

CSIRO Publishing

Australian *Journal* of Soil Research



VOLUME 39, 2001

© CSIRO 2001

An international journal for the publication of original research into all aspects of soil science

All enquiries and manuscripts should be directed to:

Australian Journal of Soil Research
CSIRO Publishing
PO Box 1139 (150 Oxford St)
Collingwood, Vic. 3066, Australia



Telephone: +61 3 9662 7628
Fax: +61 3 9662 7611
Email: sr@publish.csiro.au

Published by CSIRO Publishing
for CSIRO and the Australian Academy of Science

www.publish.csiro.au/journals/ajsr

Phosphorus sorption and desorption in oxide-rich Ferralsols of New Caledonia

I. G. Dubus^A and T. Becquer^B

I.R.D., Agropedology Laboratory, B.P. A5, 98848 Nouméa cedex, New Caledonia.

^A Corresponding author; e-mail: i.dubus@cranfield.ac.uk; present address: Soil Survey and Land Research Centre, Cranfield University, Silsoe, Beds MK45 4DT, UK.

^B Present address: I.R.D., c/o C.N.R.S., Centre de Pédologie Biologique, UPR 6831 associée à l'Université de Nancy I, B.P. 5, 54501 Vandoeuvre-lès-Nancy cedex, France.

Abstract

Phosphorus (P) availability in soils is one of the main limiting factors for crop production in Ferralsols that contain high amounts of aluminium and iron oxides. Highly weathered Geric Ferralsols cover large surface areas of south Pacific islands, some of which are required for agricultural development. Sorption and desorption of P in Geric Ferralsols of the island of Maré (New Caledonia) were investigated. The soils contain large quantities of oxides, especially of aluminium. The clay fraction consisted exclusively of fine, discrete oxide particles. Both Freundlich and Langmuir equations provided a good fit to the data for equilibrium P concentrations ranging from 0.05 to 850 mg P/L. The extremely high P sorption capacities of New Caledonian Geric Ferralsols were exemplified by the large Langmuir sorption maxima which ranged from 6400 to 9250 mg P/kg. A strong negative correlation between P sorption and organic matter was noted, resulting in a larger P availability in topsoils. This relationship can be used to provide a first assessment of P sorption capacities of Geric Ferralsols across the island. Management of organic matter is likely to be of major importance in the control of P availability in Geric Ferralsols of south Pacific islands.

Additional keywords: Ferralsols, phosphate, oxides, soil.

Introduction

In the warm humid tropics, alteration of parent materials has generally led to the formation of Ferralsols, which are characterised by the presence of 1:1 clay minerals and aluminium (Al) and iron (Fe) oxides. The high phosphorus (P) sorption capacity of Ferralsols has often been related to the presence of high amounts of oxides (Uehara and Gillman 1981). Iron and Al oxide-rich Geric Ferralsols represent an extreme evolution of these soils in which silica and, subsequently, aluminosilicate clays are virtually absent. Geric Ferralsols are found in the uplifted coral atolls of Loyalty islands (New Caledonia), on Tahiti, Salomon, and Fiji (Latham 1980; Segalen 1995), and in the Caribbean (Segalen 1995).

Although Geric Ferralsols are shallow (up to a maximum 60 cm depth) and relatively infertile due to the large amounts of oxides and the low cation exchange capacities in the subsoil, they support 60% of the agricultural production in Maré (Loyalty islands). Increasing economic and demographic pressures on the island have resulted in an intensification of agriculture on these soils, and a major concern is the magnitude of P sorption in these soils. Phosphorus is one of the main factors that prevent an increase in crop yields on such soils. Phosphorus availability to plants was found to severely limit the increase in maize yield in a glasshouse experiment (Bonzon and Becquer 1994), although P is naturally present at a high concentration in Geric Ferralsols from the Maré island (6–13 g P/kg). The strong binding of P to oxides is likely to limit the success of a more intensified agriculture on the soils of the island.

This paper reports on results of laboratory experiments conducted on samples collected on the island of Maré as a first assessment of the P-fixation properties of Geric Ferralsols from the island. The aim of the study was (i) to provide data on the P sorption and desorption properties of these highly weathered soils, (ii) to investigate P sorption variation down the soil profiles, and (iii) to determine the relationship between soil properties and P sorption data.

Materials and methods

Soil samples and basic analytical methods

Soil samples were taken from three soil profiles for each of two experimental sites (Tawaïnèdre and Taodé) on the island of Maré, New Caledonia. The Tawaïnèdre site represents regularly burnt bush fallow with 1–4-m shrubs; the Taodé site is old fallow with regrowing forest of 10–15 m. The 15 samples were dried at 40°C for 3 days in a drying tunnel, passed through a 2-mm sieve, and stored before analysis.

Soil pH was measured in a 1:2.5 soil:solution (H₂O or 1 M KCl) with a combined glass electrode. Organic carbon concentration was derived using the approach proposed by Walker and Black (1934). Exchangeable Ca and Mg were analysed according to the methodology proposed by Tucker (1954) and labile P was determined using anion exchange membranes (Qian *et al.* 1992). Specific surface areas for selected samples were measured (Feller *et al.* 1992).

Selective dissolution of Al and Fe compounds was carried out using extractions with pyrophosphate (Loveland and Digby 1984), oxalate (McKeague and Day 1966) and dithionite–citrate–bicarbonate (DCB) (Mehra and Jackson 1960). The subscripts p, O, and D were used to characterise Al and Fe forms extracted by pyrophosphate, oxalate, and dithionite-citrate-bicarbonate, respectively.

Phosphorus sorption curves

Phosphorus sorption curves (or quantity/intensity relationships) were determined by shaking 1 g of soil with 10 mL of solutions of KH₂PO₄ from 0 to 1500 mg P/L prepared in 0.01 M CaCl₂, end-over-end for 24 h at room temperature (26 ± 1°C). The supernatants resulting from centrifugation at 1240G for 15 min were filtered and the filtrates analysed for P by the molybdenum blue method (Murphy and Riley 1962). The difference between P concentration before and after equilibration with the soil sample was considered to represent the quantity of P sorbed to soil. Since P sorption usually varies with pH, experiments were conducted at naturally occurring soil pH. The analytical results are the means of duplicates.

Phosphorus desorption measurements

Phosphorus desorption characteristics were measured for samples that were initially treated as in the sorption experiments with 10 mL of solution with an initial concentration of 2000 mg P/L. After removal of the clear supernatant, the same volume of P-free 0.01 M CaCl₂ was added to the centrifuge tubes. The tubes were shaken thoroughly to disperse the soil pellets, further shaken for 24 h at room temperature (26 ± 1°C), centrifuged at 1240G for 15 min, and filtered as for the sorption protocol. The supernatants were analysed for P. This desorption process was repeated 8 times. The data presented are the averages of 3 replicates.

Fitting P sorption curves

Data obtained [P sorbed by unit weight of soil (X), and equilibrium P concentrations (C)] were described by the Freundlich (Eqn 1), Langmuir (Eqn 2), and Tempkin (Eqn 3) models:

$$X = K_f C^n \quad (1)$$

$$X = (K_l C X_{\max}) / (1 + K_l C) \quad (2)$$

$$X = K_\alpha + K_\beta \ln C \quad (3)$$

where K_f , n , K_l , X_{\max} , K_α , and K_β are constants determined by non-linear curve fitting.

K_f may be considered a hypothetical index of P sorbed from a solution having a final unit equilibrium P concentration, and may thus be taken to provide a measure of relative P sorption capacity of different

soils. The parameter n of Eqn 1 is a shape-governing factor. In Eqn 2, X_{\max} is the Langmuir sorption maximum, and K_l an equilibrium constant related to sorption energy. The Tempkin (Eqn 3) was selected because its method of plotting (X v. $\ln C$) is useful to represent a large range of concentrations.

Results and discussion

Analytical results

Selected chemical properties of the soil samples are presented in Table 1. The soils are slightly acid in the topsoil and soil pH declines with increasing depth. The ΔpH ($\text{pH}_{\text{KCl}} - \text{pH}_{\text{H}_2\text{O}}$) is negative in the surface samples, but becomes nil in deeper horizons, suggesting that negative charges are predominant in the upper horizons, but tend to be balanced by positive charges in deeper horizons. Large organic carbon contents (up to 145 g/kg) may be attributed to the large amounts of poorly crystalline Al and Fe oxides which stabilise organic matter (Boudot *et al.* 1986). The cation exchange capacity (CEC) was highly correlated to organic carbon ($r = 0.98$) and was therefore not included in Table 1. In highly weathered tropical soils where silicate clays are absent, the CEC is mainly determined by organic matter. Calcium and magnesium were the two main exchangeable cations, with a mean Ca/Mg ratio of 1.47. This was one of the reasons for choosing CaCl_2 as the background electrolyte in sorption experiments.

These highly weathered soils are dominated by Fe and Al compounds, free silica being almost absent ($\text{SiO}_2 < 2\%$). The crystalline fraction is mostly present as boehmite and gibbsite for Al and goethite for Fe (Latham 1980). Total Al concentrations are fairly constant within the profiles, while Fe concentrations tend to increase with depth.

Pyrophosphate, oxalate, and DCB extractions are usually considered to be specific for Al and Fe compounds. However, sequences of extraction varied between the two elements ($\text{Fe}_D > \text{Fe}_O > \text{Fe}_P$ for iron, but $\text{Al}_O > \text{Al}_D > \text{Al}_P$ for aluminium). DCB-extracted iron ranged from 10% to 15% of total iron, and the extraction of well-crystallised iron oxides and hydroxides ($\text{Fe}_D - \text{Fe}_O$) is thus incomplete in these soils. This is probably due to the substitution of Fe in Fe oxides by Al, which is likely in soils with large amounts of aluminium. Indeed, Cornell and Schwertmann (1996) reported a decrease in dissolution rate of synthetic and natural goethite with increasing Al substitution. Poorly crystalline Fe oxides ($\text{Fe}_O - \text{Fe}_P$) and organically bound (Fe_P) iron contents were small, with average values of 2.1% and 0.6% of total iron, respectively. With the exception of the organically bound fraction (Fe_P), the different iron fractions increased with depth. Oxalate-extractable aluminium (Al_O) ranged between 4.6 and 15.3 g/kg, with a mean of 11.3 g/kg, and was higher than DCB-extracted aluminium (Al_D). Amorphous Al concentration increased slightly in the first two horizons, but decreased further down the profile. Organically bound aluminium concentrations (Al_P) decreased with depth within the soil profiles and organic carbon content.

The two sites do not show marked compositional differences. Nevertheless, the Tawainèdre soil has slightly more total Al and Fe than that of Taodé ($P < 0.05$), with an average Al_2O_3 content of 591 g/kg v. 546 g/kg and an average Fe_2O_3 content of 332 g/kg v. 317 g/kg. Organically bound Al (Al_P) was lower for Tawainèdre soil samples than Taodé ($P < 0.05$).

Phosphorus sorption data and fitting

The maximum initial concentration (1500 mg P/L) is significantly higher than concentrations usually found in P sorption studies. This choice was based on the

Table 1. Selected analytical properties of the 15 soil samples

Sample	Profile	Depth (cm)	pH _{H₂O}	pH _{KCl}	Org.C (g/kg)	Exchangeable		Pyrophosphate ^A		Oxalate ^A		DCB ^A		Total elements		
						cations (cmol/kg) Ca	Mg	Al _P	Fe _P	Al _O	Fe _O	Al _D	Fe _D	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃
TW11	1	0–7	6.8	6.4	80.9	15.4	11.6	2.34	0.77	13.18	4.07	7.79	21.67	10.1	583.7	324.0
TW12	1	7–20	6.7	6.3	43.2	6.4	5.4	2.39	0.95	13.55	4.78	8.00	21.95	9.4	592.6	332.0
TW13	1	20–40	6.3	6.1	33.8	3.8	3.5	2.10	0.83	11.36	4.64	8.19	21.97	7.9	596.6	334.2
TW21	2	0–10	6.7	6.3	71.0	14.9	9.2	2.64	1.02	12.44	3.80	8.35	21.16	12.4	582.2	326.0
TW23	2	32–75	6.1	6.0	15.7	1.4	1.2	1.38	0.68	6.18	4.12	8.06	24.45	10.2	599.3	337.0
TW31	3	0–15	6.7	6.3	76.8	15.8	10.1	2.67	1.07	11.34	4.41	8.10	20.98	n.d.	581.7	325.5
TW33	3	35–60	5.8	6.0	8.4	0.3	0.3	0.96	0.14	4.59	4.07	7.65	25.88	19.9	598.6	342.0
TA41	4	0–10	6.9	6.6	97.3	21.1	15.4	4.05	1.45	12.38	3.47	6.55	15.45	15.6	541.6	312.0
TA42	4	10–25	6.2	5.9	31.9	4.5	3.7	3.01	0.70	12.88	4.45	6.91	18.03	16.0	558.6	319.2
TA43	4	25–60	5.9	5.8	16.1	1.7	1.1	1.88	0.48	8.82	4.85	7.13	19.88	16.2	561.8	324.4
TA44	4	60–80	5.8	6.0	13.9	1.6	1.3	1.21	0.38	7.21	3.15	6.47	20.10	16.7	568.8	326.9
TA51	5	0–12	6.3	5.9	121.0	19.9	12.4	5.97	1.83	12.43	3.76	8.78	20.10	16.7	542.7	313.9
TA52	5	12–25	6.2	5.9	32.9	3.5	4.2	3.62	0.75	12.76	4.97	6.82	17.13	15.6	555.0	326.0
TA61	6	0–12	6.7	6.4	145.8	26.4	11.9	4.48	1.28	15.25	3.41	8.04	17.84	13.2	491.4	290.2
TA62	6	12–25	6.5	6.1	38.8	5.2	5.2	3.30	0.76	15.04	4.10	7.32	18.21	13.8	549.3	326.8

n.d., no data.

^A The subscripts P, O, D denote selective extractions by pyrophosphate, oxalate, and dithionite–citrate–bicarbonate (DCB), respectively.

assumptions that (i) preliminary experiments conducted on Ferralsols of New Caledonia with widely used P concentrations resulted in total disappearance of P from the equilibrium solution (data not shown); (ii) results of glasshouse experiments on P deficiencies in maize, lettuce and beans grown on Geric Ferralsols from the main island have shown that the optimum application of P is as high as c. 3 t P/ha (L'Huillier *et al.* 1998); (iii) P inputs by some New Caledonian farmers for some crops (e.g. vegetables) are much larger than elsewhere in the world.

The time to reach equilibrium was not investigated in these studies. Phosphorus sorption is characterised by an initial fast reaction followed by a slower one which may continue for a long time (e.g. Barrow 1985). Evidence of the long-lasting reaction between P and soils in Geric Ferralsols was given by a field trial in which P availability to maize decreased progressively during the 3 years of experiment (L'Huillier *et al.* 1998). The 24-h shaking period, which was chosen for experimental convenience in this study, may therefore not reflect the long-term sorption characteristics of Geric Ferralsols.

The comparison of Freundlich and Langmuir equations is well documented (Sibbesen 1981). Fitting sorption data to Freundlich and Langmuir equations gave r^2 values >0.95 ($n = 7$), but a curvature was found when plotting X_{\max} for the Langmuir equation (Fig. 1b). The deviation from linearity has often been reported when using large P concentrations (e.g. Syers *et al.* 1971). Whenever there is a curvature, the calculated slope from linear regression analysis is dependent upon the maximum value of C (Gunary 1970). Here, X_{\max} tended to be overestimated due to the relationship between X/C and C (Fig. 1b). The introduction of a curvature has been attributed to (i) the assumption that the energy of adsorption does not vary with the surface coverage (Bowden *et al.* 1977), (ii) the diffusion of P within minerals (Bache and Williams 1971), (iii) a modification of sorption mechanisms (Taylor and Ellis 1978).

The Langmuir equation gave a good fit even though high P concentrations were used in this study (0–1500 mg P/L), despite the equation having been used successfully only in a restricted range of equilibrium P concentrations (Vo Dinh Quang *et al.* 1996). The explanation may be that, despite being known as an 'adsorption' equation, the Langmuir equation is suitable for describing secondary precipitation data (Veith and Sposito 1977). Secondary precipitation is likely to have occurred in our study, therefore no conclusions on P sorption mechanisms can be drawn using the Langmuir equation. Parameters resulting from the fitting of the Langmuir equation to the data were therefore used as sorption extent parameters, irrespective of the sorption mechanisms that occur.

The Freundlich equation is assumed to fit the data best when the labile P is included. However, considering the relative similarity of total P among our samples, the introduction of the labile P in the equation is of less value for comparing P sorption data. In spite of a high total P content in the samples (6–9 g P/kg for Tawainèdre samples, 7–13 g P/kg for Taodé samples), the labile P remains very low (data not shown). The labile P was therefore not taken into account in the Freundlich equation.

The better fit of the Freundlich equation ($r^2 = 0.989$) over the Langmuir equation ($r^2 = 0.967$), for all samples except one, has already been observed for many soils (e.g. Barrow 1978; Sanyal *et al.* 1993). This may be explained by the fact that despite being an empirical equation, the Freundlich equation corresponds to a model in which the affinity term decreases exponentially with increasing amount of adsorption (Barrow 1978). However, the Langmuir equation does not take into account a variation of the binding energy in relation to surface saturation by P (Bowden *et al.* 1977).

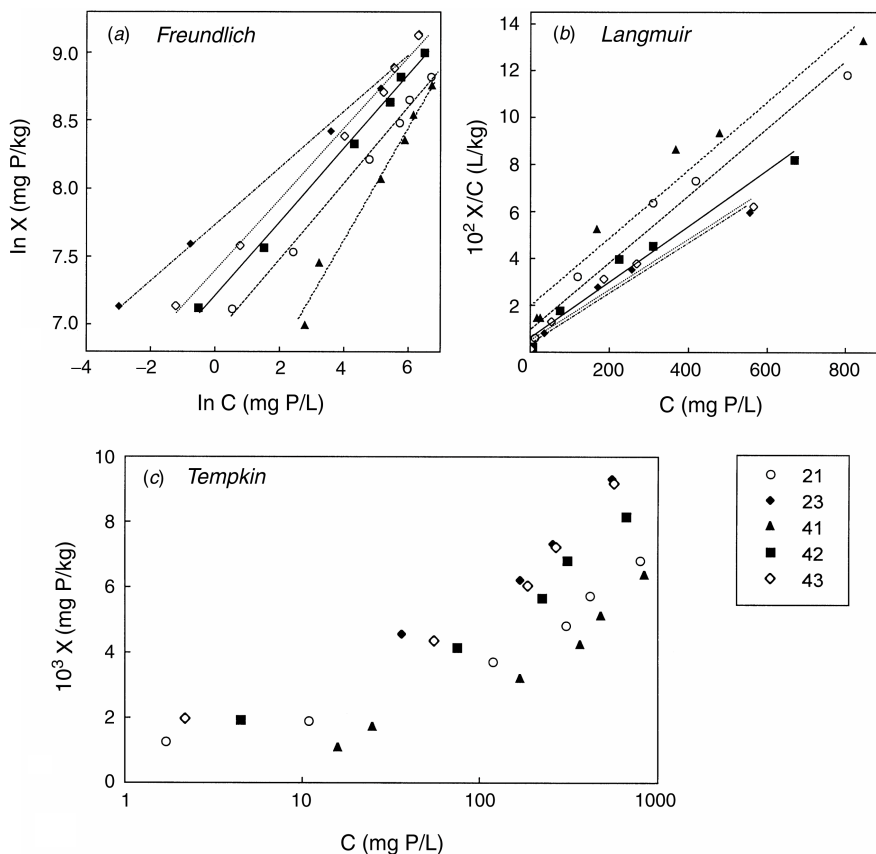


Fig. 1. Sorption data of selected samples according to Freundlich (plot *a*), Langmuir (plot *b*) and Tempkin (plot *c*) equations. X is the amount sorbed per unit weight (mg P/kg), C is the equilibrium concentration (mg P/L).

In the simplified Tempkin equation (Eqn 3), the adsorption energy decreases linearly with increasing surface coverage. The relationship between amounts of P sorbed and the logarithm of concentrations of P should give a straight line if the model is suitable for describing sorption. However, this was not found to be so in our study (Fig. 1c). These results agree with Sanyal *et al.* (1993). The Tempkin equation thus has limited value, despite its potential usefulness over large concentration ranges.

All P sorption parameters (K_f and X_{\max}) were significant at $P = 0.05$ (Table 2). The Langmuir X_{\max} ranged from 6334 to 9249 mg P/kg, while the Freundlich K_f ranged from 393 to 2289 mg P/kg. Such large sorption parameters are rare for soils or synthetic materials, and stress the high P-sorption properties of Geric Ferralsols. Synthetic goethites of various crystal morphologies and goethite-rich natural samples sorb *c.* 2.5–2.6 $\mu\text{mol P/m}^2$ (Cornell and Schwertmann 1996). Average surface areas of 103 m^2/g were measured for subsoil samples from the Tawainèdre and Taodé sites and maximum sorption maxima calculated from surface area measurements (8000–8300 mg P/kg) were therefore in relative agreement with those obtained in this study.

Table 2. Phosphorus sorption parameters for the Freundlich and Langmuir equations

Sample	Freundlich		Langmuir	
	K_f (L/kg)	r^2	X_{max} (mg P/kg)	r^2
TW11	1013.0	0.995	6880.3	0.971
TW12	1920.5	0.997	8216.3	0.981
TW13	2245.6	0.990	8388.7	0.977
TW21	1009.4	0.995	6948.8	0.971
TW23	2288.6	0.994	9249.3	0.970
TW31	953.7	0.992	6982.6	0.960
TW33	2151.8	0.958	8714.0	0.972
TA41	393.1	0.982	6911.5	0.955
TA42	1355.3	0.995	8313.1	0.974
TA43	1633.4	0.995	9248.5	0.963
TA44	1740.6	0.992	8330.3	0.963
TA51	631.4	0.986	6505.8	0.951
TA52	1314.8	0.997	8672.3	0.966
TA61	576.6	0.967	6333.7	0.955
TA62	1359.2	0.996	8592.2	0.970
Mean	1372.5	0.989	7885.8	0.967

Correlation between P sorption and soil properties

Correlation between soil properties and P sorption has been widely used in recent years to determine the soil components involved (e.g. Brennan *et al.* 1994; Vo Dinh Quang *et al.* 1996). However, correlation studies require caution as some soil properties are often interrelated. Correlation coefficients between the sorption parameter K_f and soil properties are presented in Table 3. For both the Tawainèdre and Taodé soils, P sorption was negatively correlated ($P < 0.05$) to organic carbon, pH, Al_p , and very poorly ordered aluminium compounds ($Al_D - Al_p$), although Fe_p and amorphous iron ($Fe_O - Fe_p$) were also similarly correlated for the Taodé soils (Table 3). All soil properties except some amorphous aluminium compounds and well-crystallised iron oxides appeared to be correlated to Freundlich K_f when both sites were combined.

A decrease in P sorption with increasing pH has often been reported (Parfitt 1977; Eze and Loganathan 1990). It has been attributed to increased charge repulsion between P ions and surface negative charges, to increased concentration of solution hydroxyl ions, leading to competition with P ions for sorption sites (Eze and Loganathan 1990), and to enhanced solubilisation of the amorphous aluminium phosphate (White and Taylor 1977). The role of pH variation in P sorption is of great importance in oxide-rich soils, because pH influences both the degree of ionisation of the orthophosphate ion and the oxide surface charge which is the main P-fixing component.

The clay content of highly weathered tropical soils is not a reflection of the amount of layer silicates present. A large part of the clay-sized fraction consists of particles of Fe and Al compounds (often, but not always, well-crystallised oxides), which are very fine, discrete particles. Geric Ferralsols have been shown to have very low silica contents ($SiO_2 < 2\%$), and are free from layer-silicate clays (Latham 1980). Thus, although P sorption correlated positively with clay content in tropical soils in some studies (Owusu-Bennoah and Acquaye 1989; Sanyal *et al.* 1993; Vo Dinh Quang *et al.* 1996), we chose not to include the clay percentage in our correlation study. Owusu-Bennoah and Acquaye (1989) related the significant correlation to the sorption of P onto clay particles in their study, while

Sanyal *et al.* (1993) considered it a reflection of the effect of specific area on P sorption. A linear regression between the clay content and the free oxides contents performed on the most weathered Ghanaian soils used by Owusu-Bennoah and Acquaye (1989) in their study gives a large positive correlation coefficient ($r = 0.97$). Hence, as in our case, the 'clay' fraction of some soils of their study may in fact be constituted of oxides.

In this study, the influence of organic carbon on P sorption was investigated by relating P-sorption parameters statistically to organic carbon concentration. Two other methods have been used to study the influence of organic carbon on P retention. The first method has been to reduce the organic carbon content of soil samples by chemical treatments (usually H_2O_2), while trying to minimise the effects of the treatment on other soil components. Borggaard *et al.* (1990) found no influence of organic carbon removal on P sorption in five Danish sandy soils, whereas de Mesquita Filho and Torrent (1993) noted a large increase in P sorption after similar treatment of Brazilian soils. The H_2O_2 treatment of Geric Ferralsols is relatively ineffective, and successive treatments are necessary to obtain a significant decrease of organic carbon content (data not shown), thereby affecting other soil components. The second method of studying the influence of organic carbon on P sorption consists in adding dissolved organic matter to soil suspensions. This method has the advantage of identifying the organic acids that are responsible for the P sorption. Organic carbon was the main soil property that correlated ($P < 0.001$) with the Freundlich sorption parameter K_f for the soils (Table 3). The organic carbon effect on P sorption can be positive (Brennan *et al.* 1994) or negative (Parfitt 1978), or there may be no effect (Borggaard *et al.* 1990). These conflicting results occur with different experimental conditions, especially the time of reaction between organic substances and oxides (Gerke 1993). Organic carbon was associated with mineral components, as measured by the large positive correlation between organic carbon and Al_P ($r^2 = 0.83^{***}$) and Fe_P ($r^2 = 0.91^{***}$) and the difficulty in removing organic carbon by H_2O_2 treatment. The positive effect of organic carbon can be explained by the need for orthophosphate ions to diffuse through organic matter–oxide complexes to reach sorption sites, and by the competition between organic acids and orthophosphate for them.

Aluminium and iron compounds provide the major P-sorbing surfaces in tropical soils (Uehara and Gillman 1981). Negative correlations were, nevertheless, found between K_f and pyrophosphate-extractable Fe and Al (Fe_P and Al_P) for soils of this study. The highest correlation coefficient was obtained with the poorly crystalline aluminium oxides ($Al_D - Al_P$, $r = 0.74$), which occupy a large proportion of sorption surfaces in these soils. Aluminium amorphous compounds have a larger sorbing capacity than Fe compounds in highly weathered soils (Syers *et al.* 1971).

As P sorption was related to several soil properties, a multiple regression analysis relating P sorption and other independent soil variables was carried out. Fe_P and Al_P were related to organic matter ($r = 0.91$ and $r = 0.82$, respectively) and were therefore not included. The multiple regression equations selected by the models were:

$$K_f = 2062.6 - 12.5 \text{ Org.C} + \varepsilon \quad (r^2 = 0.73)$$

$$K_f = 737.8 - 14.37 \text{ Org.C} + 135.1 (Fe_D - Fe_O) + \varepsilon \quad (r^2 = 0.85)$$

where ε is the model error.

The equation terms can be easily determined by routine chemical analyses and both equations may be used as predictive tools for estimating the P-sorption characteristics of Geric Ferralsols of the island.

Table 3. Simple correlation coefficients (Pearson *r*) between soil properties and between K_f and soil properties

Correlations between soil properties were calculated with the all samples data set. The subscripts P, O, D denote selective extractions by pyrophosphate, oxalate and dithionite-citrate-bicarbonate, respectively

	Soil properties							Freundlich K_f^A		
	pH _{H2O}	Fe _P	Fe _O - Fe _P	Fe _D - Fe _O	Al _P	Al _O -Al _P	Al _D -Al _P	K_f	$K_{f_{TW}}$	$K_{f_{TA}}$
Org. C	0.71**	0.91***	0.89***	0.35	0.82***	0.48	-0.54*	-0.85***	-0.94***	-0.93***
pH _{H2O}		0.62*	0.56*	0.10	0.45	0.70	-0.33	-0.65**	-0.81*	-0.86**
Fe _P			1.00***	0.24	0.89***	0.34	-0.66**	-0.78***	-0.66	-0.94***
Fe _O - Fe _P				0.24	0.90***	0.31	-0.66**	-0.75***	-0.60	-0.91***
Fe _D - Fe _O					-0.04	-0.29	0.47	0.03	-0.10	-0.47
Al _P						0.46	-0.85***	-0.79***	-0.76*	-0.87**
Al _O - Al _P							-0.40	-0.48	-0.57	-0.28
Al _D - Al _P								0.74***	0.76*	0.78*

* $P < 0.05$; ** $P < 0.01$; *** $P < 0.001$.

^A K_f for all samples, $K_{f_{TW}}$ for Tawainèdre samples and $K_{f_{TA}}$ for Taodé samples, successively.

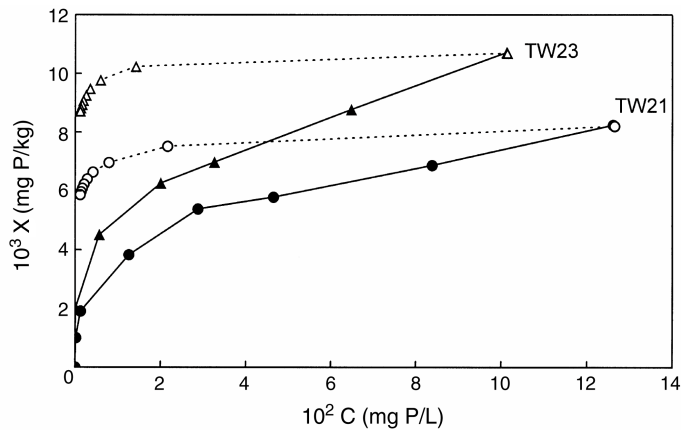


Fig. 2. Relationship between P sorbed per unit weight (*X*, mg P/kg) and equilibrium P concentration (*C*, mg P/L) during sorption (solid lines) and desorption (dotted lines) for two samples.

Phosphorus desorption

Desorption plots for 2 soil samples (TW21 and TW23) are presented in Fig. 2. The large shift between sorption and desorption lines is the expression of an hysteresis phenomenon. The first desorption step removed only 4–8% of the P added during the adsorption step, as can be seen by the low slope of the first part of the desorption curve (Fig. 2). Further, there is a highly significant ($P < 0.01$) exponential decrease in the quantities of P desorbed sequentially at each stage of the desorption process ($r^2 > 0.997$).

The total desorption was very small, as 8 successive desorptions on TW21 and TW23 resulted in a decrease of 30% (topsoil sample) and 20% (subsoil sample) of the P initially added. There are 3 possible reasons for this desorption. First, it may correspond to irreversible reactions of adsorbed P with soil compounds that lead to a stronger bond by rearrangement of the phosphate ions on the surfaces (Kuo and Lotse 1974). Second, it may be attributed to the presence of precipitation processes at high P concentrations and to the difficulty of dissolving P from precipitates. Third, it may be due to the fact that desorption equilibrium was not reached. Desorption is a slower process than adsorption (Barrow 1983), occurring for long periods. The 24-hour shaking period between desorptions appears to be not long enough to reach an equilibrium, which is essential if sorption is to be regarded as irreversible. However, even in the absence of an equilibrium, the magnitude of the hysteresis between P sorption and P desorption in these soils is very large. This clearly may relate to the known unavailability of P to plants grown in these soils.

Conclusions

Geric Ferralsols from New Caledonia are extremely rich in Fe and Al oxides, but almost free of silicate clays. Geric Ferralsols from the island of Maré showed very large P sorption capacities due to their large amounts of Al and Fe oxides. The Freundlich and Langmuir equations both provided a good fit to the data, although the concentration range was large and precipitation was likely to occur. A significant, negative correlation between P sorption and organic carbon content was found, resulting in a larger P availability in topsoils. This relationship provides a first estimate of P availability in these soils. The desorbability of P in these soils was very low. Further investigations in these P-sorbing soils should concentrate on the confirmation of these results for lower P concentrations and the management of organic matter, which increases P availability.

Acknowledgments

This research was supported by the 'Contrat de développement entre la Province des Iles et l'ORSTOM pour l'étude des risques de dégradation de la fertilité des sols et de pollution des lentilles d'eau douce' and by the French Ministry of University Education and Research for operation no. 6DEF.

References

- Bache BW, Williams EG (1971) A phosphate sorption index for soils. *Journal of Soil Science* **22**, 289–301.
- Barrow NJ (1978) The description of phosphate adsorption curves. *Journal of Soil Science* **29**, 447–462.
- Barrow NJ (1983) A mechanistic model for describing the sorption and desorption of phosphate by soil. *Journal of Soil Science* **34**, 733–750.
- Barrow NJ (1985) Reaction of anions and cations with variable-charge soils. *Advances in Agronomy* **38**, 183–230.
- Bonzon B, Becquer T (1994) Mise en valeur des sols ferrallitiques allitiques des îles Loyauté. Note de synthèse. Convention Sciences de la Vie: Agropédologie 28. ORSTOM, Nouméa.
- Borggaard OK, Jorgensen SS, Moberg JP, Raben-Lange B (1990) Influence of organic matter on phosphate adsorption by aluminium and iron oxides in sandy soils. *Journal of Soil Science* **41**, 443–449.
- Boudot JP, Bel Hadj BA, Chone T (1986) Carbon mineralization in Andosols and aluminium rich highland soils. *Soil Biology and Biochemistry* **18**, 457–461.
- Bowden JW, Posner AM, Quirk JP (1977) Ionic adsorption on variable charge surfaces mineral surfaces. Theoretical charge development and titration curves. *Australian Journal of Soil Research* **15**, 121–136.

- Brennan RF, Bolland MDA, Jeffery RC, Allen DG (1994) Phosphorus adsorption by a range of western Australian soils related to soil properties. *Communications in Soil Science and Plant Analysis* **25**, 2785–2795.
- Cornell RM, Schwertmann U (1996) 'The iron oxides. Structure, properties, reactions, occurrence and uses.' (VCH Publishers: Weinheim, Germany)
- de Mesquita Filho MV, Torrent J (1993) Phosphate sorption as related to mineralogy of a hydrosequence of soils from the Cerrado region. *Geoderma* **58**, 107–123.
- Eze OC, Loganathan P (1990) Effects of pH on phosphate sorption of some Paleudults of southern Nigeria. *Soil Science* **140**, 251–255.
- Feller C, Schouller E, Thomas F, Rouiller J, Herbillon AJ (1992) N₂-BET specific surface areas of some low activity clay soils and their relationships with secondary constituents and organic matter contents. *Soil Science* **153**, 293–299.
- Gerke J (1993) Phosphate adsorption by humic/Fe-oxide mixtures aged at pH 4 and 7 and by poorly ordered Fe-oxide. *Geoderma* **59**, 279–288.
- Gunary D (1970) A new adsorption isotherm for phosphate in soil. *Journal of Soil Science* **21**, 72–77.
- Kuo S, Lotse EG (1974) Kinetics of phosphate adsorption and desorption by lake sediments. *Soil Science Society of America Journal* **38**, 50–54.
- L'Huillier L, Dupont S, Dubus I, Becquer T, Bourdon E, Laubreaux P, Bonzon B (1998) Carence et fixation du phosphore dans les sols ferrallitiques ferritiques de Nouvelle-Calédonie, 16th World Congress of Soil Science, Montpellier, France.
- Latham M (1980) Les oxydisols dans quelques milieux insulaires du Pacifique Sud. *Cahiers ORSTOM Série Pédologie* **XVIII**, 305–316.
- Loveland PJ, Digby P (1984) The extraction of Fe and Al by 0.1 M pyrophosphate solutions: a comparison of some techniques. *Journal of Soil Science* **35**, 243–250.
- McKeague JA, Day JM (1966) Dithionite and oxalate-extractable Fe and Al as aids in differentiating various classes of soil. *Canadian Journal of Soil Science* **19**, 13–22.
- Mehra OP, Jackson ML (1960) Iron oxide removal from soils and clays by a dithionite–citrate system buffered with sodium bicarbonate. In 'Clays and Clay Minerals, 7th National Conference, Washington DC, 1958'. (Ed. A Swineford) pp. 317–327. (Pergamon Press: New York)
- Murphy J, Riley JF (1962) A simplified single solution method for the determination of phosphate in natural waters. *Analytica Chimica Acta* **27**, 31–36.
- Owusu-Bennoah EO, Acquaye DK (1989) Phosphorus sorption characteristics of selected major Ghanaian soils. *Soil Science* **148**, 114–123.
- Parfitt RL (1977) Phosphate adsorption on an Oxisol. *Soil Science Society of America Journal* **41**, 1064–1067.
- Parfitt RL (1978) Anion adsorption by soils and soil materials. *Advances in Agronomy* **30**, 1–50.
- Qian P, Schoenau JJ, Huang WZ (1992) Use of ion exchange membranes in routine soil testing. *Communications in Soil Science and Plant Analysis* **23**, 1791–1804.
- Sanyal SK, De Datta SK, Chan PY (1993) Phosphate sorption–desorption behavior of some acidic soil of south and south-east Asia. *Soil Science Society of America Journal* **25**, 937–945.
- Segalen P (1995) Les sols ferrallitiques et leur répartition géographique. Tomes 2 et 3. ORSTOM, Collection Etudes et Thèses, Paris, France.
- Sibbesen E (1981) Some new equations to describe phosphate sorption by soils. *Journal of Soil Science* **32**, 67–74.
- Syers JK, Evans TD, Williams JDH, Murdock JT (1971) Phosphate sorption parameters of representative soils from Rio Grande do Sul, Brazil. *Soil Science* **112**, 267–275.
- Taylor RW, Ellis BG (1978) A mechanism of phosphate adsorption on soil and anion exchange resin surfaces. *Soil Science Society of America Journal* **42**, 432–436.
- Tucker BM (1954) The determination of exchangeable calcium and magnesium in carbonate soils. *Australian Journal of Agricultural Research* **5**, 706–715.
- Uehara G, Gillman G (1981) 'The mineralogy, chemistry and physics of tropical soils with variable charge clays.' (Westview Press: Boulder, CO)
- Veith JA, Sposito G (1977) On the use of the Langmuir equation in the interpretation of 'adsorption' phenomena. *Soil Science Society of America Journal* **41**, 697–702.
- Vo Dinh Quang, Vu Cao Thai, Tran Thi Tuong Linh, Dufey JE (1996) Phosphorus sorption in soils of the Mekong Delta (Vietnam) as described by the binary Langmuir equation. *European Journal of Soil Science* **47**, 113–123.

- Walker A, Black IA (1934) An examination of the Degtjareff method for determining soil organic matter and a proposed modification of the chromic acid titration method. *Soil Science* **37**, 29–38.
- White IR, Taylor AW (1977) Effect of pH on phosphate adsorption and isotopic exchange in acid soils at low and high additions of soluble phosphate. *Journal of Soil Science* **28**, 48–61.

Manuscript received 4 January 2000, accepted 27 September 2000