

PHOSPHORUS DESORPTION KINETICS IN RELATION TO PHOSPHORUS FORMS AND SORPTION PROPERTIES OF PORTUGUESE ACID SOILS

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Although much information exists on the quantitative relationships between phosphorus (P) sorption and soil properties, comparatively less attention has been given to the influence of soil properties and P forms on the kinetics of P desorption and to the relationships between desorbable and sorbed P. The aim of this study was to rationalize the P desorption properties of a group of 29 acid soils representative of agricultural areas of Portugal. The soils differed widely in basic properties, total P concentration (91–1730 mg kg⁻¹), Olsen P (2.5–116 mg kg⁻¹), and relative contents of the “P fractions”—defined operationally in accordance with the seven-step fractionation scheme of Ruiz et al. (1997). P sorption capacity was accurately predicted from the concentrations of oxalate-extractable Al and Fe, as is generally the case with acid soils. Desorption of sorbed P to an anion exchange resin could be described by a combination of two kinetic equations of the Michaelis-Menten type for fast and slowly desorbable P pools. Although the concentrations of both pools were correlated with those of various P fractions, they could not be unambiguously assigned to specific chemical P species. The high correlation found between fast desorbable P and Olsen P testifies to the usefulness of this agricultural P test for acid soils; however, Olsen P tended to overestimate and underestimate fast desorbable P for Olsen P values lesser and greater than ~80 mg kg⁻¹, respectively. The average ratio of fast desorbable P to sorbed P was 0.21 and that of total desorbable P to sorbed P 0.60; both ratios increased with increasing degree of P saturation in the soil. (Soil Science 2007;172:631–638)

Key words: Phosphorus desorption, phosphorus sorption, acid soils, Olsen P.

THE concentration of orthophosphate-P in the soil solution is basically controlled by adsorption/desorption and precipitation/dissolution processes and also by the immobilization and mineralization of organic P forms (Sanyal and de Datta, 1991; Condrón et al., 2005; Pierzynski et al., 2005). Phosphorus (P) sorption (a term used here to designate the passage of orthophosphate-P from the soil solution to the solid phase) involves electrostatic and ligand

exchange adsorption processes in addition to various types of precipitation reactions (Frossard et al., 1995). The main phosphate-sorbing surfaces in soils are those of Al and Fe oxides, hydroxides, and oxyhydroxides—which are collectively referred to as *oxides*—(Frossard et al., 1995; Torrent, 1997), organic complexes of Al and Fe (Gerke and Hermann, 1992; Borggaard et al., 2004a), edges of silicate clays, and calcite (Matar et al., 1992). The sorption of phosphate by soil is conventionally described by so-called quantity/intensity (Q/I), P-sorption curves, or isotherms, which are usually described with the Langmuir or Freundlich equations. In these curves, the amount of phosphate-P sorbed under specific sorption conditions (basically, temperature, time of contact between soil and

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Received Dec. 14, 2006; accepted Feb. 28, 2007.

DOI: 10.1097/ss.0b013e3180577270

solution, soil/solution ratio, and type of supporting electrolyte) is plotted against the concentration of phosphate-P in solution.

The desorption of sorbed P (i.e., the passage of phosphate from the solid phase to the solution, either by dissolution or desorption proper) is markedly hysteretic. This is partly a result of slow sorption processes (Barrow, 1983a,b, 1985) and obviously leads to overestimating the P desorption capacity of soil from Q/I curves (Okajima et al., 1983). Although careful use of sorption curves can be useful with a view to estimating the amount of P that can be released to the soil solution (e.g., Memon and Fox, 1983), the best results are obtained with long-term desorption experiments; so, Koopmans et al. (2004a) found the Langmuir equation to provide a good description of the P desorption curve in a pot experiment where grass was grown on a P-rich acid sandy soil.

The rate of P desorption from the soil solid phase is obviously dependent on the particular desorption conditions, which include the soil/solution ratio, the vigor of shaking, the gradient of phosphate concentration near the solid phase, concentrations of various cations in solution, and temperature. These factors need to be considered when developing and calibrating desorption models (Koopmans et al., 2004b). The rate of desorption also depends on the nature and concentrations of the different P pools (e.g., the different metal phosphates or phosphate adsorbed on various P-adsorbing mineral surfaces). Although long-term P desorption can be described in terms of two discrete P pools (viz. "fast" and "slowly" desorbable P; Lookman et al., 1995), one should bear in mind that most soils appear to exhibit a continuum of desorbable P forms as illustrated, for instance, by the complex chemistry of P-rich soil particles (Pierzynski et al., 1990). Starting with the pioneering work of Chang and Jackson (1957), a number of sequential P fractionation schemes based on chemical extractants have been proposed to measure the different soil "P forms" or "P fractions." Because these operationally defined forms exhibit disparate solubility in the extracting solutions, one can hypothesize that they will exhibit also disparate rates of P desorption to the soil solution (i.e., P desorption kinetics are likely to be related to the concentration of the different P forms).

The agricultural soils of Portugal, which are mostly acid, exhibit a wide range of available and total P contents, mainly as a result of the

uneven application of P fertilizers during the last decades (Torrent et al., 2007). Consequently, they are likely to exhibit substantial differences in concentration among different P forms and hence in P desorption capacity and kinetics. A better understanding of the P sorption/desorption characteristics of these soils is thus crucial with a view to supporting management strategies intended to reduce P losses—and freshwater eutrophication by P as a result. The aim of this work was to characterize the P desorption kinetics of representative acid soils from Portugal and examine their relationship with the different P forms and P sorption properties.

MATERIALS AND METHODS

The 29 soil samples studied were obtained from A or upper B horizons of Portuguese acid soils developed on widely different parent materials that were used for cropping or grazing. The soils belonged to the following reference groups as per the World reference base for soil resources 2006 (IUSS Working Group WRB, 2006): Fluvisols (3), Regosols (3), Lithosols (1), Vertisols (1), Luvisols (7), and Cambisols (14). Samples were air-dried, sieved to <2 mm, and analyzed for particle size distribution, organic matter, pH, cation exchange properties, citrate/bicarbonate/dithionite-extractable Fe (Fe_d), acid oxalate-extractable Al, Fe, and P (Al_{ox} , Fe_{ox} , and P_{ox} , respectively), sodium pyrophosphate extractable Fe and Al (Fe_p and Al_p , respectively), and total, organic, and inorganic P (P_t , P_o , and P_i , respectively) as described by Horta and Torrent (2007). Olsen P was quantified according to Olsen et al. (1954). The equilibrium P concentration (EPC) was measured in a 1:1 soil/water extract obtained by shaking the soil suspension 30 min daily for 6 days.

We used the sequential fractionation scheme of Ruiz et al. (1997) to estimate the concentration of different P forms. The extracting solutions used and the corresponding putative P forms were as follows: (1) 0.1 M NaOH + 1 M NaCl solution (NaOH-P) for P adsorbed on mineral surfaces and organometallic complexes and in Al- and Fe-rich phosphates hydrolyzed at a high pH; (2) 0.267 M sodium citrate + 0.11 M sodium bicarbonate (CB-P) for P readsorbed at the first step and in some soluble Ca-containing pedogenic phosphates; (3) 0.2 M citric acid/sodium citrate at pH 6.0 (CC-P) for P in the more soluble pedogenic Ca phosphates; (4) 0.2 M sodium citrate + ascorbic acid at pH 6.0

(CA-P) for P in poorly crystalline Fe hydroxides; (5) 0.27 M sodium citrate + 0.11 M sodium bicarbonate + solid sodium dithionite (CBD-P) for P occluded in crystalline Fe hydroxides; (6) 1 M acetic acid/sodium acetate at pH 4.0 (Ac-P) for P in poorly soluble pedogenic calcium phosphates; and (7) 1 M HCl (HCl-P) to dissolve lithogenic apatite.

The method of Fox and Kamprath (1970) was used to construct the P sorption (i.e., Q/I) curves; however, the supporting electrolyte used was 0.002 M CaCl_2 . Sorption data were fitted to the following modified Freundlich curve (Fitter and Sutton, 1975):

$$Q_s + Q_{nat} = AC^b \quad (1)$$

where A and b are constants typical of each soil. The amount of P sorbed by the soil is the combination of that P sorbed in the sorption experiment (Q_s) and that sorbed previously by the soil (i.e., native sorbed P, or Q_{nat}). We used Olsen P rather than isotopically exchangeable P (Beckett and White, 1964; Olsen and Khasawneh, 1980), P desorbed to an anionic resin (Fitter and Sutton, 1975), or P_{ox} (Freese et al., 1992) to estimate Q_{nat} . This was done by first measuring the amount of P sorbed by the soil at an EPC of 3 mg P L^{-1} (Q_{s3}) and then conducting a stepwise multiple regression analysis to predict Q_{s3} from the variables reflecting those soil properties assumed to be related to P sorption (e.g., Al_{ox} and Fe_{ox}), Olsen P, and the Olsen P/pH ratio. The stepwise multiple regression procedure yielded no significant increase in the accounted variance of Q_{s3} after the equation

$$Q_{s3} = 2.12 + 0.072\text{Al}_{ox} + 0.062\text{Fe}_{ox} - 12.1(\text{Olsen P}/\text{pH}), \quad (2)$$

in which all variables, except Olsen P (mg kg^{-1}) and pH are expressed in millimoles per kilogram. This equation accounted for 91% of the variance of Q_{s3} versus only 78% when Olsen P/pH was excluded. Because the regression coefficient for this variable was negative, we assumed that its absolute value [viz. 12.1(Olsen P/pH)] provided a reasonable estimate of the concentration of native sorbed P (Q_{nat}). When both this value and experimental P sorption data were considered, the fit to Eq. (1) was excellent (mean $R^2 = 0.968$).

An anion exchange resin was used to study the kinetics of P desorption. Resin is less effective as a phosphate sink than is paper

impregnated with iron oxide (van der Zee et al., 1987) or iron oxide in dialysis membrane tubes (e.g., Lookman et al., 1995; Delgado and Torrent, 2001). However, methods based on iron oxides have some problems (e.g., soil adhering to the paper strips or long-term degradation of the dialysis membranes) that the use of coarse resin beads in nylon bags does not. Because resin bags can be removed from the soil suspension with little soil and solution entrained, they can be frequently replaced to keep the phosphate concentration in solution low. In the desorption experiment, nylon bags containing 2.2 g of Dowex 1 \times 4 resin in Cl^- form were placed in a 120-mL polyethylene bottle containing a suspension of soil in 100 mL of 2×10^{-3} M CaCl_2 . An amount of soil capable of desorbing $\sim 5 \mu\text{g}$ of P in 24 h as estimated in a preliminary desorption test was used. The suspension was then shaken at 1.3 Hz in a reciprocating shaker at 25 °C, and the resin bag replaced with a fresh one at times that were logarithmically spaced (ratio = 2.3) after the first replacement at 1 h (i.e., after 1, 2.3, 2.3^2 , 2.3^3 , ... 1801.2 h). The bags were gently rinsed with deionized water to remove the phosphate adsorbed on the resin and then washed three times with 0.25 M HCl to collect 100 mL of leachate. Phosphate-free resin was regenerated by washing with a 10% NaCl solution three times and then with deionized water. The concentration of dissolved reactive phosphate in each solution was determined by using the molybdate blue method of Murphy and Riley (1962).

Statistical analyses (Pearson's correlation coefficients, linear regression, stepwise multiple regression) were done with STATISTIX 7 (Analytical Software, 2000). To compare the regression coefficients of equations of the type $Z = aX + bY + \langle \text{other terms} \rangle$, the transformation expressions $V = X + Y$ and $W = Y - X$ were used to estimate the model $Z = cV + dW + \langle \text{other terms} \rangle$; then, the test for $d = 0$ is equivalent to the test for $a = b$. Nonlinear curve fitting was done with CurveExpert software (available from <http://curveexpert.webhop.biz/>). Unless otherwise stated, the term *significant* is used here to denote significance at the 0.05 probability (P) level.

RESULTS

Basic Soil Properties and P Forms

Table 1 summarizes the properties of the soils. Particle size distribution, organic carbon

content, pH, and exchange properties varied over wide ranges. On average, the soils were light-textured, moderately acidic, and relatively poor in organic carbon. Also, they differed widely in their concentrations of P-reactive compounds (as represented by Fe_d , Al_{ox} , Fe_{ox} , Al_p , and Fe_p) and of total, inorganic, and organic P. Differences in fertilizer P application rates are clearly reflected in the ranges of Olsen P (2.5–116 mg kg⁻¹), EPC (0.02–4.40 mg P L⁻¹), and degree of P saturation—defined as $P_{ox}/0.5(Fe_{ox} + Al_{ox}) - (0.03–0.93)$. On average, NaOH-P accounted for 50% of the inorganic P extracted in the seven-step sequential extraction procedure. This fraction was followed in order of abundance by CB-P, CBD-P, CC-P, CA-P, HCl-P, and Ac-P.

Phosphorus Sorption Properties

Table 2 shows the most salient P sorption and desorption properties of the soils. The value of A in Eq. (1) (i.e., total P sorbed at an equilibrium solution concentration of 1 mg P

L⁻¹ per unit soil mass) ranged from 25 to 580 mg P kg⁻¹ soil and was significantly correlated with Al_{ox} ($R^2 = 0.88$), Fe_{ox} ($R^2 = 0.45$), Al_p ($R^2 = 0.83$), Fe_p ($R^2 = 0.64$), and organic C concentration ($R^2 = 0.34$) but not with Fe_d , pH, or the clay concentration. In the stepwise multiple regression procedure, no further increase in the accounted variance of A was obtained after the following equation:

$$A = 1.94 + 0.053Al_{ox} + 0.039Fe_{ox} (R^2 = 0.92) \quad (3)$$

Equation (3), where A , Al_{ox} , and Fe_{ox} are expressed in millimoles per kilogram of soil, exposes that the Al and Fe oxides and organic complexes of Al and Fe play a dominant role in P sorption. Because the regression coefficient for Al_{ox} is higher than that for Fe_{ox} in Eq. (3), one can hypothesize that the oxalate-extractable Al forms are better P sorbents than the corresponding Fe forms, as suggested by previously reported pedotransfer functions (e.g., Borggaard et al., 2004b). However, this hypothesis is contradicted by the fact that the two regression

TABLE 1
Selected properties of the soils

| Property | Minimum | Maximum | Mean ± SD | Median |
|-------------------------------------------------------|---------|---------|-------------|--------|
| Clay (g kg ⁻¹) | 2 | 360 | 107 ± 78 | 80 |
| Sand (g kg ⁻¹) | 380 | 997 | 719 ± 163 | 740 |
| Organic C (g kg ⁻¹) | 1.7 | 30.5 | 10.5 ± 6.6 | 9.0 |
| pH _{water} | 4.9 | 7.1 | 5.8 ± 0.6 | 5.7 |
| Exchangeable Al (cmol _c kg ⁻¹) | 0 | 1.9 | 0.28 ± 0.53 | 0.44 |
| Fe_d^* (mmol kg ⁻¹) | 4 | 560 | 121 ± 153 | 52 |
| Al_{ox}^* (mmol kg ⁻¹) | 2.4 | 283 | 35.0 ± 56.7 | 19.2 |
| Fe_{ox}^* (mmol kg ⁻¹) | 1.3 | 82.7 | 26.0 ± 20.3 | 17.2 |
| Al_p^* (mmol kg ⁻¹) | 0 | 131 | 22.5 ± 33.3 | 11.4 |
| Fe_p^* (mmol kg ⁻¹) | 0.7 | 72 | 16.8 ± 15.4 | 10.8 |
| $P_{ox}/0.5(Fe_{ox} + Al_{ox})^\dagger$ | 0.03 | 0.93 | 0.26 ± 0.22 | 0.19 |
| Total P (mg kg ⁻¹) | 91 | 1730 | 484 ± 387 | 355 |
| Inorganic P (mg kg ⁻¹) | 26 | 1310 | 256 ± 308 | 126 |
| Organic P (mg kg ⁻¹) | 5 | 384 | 132 ± 92 | 118 |
| Olsen P (mg kg ⁻¹) | 2.5 | 116 | 31.3 ± 29.6 | 23.4 |
| EPC (mg L ⁻¹) | 0.02 | 4.40 | 0.79 ± 1.24 | 0.19 |
| NaOH-P (mg kg ⁻¹) | 24 | 995 | 143 ± 183 | 89 |
| CB-P [‡] (mg kg ⁻¹) | 2 | 550 | 50 ± 103 | 19 |
| CC-P [‡] (mg kg ⁻¹) | 1 | 378 | 30 ± 70 | 11 |
| CA-P [‡] (mg kg ⁻¹) | 2 | 130 | 29 ± 30 | 23 |
| CBD-P [‡] (mg kg ⁻¹) | 5 | 196 | 51 ± 54 | 29 |
| Ac-P [‡] (mg kg ⁻¹) | 1 | 47 | 7 ± 9 | 4 |
| HCl-P (mg kg ⁻¹) | 1 | 505 | 27 ± 93 | 3 |

*Subscripts for extractable forms of Al and Fe: d = citrate/bicarbonate/dithionite-extractable; ox = acid oxalate-extractable; p = sodium pyrophosphate-extractable.

[†]Degree of P saturation (van der Zee and van Riemsdijk, 1988).

[‡]Abbreviations of extractants used in the P fractionation scheme: CB = citrate-bicarbonate; CC = pH 6 citrate; CA = citrate-ascorbate; CBD = citrate-bicarbonate-dithionite; Ac = acetate.

TABLE 2

Phosphorus sorption and desorption properties

| Constant | Minimum | Maximum | Mean ± SD | Median |
|----------------------------------------------------|---------------------|---------------------|----------------|--------|
| A^* (mg kg ⁻¹) | 25 | 580 | 150 ± 114 | 109 |
| b^* | 0.07 | 0.38 | 0.23 ± 0.07 | 0.25 |
| Q_{d1}^\dagger (mg kg ⁻¹) | 0.3 | 166 | 26 ± 39 | 9 |
| Q_{d2}^\dagger (mg kg ⁻¹) | 0.3 | 477 | 55 ± 111 | 11 |
| $(Q_{d1} + Q_{d2})^\dagger$ (mg kg ⁻¹) | 0.7 | 643 | 81 ± 149 | 26 |
| K_1^\dagger (h ⁻¹) | 0.10 | 1.16 | 0.29 ± 0.21 | 0.25 |
| K_2^\dagger (h ⁻¹) | 26×10^{-5} | 66×10^{-3} | 0.0067 ± 0.013 | 0.0019 |

*In Equation (1).

†In Equation (4).

coefficients in Eq. (3) are not significantly different. It should also be noted that Fe_d is not included in the regression, as is generally the case with soils of the Mediterranean region (e.g., Peña and Torrent, 1990), probably because the soils studied here are relatively poor in crystalline Fe oxides.

Constant b —which is a measure of the curvature of the sorption curve and thus decreases with increasing relative affinity for phosphate at low solution P concentrations—ranged from 0.07 to 0.38 and was correlated with neither Al_{ox} nor Fe_{ox} . It should be noted that b values less than ~0.40 indicate that adsorption proper rather than precipitation is responsible for the removal of phosphate from the solution (e.g., Castro and Torrent, 1998).

Phosphorus Desorption Properties

Under the operational conditions described before, the kinetics of P desorption was accurately described by the combination of two equations of the Michaelis-Menten type:

$$Q_{dt} = (Q_{d1}K_1t)/(1 + K_1t) + (Q_{d2}K_2t)/(1 + K_2t) \tag{4}$$

where Q_{dt} is the amount of P desorbed per unit soil mass at time t , Q_{d1} and Q_{d2} are the sizes of “fast” and “slowly” desorbable P pools, K_1 and K_2 are the respective kinetic constants, and t is time. The latter constants are related to the curvature of the desorption curve, so curvature increases with increasing K .

Equation (4) proved more accurate than other four-parameter kinetic equations we tested to fit the desorption data. Thus, the mean R^2 and root mean squared error for the 29 soils were 0.997 and 1.22 mg kg⁻¹, respectively, versus 0.994 and 1.53 mg kg⁻¹, with a combination of

a first-order kinetic equation and a power function, and 0.988 and 2.20 mg kg⁻¹ with one of two first-order kinetic equations (used, e.g., by Lookman et al., 1995). Figure 1 illustrates the results of fitting the desorption data for one of the soils to Eq. (4).

As can be seen from Table 2, both Q_{d1} and Q_{d2} varied over a wide range, and so did the total amount of desorbable P (i.e., $Q_{d\infty} = Q_{d1} + Q_{d2}$). On average, the size of the more labile, fast desorbable pool (Q_{d1}) was about one-half that of the slowly desorbable pool (Q_{d2}). Based on the data of Table 2, the average desorption half-time was about 4 h for the fast desorbable pool and 150 h for the slowly desorbable pool.

Both Q_{d1} and Q_{d2} were strongly correlated with various P forms (Table 3) but not with CA-P, CBD-P, or HCl-P, because anionic resins

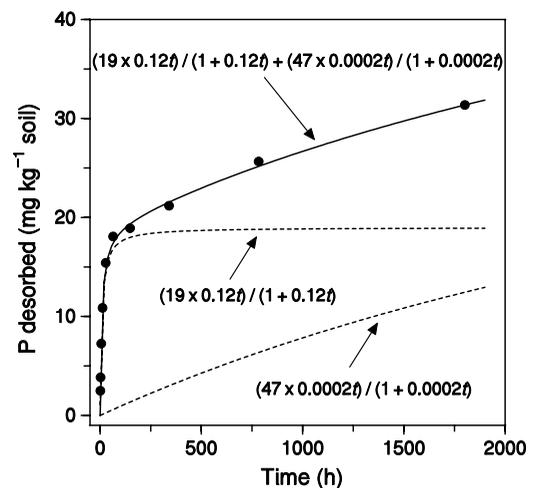


Fig. 1. Kinetics of P desorption from soil CH-219. The amount of P desorbed (continuous line) is described by a combination of two Michaelis-Menten equations corresponding to the pools of fast and slowly desorbable P (upper and lower dashed lines, respectively).

TABLE 3
Significant Pearson correlation coefficients between P desorption constants and P forms

| P form | Q_{d1} | Q_{d2} |
|-----------------|----------|----------|
| Total P | 0.835** | 0.843** |
| Inorganic P | 0.916** | 0.915** |
| Olsen P | 0.935** | 0.911** |
| NaOH-P | 0.560* | 0.595** |
| CB-P | 0.854** | 0.877** |
| CC-P | 0.847** | 0.866** |
| CA-P | 0.604** | 0.566* |
| P sorbed at EPC | 0.650** | 0.652** |

Significant at the *0.01 and **0.001 probability levels, respectively.

cannot recover phosphate occluded in Fe oxides or in poorly soluble pedogenic or lithogenic Ca phosphates. The highest Pearson correlation coefficient was that for Olsen P. However, the relationship between Q_{d1} and Olsen P was quadratic rather than linear (Fig. 2), probably because fertilizer P tends to gradually accumulate in relatively soluble phosphates in continuously fertilized soils. This indicates that Olsen P tends to overestimate and underestimate fast desorbable P at Olsen P values lesser and greater than ~ 80 mg kg⁻¹, respectively; the relationship between Q_{d2} and Olsen P (not shown) was also quadratic. A quadratic relationship was also observed between plant available P as measured in a plant cropping test conducted on the same group of

soils and Olsen P (Horta and Torrent, 2007). All these results testify to the usefulness of Olsen P as an agricultural P test for acid soils.

The correlation coefficients of Table 3 allow no unambiguous assignation of Q_{d1} or Q_{d2} to a specific P fraction. However, the correlations of these variables with NaOH-P were only modest relative to those with CB-P and CC-P, possibly because NaOH, which, unlike an anionic resin, is a strongly alkaline extractant and thus capable of desorbing phosphate from high-affinity sites on the surface of Fe and Al oxides and hydrolyzing Fe and Al phosphates. Thus, NaOH-P exceeded on average the combination of Q_{d1} and Q_{d2} . Why this combination was highly correlated with CB-P, CC-P, or CB-P + CC-P is obscure; we may speculate, however, that these citrate-based extractants are capable of dissolving those complex pedogenic phosphates that are relatively labile but are not hydrolyzed by NaOH because they are poor in Fe and Al.

The shape of the plot of $Q_{dt}/(Q_{d1} + Q_{d2})$ versus $\ln t$ differed widely among soils (see Fig. 3). Aharoni and Sparks (1991) showed that this type of plot tends to be S-shaped (concave at the beginning and convex at the end), with a small intermediate portion if the chemical reaction occurs in a homogeneous medium but tends to exhibit a dominant linear intermediate portion when the reaction occurs in a heterogeneous medium. We can, therefore, conclude that the

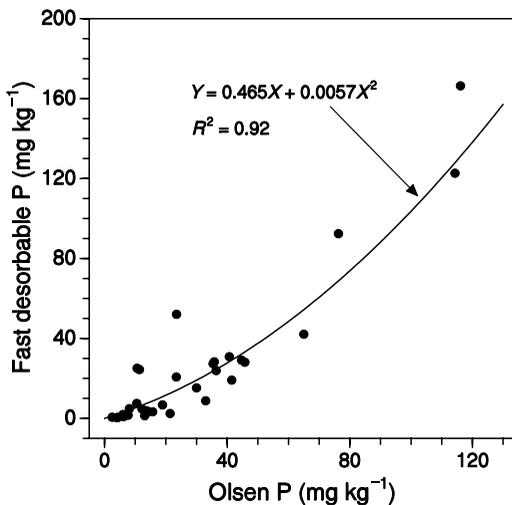


Fig. 2. Relationship between fast desorbable P (according to the Michaelis-Menten fit) and Olsen P for our soil population ($n = 29$).

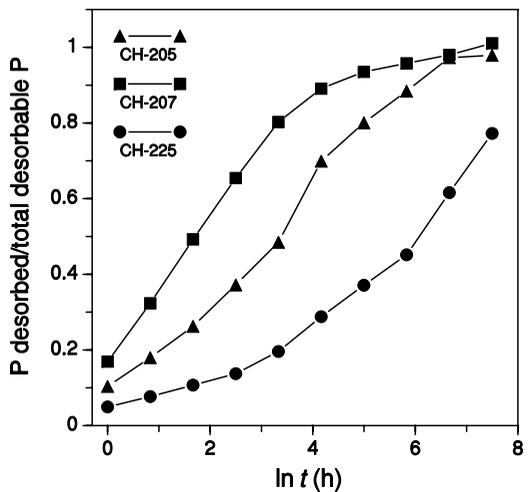


Fig. 3. Fraction of total desorbable P (according to the Michaelis-Menten fit) that is desorbed as a function of $\ln t$ in three selected soils.

pools of desorbable P in the studied soils are chemically and mineralogically diverse.

We compared the concentration of fast desorbable P (Q_{d1}) with that of P sorbed by the intact soil [i.e., the right term of Eq. (1) with $c = \text{EPC}$, which is denoted by Q_{sepc}]. The Q_{d1}/Q_{sepc} ratio ranged widely (0.01–0.82), with a mean value of 0.21 (i.e., only about one fifth of the P sorbed by the soil was rapidly desorbed on average). The mean ratio increased to about 0.5 when the amount of P desorbed after 1 day was considered. The total desorbable P ($Q_{d1} + Q_{d2}$)/ Q_{sepc} ratio also ranged widely, with an average of 0.60. These ratios exhibited significant and positively correlations (not shown) with Q_{d1} , Q_{d2} , CB-P, CC-PP, and the degree of P saturation, among other variables; therefore, as expected, the larger the amount of P sorbed was, the less firmly it was generally held in the soil solid phases.

CONCLUSIONS

Although the soils differed widely in basic properties and the concentrations of different P forms, the kinetics of P desorption were always accurately described with the combination of two equations of the Michaelis-Menten type that were assigned to the fast and slowly desorbable P pools. The concentrations of these pools were highly correlated with some of the operationally defined P fractions; however, these pools could not be unambiguously assigned to specific chemical P species. Moreover, some kinetic plots suggest that desorbable P is chemically and mineralogically diverse.

Olsen P was highly correlated with fast desorbable P; however, it tended to overestimate and underestimate fast desorbable P at Olsen P values lesser and greater than $\sim 80 \text{ mg kg}^{-1}$, respectively. The usefulness of the Olsen P test for acid soils, where other agricultural or environmental tests are generally used (e.g., the Egner-Riehm method in Portugal), thus merits some attention.

The ratio of fast desorbable P or total desorbable P to sorbed P increased with increasing degree of P saturation in the soil. All these findings stress the need for proper management of soil P to reduce the risk of the eutrophication of water bodies.

ACKNOWLEDGMENTS

The senior author acknowledges award of a grant from PRODEP III (2/2001) supported by

the Portuguese government and the European Union.

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