatively high water flow used for columns of these spodic-soil materials.

SUMMARY

Chemical reactions that govern the mobility of P during water flow in soils are complex. Nevertheless, multireaction models which assume that P can be treated as a single component, provide adequate simulations for acid, sandy soils having low capacity to retain P. Still needed are multicomponent transport models for P that include kinetic chemical interactions between P and other anions for soil microsites, and between P and Al, Fe, and Ca.

A miscible displacement technique was used to investigate the mobility of P in soil materials

FIG. 7. Best-fit P BTC's obtained for columns of soil from the Rucks dairy using 2-site kinetic, 1-site kinetic, 1-site instantaneous, and 2-site kinetic/instantaneous models ($C_0 = 51$ g m^{-3}).
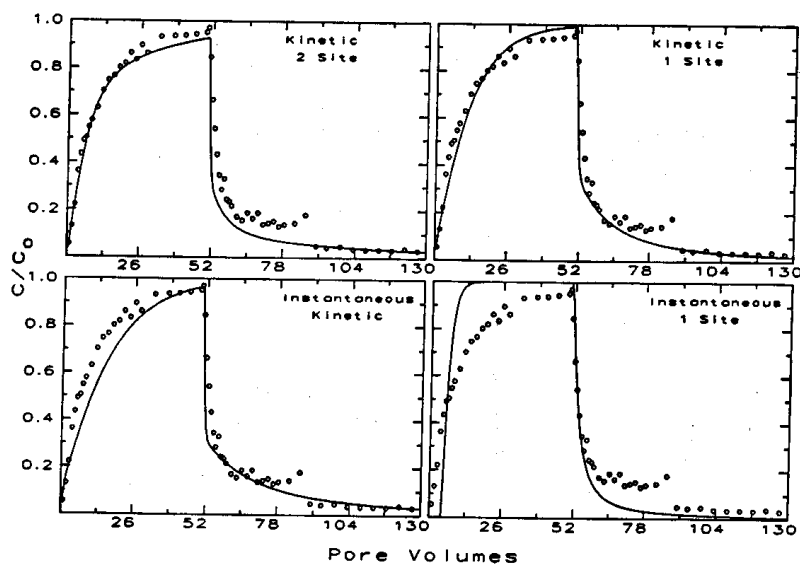
from Bh horizons from two dairies—Rucks (Myakka soil) and Dry Lake (Immokalee soil)— in the Lake Okeechobee Basin. Flow experiments were performed by applying P-laden solutions of (5, 10, 50, and 100 g P m^{-3}) to hand-packed columns of soil. Increases in C_0 increased the mobility of the P during water flow. The shape of observed P BTCs exhibited characteristics typical of kinetic and nonlinear sorption reactions, i.e., early breakthrough, clockwise rotation, and tailing. The equilibrium relationship between P sorbed and in solution was nonlinear and describable by a Freundlich isotherm.

A 2-site kinetic sorption/transport model was calibrated for one of the input solution C_0 for each of two soils and best-fit estimates were obtained for f, k_1, and k_3 parameters from the phosphorus BTC for that C_0 and soil. These parameter values were then used to simulate BTCs for the other three C_0 values. Simulations of BTCs when calibrations were based upon the three largest C_0 values—approximately 10, 50, and 100 g m^{-3}—did not provide a unique set of estimates for f, k_1, and k_3 parameters over the entire range of P concentration in the influent solutions. However, the estimates for each of these three parameters were of similar magnitude. Simulations based upon calibrations for the two highest values of C_0—50 and 100 g m^{-3}—described experimental BTCs reasonably well for all but the lowest influent concentration. However, simulations based upon a calibration using $C_0 = 5$ g m^{-3} underestimated retardation for experimental BTCs associated with the three highest concentrations in the influent. Results from these simulations of phosphorus BTCs indicate that assumptions associated with 2-site kinetic model were adequate for 11, 50 and 100 g m^{-3} C_0 values, but not for $C_0 = 5$ g m^{-3}. Assumptions of no initial residual P in the soil were obviously not applicable for the lower C_0. Further research is needed to describe the influence of residual P upon the mobility of P applied in solution to the soil.

Phosphorus BTCs were described reasonably well by the 2-site kinetic and a 2-site kinetic/ instantaneous models. A 1-site kinetic model generally described BTCs. A 1-site instantaneous model overestimated retardation and underestimated tailing of BTCs.

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