Agriculture and Environment, 7 (1982) 149—160
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

TRANSPORT AND FIXATION OF PHOSPHATE IN ACID, HOMOGENEOUS SOILS

I. PHYSICO-MATHEMATICAL MODEL

P.A.C. RAATS, P. DE WILLIGEN and R.G. GERRITSE

Institute for Soil Fertility, Postbus 30003, 9750 RA Haren (Gn.) (The Netherlands)

(Accepted 19 October 1981)

ABSTRACT

Raats, P.A.C., De Willigen, P. and Gerritse, R.G., 1982. Transport and fixation of phosphate in acid, homogeneous soils. I. Physico-mathematical model. *Agric. Environm.*, 7: 149—160.

A physico-mathematical model describing convective and diffusive transport, nonlinear reversible adsorption, and irreversible fixation is formulated. The rate of fixation is assumed to be proportional to the amounts of mobile phosphate above an equilibrium level and to the amount of Al + Fe available for binding phosphate. The finite fixation capacity implies that, with a continuous supply of phosphate at the soil surface, all fixation occurs in a front moving downward at a certain velocity and having a constant shape. The fixation front separates a transmission zone near the soil surface in which all available aluminum and iron has been used and a zone in which the equilibrium values prevail. If the fixation capacity were unlimited then all fixation would occur in a zone near the soil surface. In the absence of fixation, the model reduces to one dealt with extensively in the literature.

INTRODUCTION

In areas with large livestock operations as well as in and around urban areas, large amounts of phosphorus are taken up and then released in wastes. Traditionally such wastes were an important source of minerals and organic matter for agriculture. However, economic pressures now often dictate direct release into the aquatic environment or onto soils in excessive amounts. With the advent of secondary and tertiary treatments of sewage and the substitution of poly-phosphates in detergents by non-phosphorus containing sequestering agents, the direct release of phosphorus into surface waters is decreasing. However, the excess application of animal wastes and sewage sludge to soils is increasing, resulting in a fairly rapid increase of mainly nitrate and chloride with calcium and sodium as counterion in ground and surface water, and a gradual increase in the soil surface layer of phosphorus and various trace elements (Kolenbrander, 1974).

In The Netherlands the ultimate goal of the Coordination Committee for Environmental Health is to reduce the phosphorus concentration of the surface water to 0.05 mg l^{-1}, while for the time being a limit of 0.3 mg l^{-1} is considered acceptable (RIWA, 1977). This means that agricultural practice should aim at a situation where the concentration of P in the water leaving the soil profile and entering the drains does not exceed such limits. The concentrations of orthophosphate and most trace elements in the soil solution are buffered over a wide range due to very effective retention by the soil. As a consequence the concentration in the soil solution and the mobility of orthophosphate and most trace elements will remain low. The direct measurement of the buffer capacity is hampered by the slow equilibration processes involved.

The purpose of this series of three papers is to evaluate the effects of surplus phosphate addition on the basis of a mass balance and simple models for adsorption, fixation, and transport of phosphate. In this paper (Part *I*) the physico-mathematical model will be formulated and various analytical tools will be used to indicate some of its qualitative implications. In Part II (De Willigen et al., 1982) numerical solutions of some problems will be presented. In Part III (Gerritse et al., 1982) data from batch experiments to determine the adsorption isotherm and the rate of fixation will be used in the computer program and the results will be compared with those of column experiments.

THE PHYSICO-MATHEMATICAL MODEL

Mass balance

The orthophosphate in the soil is assumed to be divided between a mobile phase and an immobile phase (e.g., Larsen, 1967). Assuming transport in the vertical direction only, the mass balance can be written as:

$$\frac{\partial \mu}{\partial t} = -\frac{\partial F}{\partial z} - \frac{\partial \sigma}{\partial t} \tag{1}$$

where t is the time (days); z is the depth (cm); μ is the mass of mobile P per unit volume (mg cm^{-3}); σ is the mass of immobile P per unit volume (mg cm^{-3}); and F is the flux of mobile P in mg cm^{-2} day^{-1}. Equation (1) will be combined with three constitutive assumptions describing, respectively, adsorption, fixation, and transport.

Adsorption

The mobile P is assumed to be distributed between an adsorbed phase and the aqueous soil solution according to:

$$\mu = \mu_a + \theta c \tag{2}$$

where μ_a is the mass of adsorbed P per unit volume (mg cm^{-3}); θ is the volumetric water content (ml cm^{-3}); and c is the concentration of P in the soil solution (mg ml^{-1}). The adsorption reaction is usually completed within 1 to 3 days (Shayan and Davey, 1978; Beek, 1979). In practice, a contact time of 24 h is often used. In the mathematical model the physical adsorption described by equation (2) is assumed to be perfectly instantaneous and reversible. Admittedly, this is an idealization, which is justified only if the rates of transport and fixation are relatively small. With fluxes of water from 1 mm to 10 mm per day, a diffusion coefficient of the order of 1 cm^2 day^{-1}, a dispersion length of the order of 3 cm, and the half-life for the fixation reaction being at least 1 week, these conditions appear to be adequately met. If they are not met, experimentally distinguishing adsorption and fixation becomes rather difficult. Adsorption isotherms are often fitted to specific functional relationships between μ_a and c (see Barrow (1978) for a discussion of the relative merits of several equations). These are particularly useful in seeking analytical or approximate solutions of flow problems. However, in the second paper of this series, measured adsorption isotherms will be introduced in tabulated form into the computer program.

The adsorption isotherms for three Dutch soils and for two U.S. soils are shown in Fig. 1. For the Dutch soils they were determined in soil—water suspensions at a temperature of 20°C and a contact time of 24 h. Those for the U.S. soils were determined under similar circumstances (Sawhney and Hill, 1975; Sawhney, 1977). Fig. 1 shows that, despite large quantitative differences, the shapes of the curves for the different soils are the same. Although much information concerning the adsorption of phosphate in soils can be found in the literature (see for example Barrow (1978) and references given there)

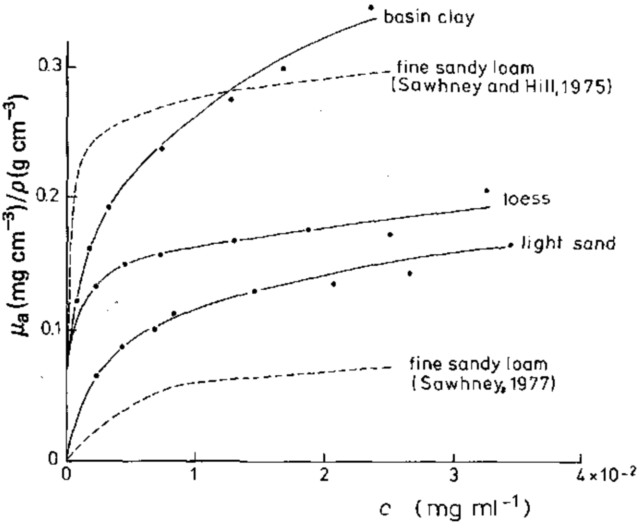

Fig. 1. Phosphate adsorption isotherms: light sand; basin clay; loess; fine sandy loam (Sawhney and Hill, 1975); fine sandy loam (Sawhney, 1977). ρ is the bulk density of the soil.

it appears difficult to compare the various results. Phosphate adsorption depends on many factors, including pH (Lopez-Hernandez and Burnham, 1974), ionic strength, and the dominant cation in the soil solution (Ryden and Syers, 1975), and, of course, on temperature (Barrow and Shaw, 1975). Another complicating factor is that there is no universally accepted method for determining phosphate adsorption isotherms.

Fixation

The rate of fixation is assumed to be proportional to $(\mu - \mu_e)$, the excess mobile solute above the equilibrium value μ_e:

$$\frac{\partial \sigma}{\partial t} = k_e(\mu - \mu_e) \qquad \text{if } \mu > \mu_e \tag{3a}$$

$$= 0 \qquad \text{if } \mu < \mu_e \tag{3b}$$

where k_e is the rate variable defined by:

$$k_e = (1 - \sigma/\sigma_\infty)k \tag{4}$$

where σ_∞ is the fixation capacity and k is the rate constant. The rate variable k_e is equal to the rate constant k when $\sigma = 0$. What we regard as "fixation" could also be called "chemisorption". Equations (3a, b) imply that the fixation is assumed to be irreversible. Equations (3) and (4) require the specification of three parameters, namely μ_e, σ_∞, and k.

To choose the equilibrium value, μ_e, several guides are available:
(1) In effluents from 90 cm long, unpolluted, undisturbed soil columns, the concentrations of phosphate were found to be in the range of 10^{-3}—10^{-1} mg l^{-1} (Gerritse, 1978). Corresponding to this equilibrium concentration c_e, there will be a certain equilibrium value μ_e.

(2) In a long term, batch adsorption/fixation experiment the decrease of mobile phosphate could be described by equations (3) with a constant value of k_e and a value of μ_e corresponding to a concentration of phosphate in solution of 0.3—0.4 mg l^{-1} (Gerritse et al., 1982).

(3) Beek (1979) assumes that the adsorbed P is distributed over two pools: pool I fills up mainly at lower concentrations and is not subject to fixation; pool II fills up mainly at higher concentrations and is subject to fixation (see Fig. 2). Beek's model does not differ very much from one in which the division between pools I and II is assumed to be sharp, with μ_e in equations (3) corresponding to the transition point. Interpreted this way, the data of Beek suggest that for his conditions the equilibrium phosphate concentration (corresponding to μ_e) is about 1 mg l^{-1}.

The simple model for the rate variable k_e involving a finite fixation capacity σ_∞ was proposed recently by Beek (1979). On the basis of data for three sandy soils with pH 4 to 5 Beek concluded that: (a) the maximum amount of phos-

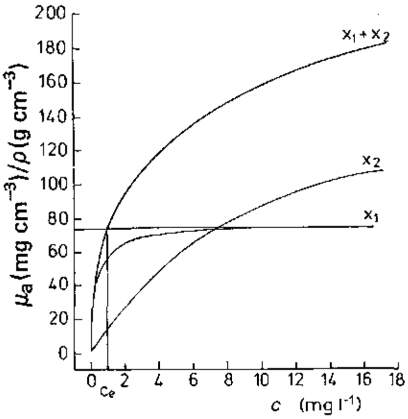

Fig. 2. Phosphate adsorption of a top soil sample described by two Langmuir isotherms (x_1 and x_2) (after Beek, 1979).

phate which can be immobilised is closely correlated with the content of oxalate-extractable aluminum and iron; (b) the percentage of the total aluminum and iron available for P fixation varies widely, mostly in the range of 5 to 20%; the aluminum and iron contents of Dutch soils vary from 0.1 to 20% (Knibbe and Schelling, 1967); (c) three moles of aluminum or iron, regarded as being available on the basis of the oxalate extraction, can bind one mole of P.

Equation (4) stipulates a finite capacity for fixing P. Earlier first-order (Larsen et al., 1965; Fitter, 1974) and higher order (Helyar and Munns, 1975; Barrow and Shaw, 1975) models implied an infinite capacity to immobilise phosphate, which is obviously not acceptable in the long term. From data reported by Larsen et al. (1965) and by Fitter (1974) one can, nevertheless, infer something about the value of the rate constant k. Over a period of several years Larsen et al. (1965) followed the decrease of the L value, the isotopically dilutable soil phosphate determined on the basis of the ^{32}P/^{31}P ratio in plants growing on a soil. They found that a first-order rate equation could describe the decrease satisfactorily. Half-life times calculated by Larsen et al. (1965) for 18 British mineral soil types ranged from 1 to 6 years. For one peat soil they found a half-life of 56 years. Fitter (1974) obtained corresponding results for the slow fixation of phosphate by colliery shale soils, with half-life times of 2—4 months. Other recent measurements also suggest half-lives of the order of a few months (Beek, 1979; Gerritse et al., 1982).

Flux of mobile solute

The flux F is assumed to be the sum of a convective component θvc and a dispersive component $-\theta D\partial c/\partial z$:

$$F = \theta vc - \theta D\partial c/\partial z \qquad (5)$$

where v is the velocity of the water (cm day^{-1}), θv is the volumetric flux (ml cm^{-2} day^{-1}); and D is the dispersion coefficient (cm^2 day^{-1}) defined by:

$$D = \alpha D_0 + lv \tag{6}$$

where $D_0 = 1$ cm^2 day^{-1} is the diffusion coefficient in the bulk liquid, $\alpha = 0.67$ is a tortuosity factor, and $l = 3$ cm is a dispersion length. Unless stated otherwise, the volumetric water content, θ, and the volumetric flux, θv, are assumed to be constant in this series of papers. In The Netherlands the flux of water below the root zone, averaged over the year, is about 1 mm day^{-1}.

Initial and boundary conditions

The initial condition is assumed to be uniform:

$$c = c_{\mathrm{i}} \qquad t = 0 \qquad z \geqslant 0 \tag{7a}$$

$$\mu = \mu_{\mathrm{i}} = \mu[c_{\mathrm{i}}] \qquad t = 0 \qquad z \geqslant 0 \tag{7b}$$

$$\sigma = \sigma_{\mathrm{i}} \qquad t = 0 \qquad z \geqslant 0 \tag{7c}$$

$$F = F_{\mathrm{i}} = \theta v c_{\mathrm{i}} \qquad t = 0 \qquad z \geqslant 0 \tag{7d}$$

For $t > 0$ the flux at the soil surface is assumed to be constant:

$$F = F_0 = \{\theta v c - \theta D \partial c/\partial z\}_{z=0} \qquad t > 0 \qquad z = 0 \tag{8}$$

ANALYTICAL SOLUTIONS OF SOME LIMITING CASES

The constitutive assumptions describing adsorption and fixation are both nonlinear. For specific initial and boundary conditions, complete descriptions of the transport, adsorption, and fixation will generally require numerical techniques (De Willigen et al., 1982). Nevertheless, as usually happens with nonlinear problems, analytical solutions of several limiting cases help to isolate the dominant characteristics.

Infinite fixation capacity

Following Beek (1979), we assumed the fixation capacity to be finite. It is instructive to first consider an effectively infinite fixation capacity, in other words to set $(1 - \sigma/\sigma_\infty) = 1$ in equation (4). The solutions of equations (1), (2), (3), and (5) subject to conditions (7)—(10) will after a long time approach a steady distribution with all the added phosphate being fixed in a zone near the soil surface. If the transport is purely convective, so that equation (5) reduces to $F = \theta v c$, then the steady concentration profile is given by:

$$z = (\theta v/k)\int_{c}^{c_0} (\mu - \mu_e)^{-1}\,dc \tag{9}$$

where

$$c_0 = F_0/(\theta v) \tag{10}$$

Given the adsorption isotherm, the integral on the right hand side of equation (9) can be evaluated numerically or graphically from plots of $(\mu - \mu_e)^{-1}$ versus c. According to equation (9), for given values of F_0 and θv, the depth at which a given value of c occurs is inversely proportional to the rate constant k. If the adsorption isotherm is linear such that $(\mu - \mu_e) = \alpha(c - c_e)$, then equation (9) reduces to:

$$c = c_e + (c_0 - c_e)\exp -bz \tag{11}$$

where the damping factor, b, is given by:

$$b = (\alpha k)/(\theta v) \tag{12}$$

Note that substituting equation (2) into the linear relation $(\mu - \mu_e) = \alpha(c - c_e)$ gives the more conventional adsorption isotherm $(\mu_a - \mu_{ae}) = k(c - c_e)$, where the equilibrium distribution coefficient $k = \alpha - \theta$.

The dispersive component in equations (5) and (8) will tend to reduce the concentration gradients near the soil surface. If the adsorption isotherm is linear, then equation (11) remains valid with equations (10) and (12) replaced by:

$$c_0 = \frac{F_0/(\theta v) + (D/v)bc_e}{1 + (D/v)b} \tag{13}$$

$$b = \frac{-1 + \{1 + 4(D/v)(\alpha k)/(\theta v)\}^{1/2}}{2\,D/v} \tag{14}$$

A related steady flow problem was discussed by Gershon and Nir (1969), Bolt (1979, equation 9.107) and Van Genuchten and Cleary (1979, equations 10.13 and 10.14). They considered a slightly different model with $(\mu - \mu_e)$ in the rate equation (3) replaced by c; in other words, they considered a model in which *all* (i.e. $c_e = 0$) the dissolved substance, but not the adsorbed substance is subject to decay. Then the solution (11) remains also valid when the adsorption isotherm is nonlinear. Such is not the case with the rate equation (3) (Raats, 1982).

If the fixation capacity σ_∞ is infinite then integration of equation (3) gives:

$$\sigma = k\int_{t_0}^{t} (\mu - \mu_e)\,dt \tag{15}$$

According to equation (15) the mass of immobile P per unit volume is equal to the product of the rate constant k and the exposure to mobile P above the equilibrium value μ_e. Unlimited increase of the exposure to mobile P would require an infinite amount of binding agent.

Finite fixation capacity

If the effective fixation capacity is given by equation (4), then integration of equation (3) gives:

$$\sigma = \sigma_\infty \{1 - \exp[-(k/\sigma_\infty) \int_{t_0}^{t} (\mu - \mu_e) \mathrm{d}t]\} \tag{16}$$

According to equation (16), the mass of immobile P will approach σ_∞ for large values of the exposure to mobile P above the equilibrium level μ_e. Any solution of the system of equations (1)—(8) will after a long time approach a rather simple limit. Near the soil surface there will eventually be a transmission zone in which all the available Al and Fe has been used so that $\sigma = \sigma_\infty$ and in which the concentration approaches the ratio of the fluxes of the phosphate and of the water. Symbolically:

$$\sigma = \sigma_\infty \tag{17a}$$

$$c = c_\infty = F_0/(\theta v) \tag{17b}$$

$$\mu = \mu_\infty = \mu[c_\infty] \tag{17c}$$

$$F = F_\infty = F_e = \theta v c_\infty \tag{17d}$$

Ultimately, such a uniform zone near the soil surface will be separated from a second uniform zone by a fixation front moving down at a velocity v_f and having a constant shape. This second uniform zone is an equilibrium zone in which σ, c, μ, and F have the following values:

$$\sigma = \sigma_e \tag{18a}$$

$$c = c_e \tag{18b}$$

$$\mu = \mu_e = \mu[c_e] \tag{18c}$$

$$F = F_e = \theta v c_e \tag{18d}$$

The solutions can be classified on the basis of the location of the equilibrium state with respect to the initial state.

(1) The equilibrium state and the initial state coincide: $c_e = c_i$, $\mu_e = \mu_i$, and $F_e = F_i$. All cases considered in Part II of this series of papers fall in this category.

(2) The equilibrium state is located above the initial state: $c_i < c_e$, $\mu_i < \mu_e$. In addition to the three zones mentioned above there will be: (a) an adsorp-

tion front moving downward at a velocity v_a and having a constant shape; (b) a zone in which the initial conditions still prevail.

(3) The equilibrium state is located below the initial state: $c_i > c_e$, $\mu_i > \mu_e$. At depths not yet influenced by the application of P, the mobile P content gradually decreases to the equilibrium level.

To describe the fixation front it turns out to be convenient to introduce a coordinate frame of reference Z that moves with the front.

$$Z = z - v_f t \tag{19}$$

For a fixation front moving down at a velocity v_f and having a constant shape, the derivatives with respect to t at constant Z vanish. Introducing equation (19) into equations (1) and (3) transforms the latter two equations from partial differential equations in (x, t) to ordinary differential equations in Z:

$$v_f \mathrm{d}(\mu + \sigma)/\mathrm{d}Z - \mathrm{d}F/\mathrm{d}Z = 0 \tag{20}$$

$$v_f \mathrm{d}\sigma/\mathrm{d}Z + k\,(1 - \sigma/\sigma_\infty)(\mu - \mu_e) = 0 \tag{21}$$

Integration of (20) gives:

$$F - v_f(\mu + \sigma) = F_r \tag{22}$$

where F_r is an integration constant. Since F is the flux of orthophosphate with respect to the fixed coordinate z and $v_f\,(\mu + \sigma)$ in the flux of orthophosphate associated with the movement of the fixation front, it follows that F_r is the flux of orthophosphate with respect to the fixation front. Both v_f and F_r are constants determined by the limiting conditions of the fixation front. Behind and ahead of the fixation front, respectively, equation (22) reduces to:

$$\theta v c_\infty - v_f(\mu_\infty + \sigma_\infty) = F_r \tag{23}$$

$$\theta v c_e - v_f(\mu_e + \sigma_e) = F_r \tag{24}$$

Solving equations (23) and (24) for the constants v_f and F_r gives:

$$v_f = \frac{c_\infty - c_e}{(\mu_\infty + \sigma_\infty) - (\mu_e + \sigma_e)}\,\theta v = \gamma_1 \theta v \tag{25}$$

$$F_r = \frac{c_e(\mu_\infty + \sigma_\infty) - c_\infty(\mu_e + \sigma_e)}{(\mu_\infty + \sigma_\infty) - (\mu_e + \sigma_e)}\,\theta v = \gamma_2 \theta v \tag{26}$$

where γ_1 and γ_2 are constants which depend only on the conditions behind and ahead of the fixation front. One can derive the expression for v_f also directly by equating the flux in the uniform zone near the soil surface to the sum of the accumulation at the moving front plus the flux ahead of the front and solving for v_f. The constant $\gamma_1\theta$ accounts for the retardation of the velocity v_f of the fixation front with respect to the velocity of the water.

An analysis of the shape of fixation fronts will be presented in a future paper (Raats, 1982). Here we only note that in the limit of purely convective transport, i.e. in the limit $F \to \theta vc$, it follows from equations (21) and (22) that the distribution of the mobile phosphate is given by:

$$Z - Z_{\text{ref}} = \frac{\sigma_\infty \gamma_1 \theta v}{k} \int_{\xi_{\text{ref}}}^{\xi} (\mu - \mu_e)^{-1} \mathrm{d}\xi \tag{27}$$

where

$$\xi = \ln(\mu - c/\gamma_1 + \gamma_2/\gamma_1 + \sigma_\infty) \tag{28}$$

Note the similarity between equations (9) and (27). According to equation (27) in the limit of negligible dispersion, the width of the fixation front is proportional to the water flux θv and inversely proportional to the rate constant k. The integral on the right hand side of equation (27) can be evaluated numerically for any adsorption isotherm and values of (c_e, μ_e), σ_e, (c_∞, μ_∞), and σ_∞.

Vanishing rate of fixation

We have met two regions in which the rate of fixation vanishes: (a) $\sigma \to \sigma_\infty$, the binding agent is depleted; and (b) $\mu \leqslant \mu_e$, the mobile P is not accessible for fixation. Of course, the rate of fixation also vanishes if $k \to 0$, i.e. if the rate of fixation is extremely slow. In the absence of fixation the model reduces to one describing the interaction between adsorption and advective/dispersive transport. Such a model has been used widely for various substances (see e.g. Bolt, 1979; Van Genuchten and Cleary, 1979). For orthophosphate, models neglecting (irreversible) fixation can be used to describe relatively short term experiments with velocities v of the water of the order of cm per day to cm per h, provided the rate of (reversible) adsorption is taken into account (Cameron and Klute, 1977; Shah et al., 1975; Novak et al., 1975; De Camargo et al., 1979). Cameron and Klute (1977) used a *linear*, nonequilibrium adsorption isotherm and presented an analytical solution for a semi-infinite continuum with a uniform initial distribution and a step increase of the concentration in the solution at the boundary. They used this model to interpret an experiment of Cho et al. (1970) (in which the velocity of the water was 6 cm/h). Shah et al. (1975), Novak et al. (1975) and De Camargo et al. (1979) used a *nonlinear*, nonequilibrium adsorption isotherm. Shah et al. and Novak et al. emphasised the convergence to moving adsorption fronts of constant shape. With a linear isotherm such convergence does not occur.

The nonequilibrium adsorption models virtually reduce to equilibrium models, whenever due to slow transport the contact time is relatively long.

Finally, as a reviewer pointed out, it should be noted that irrespective of what is stipulated in models, most measurements of adsorption isotherms are performed under quasi-equilibrium conditions.

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