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Phosphorus sorption in two Geric Ferralsols of New Caledonia

Rétention du phosphore dans deux sols ferrallitiques oxydiques de Nouvelle-Calédonie

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A large part of New Caledonia territory is covered with Geric Ferralsols. These soils are usually divided in two types, according to their mineralogy. "Ferritic" soils are characterised by a predominance of iron oxides and are located in the South of the main island of New Caledonia. On the other side, "Allitic" soils exhibit large amounts of both aluminium and iron oxides, and are found on Loyalty Islands. These soils, which are of great importance for the agricultural development of these two regions, are believed to have very large phosphorus sorption capacities that lead to a limited phosphorus availability to crops.

Sorption kinetics, sorption and desorption isotherms were built using batch equilibrium experiments for the two soil types. Phosphorus sorption data was analysed using correlations between Langmuir sorption parameter X_{max} and soil properties.

Geric Ferralsols of New Caledonia showed very large sorption capacities, and sorption appears to be governed by both organic and mineral components. Organic carbon and oxalate-extracted aluminium were the main soil properties that explained P sorption variations. An increase in shaking duration resulted in a sorption increase. The organic matter would act as a physico-chemical barrier, its role being however limited in time. Desorption data showed that the sorption-desorption process is highly irreversible.

The richness in aluminium and iron oxides combined to unusual large phosphorus sorption capacities make New Caledonian soils particularly interesting research materials.

Keywords : phosphorus, sorption, desorption, kinetic, Geric Ferralsols, New Caledonia

Mots clés: phosphore, adsorption, désorption, cinétique, Geric Ferralsols, Nouvelle-Calédonie

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Introduction

Phosphorus sorption has been intensively investigated in the past years. It is widely accepted that orthophosphate anions are principally sorbed to iron and aluminium oxides when present in soils (Holford and Mattingly, 1975 ; Hamad et al., 1992). P sorption is usually found to be large in soils that are naturally rich in sesquioxides (Saunders, 1965). A large part of New Caledonia is covered by highly-weathered Oxisols with metallic oxide contents as high as 80%. Two main types of Oxisols ("Allitic" Oxisols and "Ferritic" Oxisols, Latham, 1980) can be identified on the basis of their pedogenesis.

Maré is an uplifted coral atoll, with 16% of the island surface covered by Allitic Oxisols. These soils have usually high organic carbon contents (usually more than 10% in the topsoil), low silicium (less than 1%), and large amounts of oxides, aluminium compounds being usually predominant (40-50% Al_2O_3 , 20-25% Fe_2O_3). This soil type is also found in Fiji islands, the Caribbean and Jamaica (Latham, 1980). Although very present in the soils ($\text{P}_2\text{O}_5 > 3\%$), phosphorus is mostly incorporated in minerals and is unavailable to plants. Oxisols that are found on the main island of New Caledonia (20% of its surface) are derived from ultrabasic rocks and are chiefly composed of iron oxides (Ferritic Oxisols). They exhibit a low cation exchange capacity solely linked to the organic matter content, and high nickel contents which lead to toxicities for plants.

Both soil types are believed to be cultivated intensively in the near future because of the intensification of New Caledonian agriculture and the development of cash-cropping sector. We therefore investigated phosphate sorption to access fertilisation problems that may rise in the near future.

Material and Methods

Allitic and Ferritic Oxisols samples were collected on Maré island (Loyalty Islands) and on the main island of New Caledonia (Grande Terre), respectively.

Phosphorus sorption isotherms (or Q-I relationships) were determined by a standard batch equilibrium method. 1 g of soil was allowed to equilibrate with 10 ml of phosphorus solutions of increasing concentration (0-1.5 g P l⁻¹) by shaking in an end-over-end shaker for 24 hours at room temperature (25±1°C). CaCl₂ was used as a background electrolyte. At the end of the shaking period, the suspension was centrifuged for 15 min at 2500 rpm. The supernatant was then filtered and the filtrates analysed colorimetrically for P by the method of Murphy and Riley (1962). The parameter X_{max} was derived using the Langmuir equation (Holford et al., 1974). Because our shaking period was too short to reach an equilibrium state, the equation was only used as a numerical way to assess the sorbed amount corresponding to an unlimited concentration.

Desorption studies were conducted for two samples from each experimental site. Following a centrifugation ending a usual adsorption run as described above, the supernatant was removed and replaced with the same amount of a P-free CaCl₂ solution. After vigorous shaking to allow complete dispersion of the pellets, soils were shaken for 24 hours in the end-over-end shaker. Samples were centrifuged, the supernatant being then removed for P-determination and replaced by a P-free CaCl₂ solution once again. The process was repeated eight times.

Kinetic studies were conducted with the same four samples used in the desorption study. The method used here is similar to the one used in the adsorption study, the only difference being that the shaking time ranged from one hour to seven days. Two drops of toluene were used to limit microbial activity in the sample tubes.

Results and discussion

Preliminary batch tests conducted with initial P concentration values lower than 100 mg P l⁻¹ resulted in a total disappearance of phosphorus from the solution and it was decided to use large P concentrations values (from 0 to 1500 mg P l⁻¹). P sorption is thus likely to involve both true adsorption and precipitation (Hsu and Rennie, 1962).

The Langmuir equation gave a reasonable good fit to the equilibrium P sorption data (r²>0.95 for Maré samples ; r²>0.99 for Ouénarou samples). This equation is able to describe empirical data for both adsorption and precipitation reactions (Veith and Sposito, 1977). A deviation from linearity in the Log-Log representation was observed. This has often been reported.

P sorption as represented by X_{max} values was large in all samples, ranging from 2678 to 9250 mg P kg⁻¹ (Table 1). Such high values were seldom reported and may be attributed to the unique mineralogy of New Caledonian soils (Latham, 1980 ; Becquer et al., 1998). P sorption was higher in Allitic Oxisols from Maré that exhibit higher aluminium oxide contents than Ferritic Oxisols from Ouénarou.

For Maré samples, significant correlations (p<0.01) were found between X_{max} and organic carbon (r=-0.93, Table 2), pH (r=-0.74), pyrophosphate-extracted Fe and Al (r=-

0.77 and $r=-0.65$ respectively). The mineralogy from soils of Maré are dominated by aluminium oxides (Becquer et al., 1993) and organic matter is largely present in topsoils (Table 1). Organic carbon is known to greatly influence phosphorus sorption (Vo Dinh Quang et al., 1996) and positive (Brennan et al., 1994), negative (Singh and Jones, 1976) or nil (Borggaard et al., 1990) effects on P sorption have been observed. Whereas positive effect of organic carbon on P sorption was attributed to the inhibition of oxides crystallization (Cornell and Schwertmann, 1979), the negative resultant of organic has been explained by the competition between organic ligands and phosphorus (Nagarajah et al., 1970). Organic matter is believed to be intimately associated to sesquioxides in Oxisols from New Caledonia because a standard H_2O_2 treatment of topsoil samples is ineffective in decreasing organic matter content. This close association is likely to act as a physico-chemical barrier at least in highly organic topsoils, and decrease the accessibility of orthophosphate molecules to sorption sites. The high negative correlation between X_{max} and pyrophosphate-extracted aluminium (AIP) and iron (FeP) is supposed to be due to the high correlation between AIP and FeP and organic carbon. A negative correlation between P sorption and pH was found in our study, in accordance with previous results (e.g. Hingston et al., 1972). A pH increase leads to a decrease in positively charged aqueous sites on variable charge surfaces (Shang et al., 1992), to an increase in hydroxyl ions that can compete with orthophosphate ions for sorption sites (Eze and Loganathan, 1990), to an increase in solubilization of aluminium-phosphate complexes (White and Taylor, 1977) and to an enhanced electrostatic repulsion between orthophosphate ions and soil particles. All these effects result in a P sorption decrease.

For Ouénarou samples, X_{max} was positively related ($p<0.01$) to oxalate- and DCB-extracted aluminium ($r=0.82$ and $r=0.67$ respectively, Table 3). Oxalate and DCB extractions are often applied to iron and aluminium oxides but the selectivity of these extractions is not the same for the two elements. In particular, oxalate-extracted aluminium is usually higher than DCB-extracted aluminium, the difference between the two values accounting for an estimation of allophanes (Faivre, 1988). However, the reverse is observed here and RX analyses revealed that aluminium oxides are almost absent from Ouénarou samples. It is therefore suggested that extracted aluminium results from substitution in goethite. Oxalate- and DCB-extracted aluminium variations are related to the degree of substitution of aluminium in goethite and to the amount of aluminium in amorphous iron oxides.

P sorption in selected samples from both sites was found to be highly irreversible (Fig. 1). In particular, the first desorption step only decreased the P adsorbed by less than 10%. The parts of desorption curves related to the beginning of the desorption experiment were almost horizontal.

P sorption kinetics curves show that in case of samples having roughly the same mineralogical components but different organic matter contents (M21 and M23, Fig. 2), organic matter may delay phosphorus sorption but this effect is only transient. This observation is in accordance with previous works on Oxisols (Afif et al., 1995). The observed delay accounts for diffusion through organic coatings of minerals and P competition with organic ligands for sorption sites.

Conclusions

P sorption was found to be extremely high in New Caledonian Oxisols, X_{max} values reaching 9000 mg P kg⁻¹ in some subsoils. This is attributed to their high oxide contents. Allitic Oxisols (40-45% Al₂O₃, 20-25% Fe₂O₃) showed higher sorption properties than Ferritic Oxisols (60-80% Fe₂O₃, 5-10% Al₂O₃). In the first case, sorption was negatively related to organic matter and pH, whereas the most important parameters in Ferritic Oxisols were oxalate- and DCB-extracted aluminium. Desorption curves revealed that sorption is an irreversible process in New Caledonian Oxisols. Phosphorus sorption was delayed in organic samples but this effect seems to be only transient.

References

- Afif E., Barron V., Torrent J., 1995. Organic matter delays but does not prevent phosphate sorption by Cerrado soils from Brazil. *Soil Sci.*, 159:207-211.
- Becquer T., Bourdon E., Pétard J.A., 1993. Contribution à l'étude des sols de Maré. 2. Caractérisation physico-chimique des sols. ORSTOM Nouméa, 63p.
- Becquer T., Bourdon E., L'Huillier L., Quantin P., Herbillon A., 1998. Sources du nickel biodisponible dans les sols ferrallitiques ferritiques du sud de la Nouvelle-Calédonie. 16th World Congress of Soil Science, Montpellier. Symposium N° 6.
- Borggaard O.K., Jorgensen S.S., Moberg J.P., Raben-Lange B., 1990. Influence of organic matter on phosphate adsorption by aluminium and iron oxides in sandy soils. *J. Soil Sci.*, 41:443-449.
- Brennan R.F., Bolland M.D.A., Jeffery R.C., Allen D.G., 1994. Phosphorus adsorption by a range of western Australian soils related to soil properties. *Commun. Soil Sci. Plant Anal.*, 25:2785-2795.
- Cornell R.M., Schwertmann U., 1979. Influence of organic anions on the crystallization of ferrihydrite. *Clays Clay Min.*, 27:402-410.
- Eze O.C., Loganathan P., 1990. Effects of pH on phosphate sorption of some Paleudults of southern Nigeria. *Soil Sci.*, 150:613-621.
- Faivre P., 1988. Lessivage et planolisation dans les séquences de sols caractéristiques des milieux intrandins de Colombie. Thèse Doct., Univ. Nancy I, 563 p.
- Hamad M.E., Rimmer D.L., Syers J.K., 1992. Effect of iron oxide on phosphate sorption by calcite and calcareous soils. *J. Soil Sci.*, 43:273-281.
- Hingston F.J., Posner A.M., Quirk J.P., 1972. Anion adsorption by goethite and gibbsite. I. The role of the proton in determining adsorption envelopes. *J. Soil Sci.*, 23:177-192.
- Holford I.C.R., Mattingly G.E.G., 1975. The high- and low-energy phosphate adsorbing surfaces in calcareous soils. *J. Soil Sci.*, 26:407-417.
- Holford I.C.R., Wedderburn R.W.M., Mattingly G.E.G., 1974. A Langmuir two-surface equation as a model for phosphate adsorption by soils. *J. Soil Sci.*, 25:242-255.
- Hsu P.H., Rennie D.A., 1962. Reactions of phosphate in aluminium systems. *Can. J. Soil Sci.*, 42:197-221.
- Latham M., 1980. Les oxydisols dans quelques milieux insulaires du Pacifique Sud. *Cah. Orstom, sér. Pédol.*, 18:305-316.

- Murphy J., Riley J.F., 1962. A simplified single solution method for the determination of phosphate in natural waters. *Anal. Chim. Acta*, 27:31-36.
- Nagarajah S., Posner A.M., Quirk J.P., 1970. Competitive adsorption of phosphate with polygalacturonate and other organic anions on kaolinite and oxide surfaces. *Nature*, 228:83-85.
- Saunders W.M.H., 1965. P retention by New Zealand soils and its relationship to free sesquioxides, organic matter, and other soils properties. *N. Z. J. Agric. Res.*, 8:30-57.
- Shang C., Stewart J.W.B., Huang P.M., 1992. pH effects on kinetics of adsorption of organic and inorganic phosphates by short-range ordered aluminium and iron precipitates. *Geoderma*, 53:1-14.
- Singh B.B., Jones J.P., 1976. Phosphorus sorption and desorption characteristics of soil as affected by organic residues. *Soil Sci. Soc. Am. Proc.*, 40:389-394.
- Veith J.A., Sposito G., 1977. On the use of the Langmuir equation in the interpretation of 'Adsorption' phenomena. *Soil Sci. Soc. Am. J.*, 41:697-702.
- Vo Dinh Quang, Vu Cao Thai, Tran Thi Tuong Linh, Dufey J.E., 1996. Phosphorus sorption in soils of the Mekong Delta as described by the binary Langmuir equation. *Eur. J. Soil. Sci.*, 47:113-123.
- White R.E., Taylor A.W., 1977. Effect of pH on phosphate adsorption and isotopic exchange in acid soils at low and high additions of soluble phosphate. *J. Soil Sci.*, 28:48-61.

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	Xmax	pH	Org.C	AIP	FeP	AIO	FeO	AID
pH	-0.72							
Org.C	-0.93	0.70						
AIP	-0.65	0.46	0.80					
FeP	-0.76	0.67	0.86	0.88				
AIO	-0.54	0.74	0.63	0.69	0.63			
FeO	0.53	-0.14	-0.46	-0.19	-0.27	0.05		
AID	-0.38	0.28	0.40	0.21	0.38	0.10	0.00	
FeD	0.31	-0.35	-0.42	-0.64	-0.48	-0.66	0.13	0.53

Table 2. Simple linear correlation coefficients (r) between P sorption-parameter and soil properties from Maré samples.

	Xmax	pH	Org.C	AIP	FeP	AIO	FeO	AID
pH	-0.27							
Org.C	-0.43	-0.29						
AIP	-0.41	-0.36	0.43					
FeP	-0.56	-0.35	0.65	0.89				
AIO	0.84	-0.17	-0.33	-0.03	-0.29			
FeO	-0.26	-0.29	0.76	0.44	0.71	-0.23		
AID	0.68	-0.49	-0.05	-0.05	-0.14	0.64	0.00	
FeD	0.37	0.03	0.29	-0.16	-0.02	0.35	0.32	0.43

Table 3. Simple linear correlation coefficients (r) between P sorption-parameter and soil properties from Ouénarou samples.

Table 1. Selected analytical properties of the soil samples

Sample	Profil	Depth cm	pH _{H2O}	Org.C g/kg	PyroP. ^a		Oxalate ^b		DCB ^c		Xmax mg/kg
					Al _P g/kg	Fe _P g/kg	Al _O g/kg	Fe _O g/kg	Al _D g/kg	Fe _D g/kg	
M11	1	0-7	6.8	80.9	2.3	0.8	13.2	4.1	7.8	21.7	6880.3
M12	1	7-20	6.7	43.2	2.4	1.0	13.6	4.8	8.0	22.0	8216.3
M13	1	20-40	6.3	33.8	2.1	0.8	11.4	4.6	8.2	22.0	8388.7
M21	2	0-10	6.7	71.0	2.6	1.0	12.4	3.8	8.4	21.2	6948.8
M23	2	32-75	6.1	15.7	1.4	0.7	6.2	4.1	8.1	24.5	9249.3
M31	3	0-15	6.8	76.8	2.7	1.1	11.3	4.4	8.1	21.0	6982.6
M33	3	35-60	5.8	8.4	1.0	0.1	4.6	4.1	7.7	25.9	8714.0
M41	4	0-10	6.9	97.3	4.1	1.5	12.4	3.5	6.6	15.5	6911.5
M42	4	10-25	6.2	31.9	3.0	0.7	12.9	4.5	6.9	18.0	8313.1
M43	4	25-60	5.9	16.1	1.9	0.5	8.8	4.9	7.1	19.9	9248.5
M44	4	60-80	5.8	13.9	1.2	0.4	7.2	3.2	6.5	20.1	8330.3
M51	5	0-12	6.3	121.0	6.0	1.8	12.4	3.8	8.8	20.1	6505.8
M52	5	12-25	6.2	32.9	3.6	0.8	12.8	5.0	6.8	17.1	8672.3
M61	6	0-12	6.7	145.8	4.5	1.3	15.3	3.4	8.0	17.8	6333.8
M62	6	12-25	6.5	38.8	3.3	0.8	15.0	4.1	7.3	18.2	8592.2
O11	7	0-5	4.6	27.4	1.6	6.0	1.0	2.1	5.1	47.4	3587.1
O12	7	5-20	4.6	20.7	1.4	6.1	1.1	3.0	5.0	51.2	4025.0
O13	7	23-33	4.7	4.5	0.9	2.7	1.3	2.0	5.7	53.7	5647.5
O14	7	38-57	4.8	1.7	0.7	1.1	1.9	1.6	5.5	50.9	7214.2
O15	7	68-85	4.5	0.4	0.7	1.5	1.5	1.3	5.1	46.6	6810.5
O21	8	0-5	5.3	24.6	1.0	3.7	1.2	2.5	4.6	57.5	3787.9
O22	8	7-17	4.8	25.0	1.0	4.6	1.0	2.9	4.3	55.8	4067.2
O23	8	14-34	5.1	4.0	0.5	0.7	1.0	1.7	3.9	57.4	5297.0
O24	8	40-54	5.4	4.9	0.6	0.7	1.3	1.5	3.8	55.9	4830.8
O26	8	67-80	4.9	9.1	0.5	1.4	1.5	1.5	6.3	68.7	6520.4
O27	8	98-100	4.9	0.4	0.4	0.5	1.6	1.5	6.5	76.6	6762.5
O32	9	4-10	4.9	29.0	0.5	1.9	1.0	2.0	4.2	65.7	5032.0
O33	9	18-27	5.0	11.7	1.5	7.2	1.3	3.3	3.8	60.1	4027.6
O34	9	40-51	5.0	13.7	0.8	3.5	1.1	1.9	4.5	63.1	4528.0
O42	10	8-9	4.6	47.2	1.1	6.9	1.0	7.3	5.2	72.1	4876.0
O43	10	26-39	4.7	32.1	0.7	2.9	1.4	3.0	5.6	64.2	5374.8
O44	10	49-67	5.0	10.4	0.9	3.9	1.2	3.0	5.4	54.9	5227.7
O45	10	74-80	5.1	7.1	0.3	2.0	0.3	1.9	3.5	38.9	2678.1

^a Pyrophosphate extracted ; ^b Ammonium oxalate extracted ; ^c Dithionite-citrate-bicarbonate extracted

