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## KINETIC FREUNDLICH EQUATION APPLIED TO SOILS WITH A HIGH RESIDUAL PHOSPHORUS CONTENT

W. J. Chardon and D. Blaauw

For soils with low plant-available phosphorous (P) content, the kinetics of P sorption can be described adequately using the kinetic Freundlich equation ( $Q = at^m C^n$ ), where  $a$ ,  $m$ , and  $n$  are fitting parameters. When this equation is used for soils that already contain a large amount of plant-available P as a result of previous P additions, the problem arises as to how the initial P content,  $Q_0$ , ( $Q$  at  $t = 0$ ) can be taken into account. In this study, we tested the applicability of the equation to soils with a high level of plant-available P and several ways to include  $Q_0$ , which was estimated using nonlinear regression. Adsorption isotherms for three Dutch soils (sandy soil, loamy sand, and sandy loam soil) were determined after 1, 3, 7, and 21 days. We have shown that for these soils, a higher value of  $Q_0$  must be used for a longer equilibration time. A description of the increase of  $Q_0$  with time of the form:  $Q_0 = x t^m$  appeared to be applicable for the three soils tested. This leads to an extended kinetic Freundlich equation of the form:  $Q_{\Delta C} = (a C^n - x) t^m$ , where  $Q_{\Delta C}$  represents adsorbed P, determined from the amount that has disappeared from the shaking solution, and  $x$  is an additional fitting parameter. (Soil Science 1998;163:30-35)

**Key words:** Adsorption, kinetics, residual phosphorus.

**W**HEN phosphorus (P) is added to a soil, it may undergo several different reactions. A fast reaction indicates adsorption; a slow reaction indicates absorption, precipitation, or fixation. According to Barrow (1978) the adsorption of P by soil can be described adequately with the so-called Van Bemmelen-Freundlich equation (Sposito 1980):

$$Q = k C^n \quad (1)$$

where  $Q$  is the P sorbed ( $\text{mg kg}^{-1}$  soil),  $C$  is P in equilibrium solution ( $\text{mg L}^{-1}$ ), and  $k$  and  $n$  are fitting parameters.  $Q$  comprises both the initial amount of P sorbed,  $Q_0$ , and the amount of P that has disappeared from the solution,  $Q_{\Delta C}$  (Barrow 1978):

$$Q = Q_0 + Q_{\Delta C} \quad (2)$$

Combining Eqs. (1) and (2) gives:

$$Q_{\Delta C} = k C^n - Q_0 \quad (3)$$

with:

$$Q_{\Delta C} = \nu \Delta C W^{-1} \quad (4)$$

where  $\nu$  is volume of solution used (L) and  $W$  is weight of soil used (kg). Several methods are used to estimate  $Q_0$ . Holford et al. (1974) determined isotopic exchangeable P as a measure for  $Q_0$ , and Ryden and Syers (1977) used P extractable in 0.1 M NaOH. As an alternative, soil can be shaken with a solution to which a sink for P is added and  $Q_0$  estimated from the amount of P bound by the sink. Fitter and Sutton (1975) used anion resin as a sink, Van der Zee et al. (1987) and Van Noordwijk et al. (1990) used iron hydroxide-impregnated filter paper (FeO-paper) for this purpose. The parameter  $Q_0$  can also be determined by curve-fitting (Fitter and Sutton 1975; Barrow 1978), or it can be read from the point where the isotherm intersects the y-axis (Beckett and White 1964). In all cases,  $Q_0$  was assumed to be a fixed value characteristic of the soil sample. However, for the techniques mentioned above, the values of the parameters were shown to be influenced by the procedure. Specifically for  $Q_0$ , the length of time that a soil is left in contact with a sink for P, an extracting solution, or an equilibrating solution containing P influences the value of  $Q_0$ .

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Fardeau et al. (1985) showed this for exchangeable P, Amer et al. (1955) for resin-extractable P, Cabrera et al. (1981) for NaOH-extractable P, Van der Zee et al. (1987) and Myers et al. (1994) for FeO-paper, and Beckett and White (1964) for the intersection method. Thus, the assumption that  $Q_0$  is constant seems to be invalid.

Russell and Prescott (1916), who measured curves immediately after adding P and after 2 and 24 h, were probably the first to recognize that the shape of the P adsorption curve changes with time. Figure 1 shows their data plotted on a double-log scale with lines drawn with a constant value of  $n$ . This type of plot can be described with:

$$Q = a t^m C^n \quad (5)$$

where  $t$  is time (days) and  $a$  and  $m$  are fitting parameters. This equation was first derived by Kuo and Lotse (1973); however, they simplified the equation by substituting  $C^n$  with  $C_0$ , the initial concentration of P in solution. This simplification was shown to be less applicable than Eq. (5) over a wide range of conditions because it yields different values of  $a$  when  $C_0$  varies (Barrow 1989; Kato and Owa 1989).

The applicability of Eq. (5) has been shown in a number of studies (e.g., Kuo and Lotse 1973, 1974; Barrow and Shaw 1975, 1979; Barrow 1980 a and b; Mendoza and Barrow 1987; Torrent 1987; Kato and Owa 1989; Bramley et al. 1992; Afif et al. 1995). The equation was used in P transport models by Notodarmojo et al. (1991), Gerritse (1993), and Ho and Notodarmojo

(1995). From the studies mentioned, it can be determined that  $m$  ranges from 0.1 to 0.3.

Also in Eq. (5), the initial amount of P sorbed ( $Q_0$ ) has to be considered (Barrow 1980b; Torrent 1987). Using regression analysis, Mendoza and Barrow (1987) found an increase in  $Q_0$  with time. For a given temperature, the following equations relating  $Q_0$  to time were used:

$$Q_0 = b_1 t^{b_2} \quad (6)$$

$$Q_0 = A - B e^{-b_3 t} \quad (7)$$

where  $b_1$ ,  $b_2$ ,  $b_3$ ,  $A$ , and  $B$  are fitting parameters. Mendoza and Barrow (1987) tested five soils and used Eq. (6) and Eq. (7) for one and four soils, respectively.

Time-dependent sorption of P is unfavorable to agricultural soils because it gradually decreases P availability for plants. This is especially true in soils with low P content. For this reason, most research on time-dependent sorption has been done on soils that are deficient in P from an agronomic point of view. Neglecting time-dependent sorption leads to an overestimation of long-term P availability for plants and to an underestimation of the capability of a (sub)soil to retard the leaching of P. Therefore, a widely applicable mathematical description, including the role of  $Q_0$ , is needed for the understanding of the important role of P dynamics in soils. In order to test whether Eq. (5) is also valid for soils with high plant-available P content, the influence of time on sorption was determined on three samples of such soil. Several methods were also tested for taking  $Q_0$  into account to increase the applicability of the equation.

## MATERIALS AND METHODS

The soils used were three Dutch soils with a high level of plant-available P. Samples taken from the plough layer (0–20 cm) were air-dried and sieved using a 2-mm sieve. pH was measured in 1:5 (v:v) 1 M KCl (Anonymous 1989). Loss-on-ignition was determined by ignition for 2 h at 550°C (Anonymous 1992a). Plant-available P was determined by water extraction (60:1 v:v;  $P_w$ , mg P kg<sup>-1</sup> soil) according to Sissingh (1971). Total P content of the soil samples was determined spectrophotometrically after digestion of the soil with HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> (Anonymous 1992b).

Widemouth 100-mL polyethylene vessels were used for the determination of sorption isotherms. The determination was done in duplicate with 2 g of air-dried soil in 40 mL of 0.01 M CaCl<sub>2</sub>·2H<sub>2</sub>O. The vessels were rotated slowly

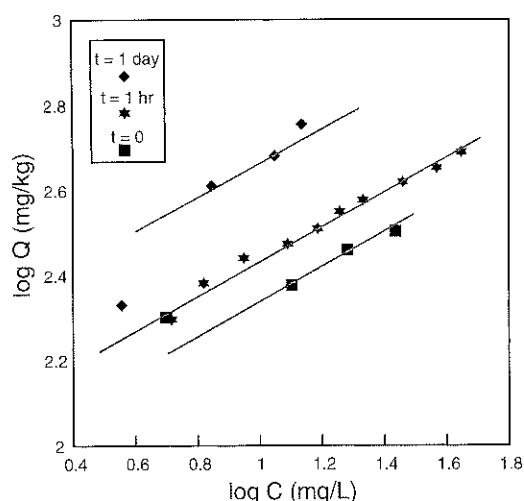


Fig. 1. Increase of amount adsorbed ( $Q$ ) as a function of  $C$  with time (Eq. (4)); data from Russell and Prescott (1916).

TABLE 1

Characteristics of soils used. pH, loss-on-ignition, total P content, water extractable P ( $P_w$ ), and  $P_i$  after 1, 3, 7, and 12 days

Soil	Soil texture	Location	pH	Loss-on-ignition (%)	P total	P <sub>w</sub>	P <sub>i</sub> after ... days			
							1	3	7	21
							(mg kg <sup>-1</sup> )			
A	Loamy sand	Haren	5.0	3.7	617	10.3	35	59	75	84
B	Sand	Giethoorn	5.1	8.1	843	9.0	43	59	74	120
C	Sandy loam	Vredepeel	6.8	3.1	584	10.0	27	38	51	72

at 4 r.p.m. during the entire period. Initial P concentrations, using  $\text{KH}_2\text{PO}_4$ , were 0, 1, 2, 4, 6, 10, 15, 20, 35, and 50 mg P L<sup>-1</sup>. After 1, 3, 7, or 21 days, the solution was filtered through 15-cm  $\emptyset$  paper filters, and the remaining P concentration was measured in the filtrate according to

Murphy and Riley (1962). Adsorption of P ( $Q_{AC}$ ) was calculated from the difference between initial and equilibrium value of C (Eq. (4)). Parameters were estimated using nonlinear regression with the statistical package GENSTAT 5, release 1.3 (Clarendon Press, Oxford, UK).

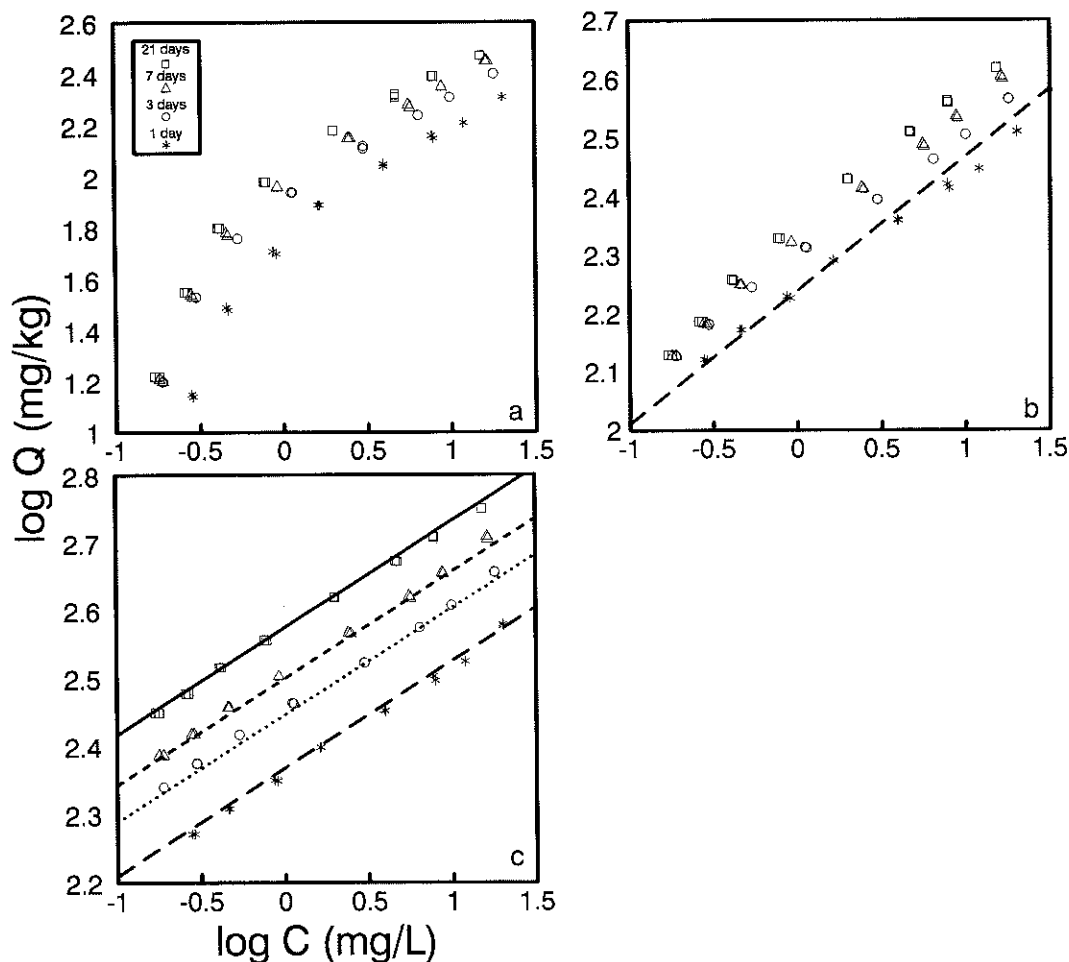


Fig. 2. Increase of amount adsorbed ( $Q = Q_0 + Q_{AC}$ ) as a function of  $C$  with time, soil A; (a)  $Q_0$  taken as zero; (b) constant value for  $Q_0$ ; (c) time-dependent value for  $Q_0$  (Eq. (9)).

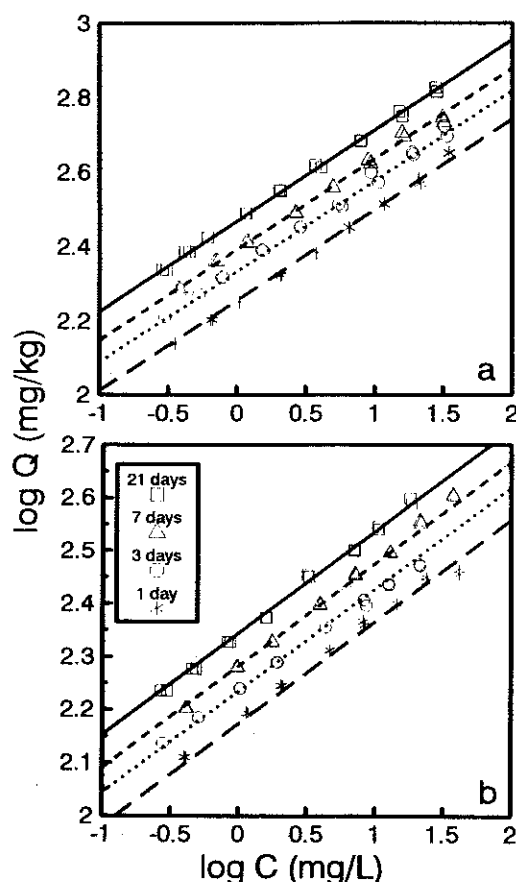


Fig. 3. Increase of amount adsorbed ( $Q = Q_0 + Q_{\Delta C}$ ) as a function of  $C$  with time; (a) soil B and (b) soil C, with time-dependent value for  $Q_0$  (Eq. (9)).

For measuring reversible sorbed P ( $P_i$ ) (Singh 1983; Chardon et al. 1996) as an indication for  $Q_0$ , two strips (20 cm<sup>2</sup>) of FeO paper were added to a widemouth 100-mL polyethylene vessel with 2 g of soil in 40 mL 0.01 M CaCl<sub>2</sub>·2H<sub>2</sub>O, in duplicate. FeO papers were refreshed weekly during the 21-day period. Before the determina-

tion of P on the FeO paper, the strips were cleaned using demineralized water to remove soil particles embedded in the paper. The FeO was dissolved in 0.1 M H<sub>2</sub>SO<sub>4</sub>, and P was determined in the acid solution according to Murphy and Riley (1962).

## RESULTS AND DISCUSSION

Table 1 gives data on soil texture, sampling location, pH, loss-on-ignition, total P content,  $P_w$  and  $P_i$ . The  $P_i$  data show that the FeO paper continued to extract P between days 7 and 21 although the rate decreases with time. This contrasts with the results of others, who found that after 16 h, P extraction by the FeO paper was almost completed (Chardon et al. 1996).

Adsorption data for soil A are shown in Figs. 2a, 2b, and 2c. In Fig. 2a,  $Q$  was not corrected for  $Q_0$ . Because all isotherms are curvilinear, it is clear that Eq. (5) is not valid without this correction.

In Fig. 2b, a constant value was used for  $Q_0$ .  $Q_0$  was calculated by fitting the sorption data of the 1-day isotherm on Eq. (3). Although the 1-day isotherm is linear, this is not the case with the 3-, 7-, and 21-day isotherms, and, thus, Eq. (5) is still not valid.

In Fig. 2c,  $Q$  was corrected for  $Q_0$  using a time-dependent value of  $Q_0$  following the equation:

$$Q_0 = x t^m \quad (8)$$

where  $x$  and  $m$  are fitted parameters. Figure 2c shows that straight lines are found for each period, implying that Eq. (5) is valid after the following extension for  $Q_0$ :

$$Q = Q_0 + Q_{\Delta C} = x t^m + Q_{\Delta C} = a t^m C^n \quad (9)$$

or:

$$Q_{\Delta C} = a t^m C^n - x t^m = (a C^n - x) t^m \quad (10)$$

The parameters  $a$ ,  $m$ ,  $n$ , and  $x$  for a specific soil were estimated using all data (three sampling times) in one fitting procedure with nonlinear regression. Note that in Eq. (9), the exponent  $m$  in the  $Q_0$  term is the same as the exponent of  $t$  on the

TABLE 2  
Fitted Parameters  $a$ ,  $n$ ,  $x$ , and  $m$  from Eq. (9); calculated values of  $Q_0$  after 21 days compared with total P content ( $P_T$ ) and  $P_i$  after 21 days

Soil	Soil texture	$a$ (mg <sup>1-n</sup> kg <sup>-1</sup> L <sup>-n</sup> day <sup>-m</sup> )	$n$	$x$ (mg kg <sup>-1</sup> day <sup>-1</sup> )	$m$	$P_T$	$P_i - 21$ (mg kg <sup>-1</sup> )	$Q_0 - 21$
A	Loamy sand	192	0.18	128	0.17	617	84	215
B	Sand	180	0.25	123	0.15	843	120	194
C	Sandy loam	136	0.20	94	0.14	584	72	144

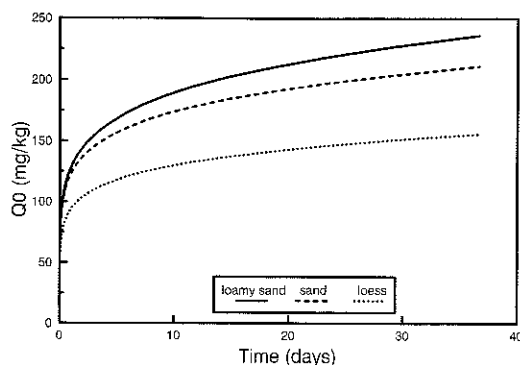


Fig. 4. Increase with time of  $Q_0$  for soils A, B, and C, calculated using Eq. (8) with parameter values from Table 2.

right side of the equation. On this point, Eq. (9) differs from Eq. (6) of Mendoza and Barrow (1987).

The sorption data of soils B and C followed the same pattern as the data of soil A. Using either no correction or a constant value for  $Q_0$  gave curvilinear isotherms (data not shown). As shown in Figs. 3a and 3b, the use of a time-dependent value for  $Q_0$  gave linear isotherms. For soils A, B, and C, the proportions of variation accounted for by Eq. (9) were 0.993, 0.994, and 0.991, respectively. Thus, the equation can describe all data, nine initial concentrations and four sampling times, using only four parameters and makes it possible to interpolate between sampling times. This would not be the case when  $Q_0$  was determined separately using one of the methods summarized above.

A physical explanation of the time-dependency of  $Q_0$  can be hypothesized as follows. The increase of sorption with time can be ascribed to a P front moving into a mineral aggregate (Willet et al. 1988). The amount of aggregate material behind the front increases with time. Thus, when the aggregate already contains a significant amount of P, the amount of P already sorbed on the material behind the front also increases, which is reflected in the increase of  $Q_0$  with time.

Table 2 gives the parameters of Eq. (9). In this table, the calculated values of  $Q_0$  after 21 days are compared with the total P content and with  $P_i$  measured after 21 days. After 21 days,  $Q_0$  represents 20 to 40% of total P. On average,  $P_i$  measured after 21 days is still 20% lower than  $x$ , which equals calculated  $Q_0$  after 1 day (Table 2). Figure 4 shows how  $Q_0$ , calculated for the three soils using parameters from Table 2, increases with time.

## CONCLUSION

A description of the sorption of phosphate requires a proper estimation of  $Q_0$  (the initial amount sorbed), which is also the case when the kinetics of P sorption is studied. For the three soils studied, all of which had a high content of plant-available P, sorption data could not be modeled with the kinetic Freundlich equation without any correction for  $Q_0$  or with a constant value. A time-dependent value had to be used for  $Q_0$ , and an increase of  $Q_0$  with time according to  $Q_0 = x t^m$  was found to be applicable. This leads to an extended Freundlich equation of the form:  $Q_{\Delta C} = (a C^n - x) t^m$ . For the description of P sorption kinetics on soils with a high content of plant-available P, we assume that this equation will be more applicable than the unextended equation.

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