NOTE

A DIFFUSION INTERPRETATION OF SOIL PHOSPHORUS DESORPTION

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ABSTRACT

In earlier papers, we showed the applicability of a power-form equation to describe the kinetics of soil P desorption for several soils in laboratory batch experiments and in a rainfall-runoff process

\[ P_d = KP_0 t^{\alpha} W^\beta \]

where \( P_d \) is the amount of P desorbed in time \( t \) at a water:soil ratio of \( W \), with \( P_0 \) being the initial amount of desorbable P present in the soil, and \( K, \alpha, \) and \( \beta \) constants for a given soil. In this note, we have attempted to explain the above equation in terms of diffusion-controlled desorption. The development utilized some empirical deductions from the literature. The basic desorption rate equation is formulated as a diffusion equation, with the diffusion coefficient taken as a power function of the fraction of \( P_0 \) yet to be desorbed. This basic formulation is tested on experimental data for different levels of \( P_0 \) and \( t \), at a large value of \( W \). The basic equation is integrated and the results are simplified to derive the equation for \( P_d \) given above.

INTRODUCTION

Several studies have reported that the desorption of soil P during a short period of time is a low-activation energy process. The work of Kuo and Lotse (1974) and Evans and Jurinak (1976) reported that the activation energy for P desorption was between 2 and 3 kcal/mole. The low activation energies led Kuo and Lotse and Evans and Jurinak to suggest that the desorption of soil P during short reaction times may be limited more by the diffusion of the desorbed P through the stagnant water films present around the soil particles and within the soil aggregates than by the chemical reaction. Although higher activation energies (20 kcal/mole) were reported by Barrow and Shaw (1975), they were determined for a longer reaction period (up to 100 days) and represent the transfer of P between desorbable and fixed forms. It has been suggested that there is a continuous range of activation energies for soil P desorption (Posner and Bowden 1980). During the initial stages of desorption, P held at low activation energies is desorbed; during the later stages, P held at higher activation energies is desorbed.

Further evidence suggesting that the rapid desorption of P is diffusion-controlled, was obtained by Cooke (1966), who found that P desorption could be described by a linear relation to \( t^{1/2} \) for the initial 100 min of reaction. Similarly, Li et al. (1972), Enfield and Bledsoe (1975), and Vig and Dev (1979) concluded that P desorption was diffusion-controlled.

The kinetics of phosphorus (P) desorption for several soils has been described by an empirical model in a recent paper by Sharpley et al. (1981b). The equation has the form

\[ P_d = KP_0 t^{\alpha} W^\beta \] (1)

where \( P_d \) is the amount of P desorbed (\( \mu g \) P/g
The diffusion path length may, however, be water or solution that surrounds the particles. The development utilizes some empirical deductions from the cited literature. The essential features of Eq. (1) are that the logarithm of \( P_d \) is linearly related to the logarithm of \( t \) at any given \( W \) and \( P \) amendment and to the logarithm of \( W \) at any given \( t \) and \( P \) amendment. In addition, \( P_d \) is directly proportional to \( P_0 \). Several earlier studies have reported the use of a power-form equation to describe the desorption of \( P \) from soil with time (Kuo and Lotse 1974; Chien 1977; Barrow 1979; Chien and Clayton 1980).

In this note, we attempt an interpretation of Eq. (1) in terms of the concept of a diffusion-controlled desorption. The development utilizes some empirical deductions from the cited literature.

**CONCEPTUAL FRAMEWORK AND SOME RESULTS**

**Relationship for diffusion-controlled desorption**

A thin stagnant layer of water is usually assumed to be the diffusion barrier between the surface of the soil particles and the well-stirred water or solution that surrounds the particles. The diffusion path length may, however, be spatially variable, as the phosphate ions may be located inside a soil particle or aggregate, as well as on the external surface. The rate of diffusion would be inversely proportional to this path length. In the treatment given below, the thickness of the stagnant layer and the diffusion coefficient of \( P \) through this layer are considered as one parameter for convenience, called diffusivity. The diffusivity is equal to the diffusion coefficient \( \text{cm}^2/\text{s} \) in the traditional sense divided by the thickness of the stagnant layer \( \text{cm} \). The diffusivity implicitly includes any changes in the diffusion coefficient resulting from the differences in activation energy of the \( P \) desorption from the surface sites or the changes in the activation energy with time during desorption. For a general description, the diffusivity is considered a variable function. Its value decreases as the desorption progresses, as a result of changes in the effective diffusion coefficient, the length of the diffusion path or both. The differential equation for desorption is written as

\[
dP_d/dt = A \cdot a\left(\frac{P_0 - P_d}{P_0}\right)^m \cdot \left[\frac{P_0 - P_d}{V} - \frac{P_d}{W}\right]
\]

where \( dP_d/dt \) is the rate of desorption, \( A \) is the specific surface area \( \text{cm}^2/\text{g} \) of the soil particles, the expression \( a(P_0 - P_d)/P_0^m \), with \( a \) and \( m \) parameters is the variable diffusivity function \( \text{cm}/\text{s} \), and \( (P_0 - P_d)/V \) is the effective concentration of desorbable \( P \) at the soil surface at any time, \( t \), with \( V \) a constant that relates the amount of desorbable \( P, P_0 - P_d, \) to the effective concentration. This constant \( V \) may be interpreted as the volume of the diffusion layer \( \text{cm}^3 \) on the surface or inside the particles that is envisioned to contain the \( P \) on the soil. In the present analysis, we assume that \( V \) is a constant for a given soil, incorporating the effect of different particle sizes and their aggregation. The term within the brackets represents the \( P \) concentration gradient between soil and water. The diffusivity has been taken as a power function of the fraction of the initial \( P \) remaining on the soil; as this fraction decreases from the initial value of 1, the diffusivity decreases. The diffusivity is, thus, assumed to be dependent on distance from equilibrium. The specific function will allow the relationship to be linear or nonlinear, as determined by the value of \( m \). The choice of this function is somewhat arbitrary, but the general form of it may be intuitively justified in view of the various factors given above, which are thought to determine its value, and in view of the empirical evidence that can be deduced from the literature.

An important assumption that leads to the proposed form of diffusivity is that the initial desorbable \( P, P_0 \), is distributed among the var-
ious sites on the surface and inside the soil particle in a certain proportion, at any given level of $P_0$. This leads to the diffusivity being a function of the fraction $(P_0 - P_0)/P_0$, rather than of the absolute amount desorbable $(P_0 - P_d)$. The former formulation in Eq. (2) makes the rate of desorption $dP_d/dt$ at small times, when $P_d = 0$, directly proportional to the level of $P$ (Sharpley et al. 1981b). The same cannot be said for diffusivity as a function of $(P_0 - P_d)$.

**Test of the basic relationship for large water:soil ratio**

We tested Eq. (2) for a large water:soil ratio, $W$. By setting $P_d/W = 0$ in Eq. (2), we obtain

$$\frac{dP_d}{dt} = \frac{A \cdot a}{v} \left(\frac{P_0 - P_d}{P_0}\right)^m \cdot [P_0 - P_d] \tag{3}$$

Dividing both sides by $P_0$ gives

$$\frac{1}{P_0} \frac{dP_d}{dt} = \frac{A \cdot a}{v} \left(\frac{P_0 - P_d}{P_0}\right)^{m+1} \tag{4}$$

which indicates that the normalized rate of desorption, $(dP_d/dt)/P_0$, is a unique function of the fraction of desorbable $P$ remaining on the soil. Figure 1 shows such a plot for Bernow fine sandy loam (fine-loamy, siliceous, thermic Gisso- sic Paleudalfs), using the data of Sharpley et al. (1981b). The data points for all the $P_0$ levels coalesce fairly well into one curve. In accordance with Eq. (4), the data can be represented by a power function of $(P_0 - P_d)/P_0$, as shown by a solid curve drawn in Fig. 1. When the desorption rate was plotted against $(P_0 - P_d)$, the data points for different $P_0$ levels were widely separated. The basic ingredients of Eq. (2), thus, hold. Equation (4) has the same form as that proposed by Barrow (1974) to describe $P$ transformations between labile and fixed forms of $P$ in soils.

**Integrated solution for large water:soil ratio**

By introducing a transformation $X = P_d/P_0$, Eq. (2) may be rewritten as

$$\frac{dX}{dt} = B(1 - X)^m[1 - GX] \tag{5}$$

where $B = Aa/v$, and $G = 1 + V/W$. Separation of the variables gives

$$(1 - X)^{-m}(1 - GX)^{-1} \frac{dX}{dt} = B \ dt \tag{6}$$

For $G = 1$, the case of a very large water:soil ratio or an infinite sink, the solution of Eq. (6) is (Selby 1967)

$$(1 - X)^{-m} = mBt + 1 \tag{7}$$

According to this equation, a log-log plot of the fraction of the initial desorbable $P$ remaining in the soil and time will be essentially a straight line with slope $= -1/m$, for $mBt \gg 1$. Solving Eq. (7) for $X$ yields

$$X = 1 - (1 + mBt)^{-1/m} \tag{8}$$

This expression is consistent in that $X = 0$ at $t = 0$, and $X$ approaches unity as $t \to \infty$, or at a very large value of $t$. Values of $X$ at several times were calculated using Eq. (8), with $m$ and $B$ equal to 3.0 and 0.82, respectively, obtained from our experimental data (presented in Fig. 1). The results of these calculations are shown in Fig. 2. For short to intermediate time periods, a log-log plot of $X$ and time can be represented by a straight line (Fig. 2). Both functions will converge for $t = 0$. We, thus, obtain a simplified expression

$$X = Ct^m \tag{9}$$
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where $C$ and $n$ are constants, and $n < 1$. Equation (9) has been successfully used for describing desorption to an infinite sink in several studies cited earlier. Equation (8) can also be expanded into a series of power terms or of exponential terms, such as have been used by Amer et al. (1955). Equations (7) and (9) also indicate that after early stages of desorption the relationship between the amount of P on the soil, $1 - X$, and the amount in solution, $X$, at any given time (Fig. 2, inset) is approximately similar to that of a Freundlich equation ($1 - X \approx EX^{1/m}$), which was also found experimentally by Barrow (1979) during desorption and by Kuo and Lotse (1974) during adsorption.

Rewriting Eq. (9) in terms of $P_d$ and $P_o$ gives

$$P_d = CP_0t^n$$

which shows that for a fixed time of desorption, the amount desorbed will be linearly related to the initial desorbable P on the soil, a finding that has been reported earlier and confirmed (Romkens and Nelson 1974).

Solution for general relationship

For $G > 1$, involving the cases of small to intermediate water:soil ratios or a finite sink, a closed-form solution of Eq. (6) can be obtained for integer values of $m$. For $m = 3$, the solution is (Selby 1967)

$$\frac{1}{2(G - 1)} \left[ -1 \right] \frac{2G}{(1 - X)^2} \left[ \frac{2G^2}{(1 - X)^2} \ln \frac{1 - X}{1 - GX} \right]$$

$$\frac{1}{(1 - X) + \frac{b}{(G - 1)^2} = Bt}$$

The form of the dependence of $X$ upon $Bt$ was calculated for several values of $G$ (originally defined as $1 + (V/W)$ and presented in Fig. 3a. It should be noted that Eq. (11) will hold only for $GX < 1$, which limits the calculation of $X$ for certain $G$ values. The relationship between the logarithm of $X$ and logarithm of $Bt$, for a given $V/W$ value, can be represented by a straight line over short time periods. The curves for different $V/W$ values have nearly the same slope. The dependence of $X$ on $V/W$ was determined using Eq. (11) for $Bt$ equal to 10. A log-log plot of the data gave a nearly straight line (Fig. 3b). Consequently, for small to intermediate time periods and within a limited range of $W$ values, the above functional dependence may be incorporated into a simplified form of Eq. (11)

$$X = Kt^n W^b$$

From Eq. (12), the expression for $P_d$ is given by Eq. (1).

**FIG. 3.** Relationship between logarithm of $X$ and (a) logarithm of $Bt$ at several $V/W$ values and (b) logarithm $V/W$ when $Bt$ is 10, according to Eq. (11) for Bernow soil.
Equation (12) gave a reasonably good description of P desorption from several soils and provided similar values of the constants $K$, $\alpha$, and $\beta$ for each soil over a range in $t$ (5 to 180 min), $W$ (10:1 to 1000:1), and $P_0$ (2 to 140 $\mu$g P/g soil) (Sharpley et al. 1981b). It should be noted that these are the limits within which the model can be applied and are equivalent to contact times and water:soil ratios existing in runoff-surface soil interaction. A more rigorous application of the kinetic model may be made using Eq. (11). In an earlier paper, Sharpley et al. (1981a) showed that Eq. (12) described the concentration of soluble P of runoff from soil under simulated rainfall.

We have not provided a rigorous proof of the effect of the $W$ term in the basic Eq. (2). From our experimental studies (Sharpley et al. 1981b), it appeared that breakdown of soil aggregates during desorption might have influenced the value of $\beta$, which expresses the effect of water:soil ratio. If soil aggregates break down, both the constant $V$ and "diffusivity" will change, resulting in a change in the rate of $P$ desorption. Although the breakdown effects are not included in the present model, the $W^\delta$ term of Eq. (1) still described the effects of water:soil ratio fairly well (Sharpley et al. 1981a, b). Further work is, however, needed in this regard.

REFERENCES


