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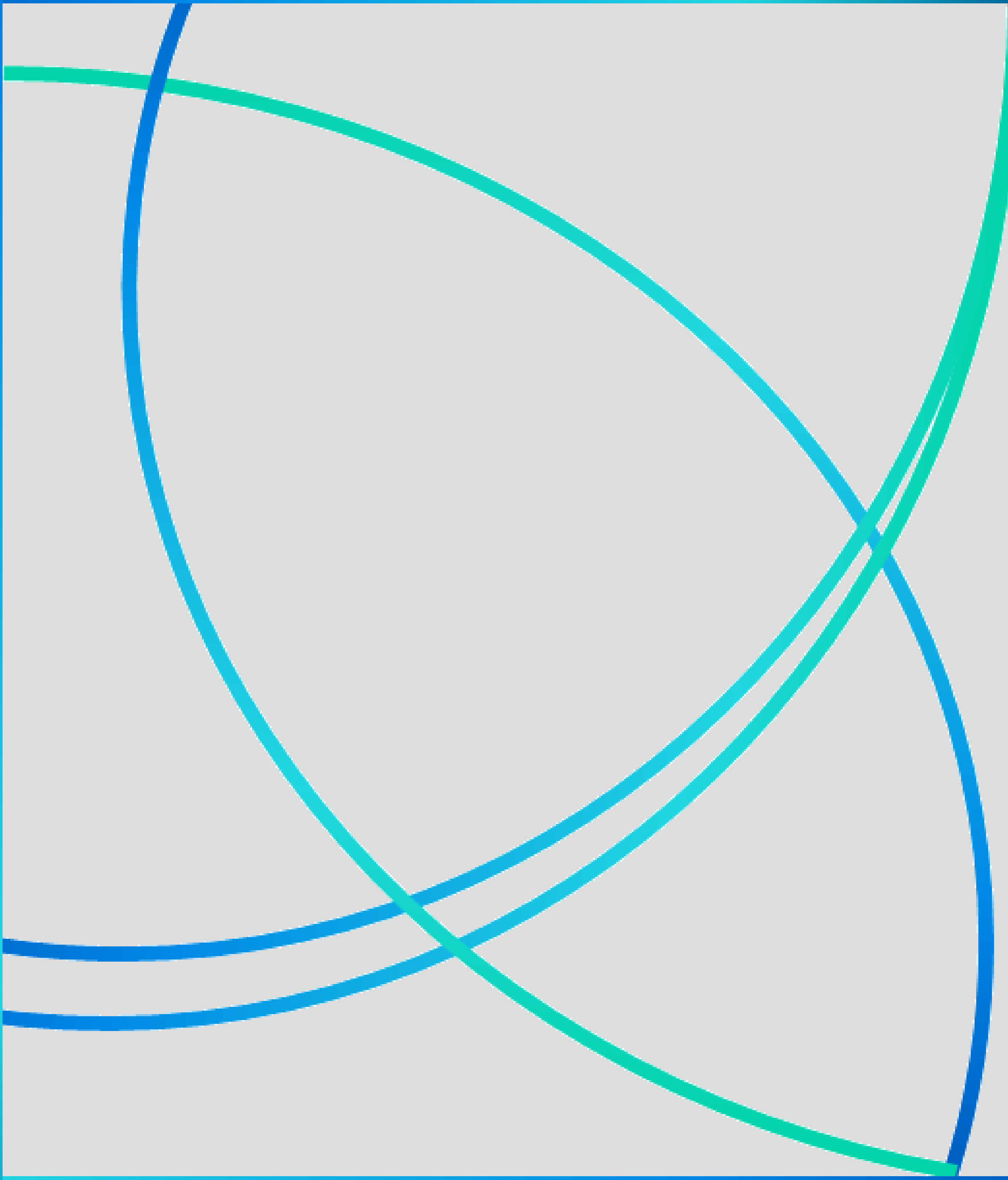

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Soils with hardened laterites are they really high P-sorbing?

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Abstract

In well weathered tropical soils, a common feature of the environment is the presence of laterite within the soil profile. The soils with laterites are considered agriculturally poor because of many major agro-management-related problems such irreversibility hardening upon exposure and phosphorus fixation. In those soils, amorphous and crystalline forms of Fe and Al are the main responsible for P-sorbing sites; however adsorption tends to decrease as long as the amorphous forms are aged. In this contribution, fourteen tropical soil series (or sites) which differ according with the presence of hardened laterites in the profile, were compared for P-sorption and associated soil properties. It was found that P-sorption was lower in the case of the soil with hardened laterite none-the-less that the laterite presented a higher amount of free iron in the subsoil. Basically, lateritic soils sorb less P than the non-lateritic ones probably because the clay fraction is diluted by coarse laterite fragments that due to the cementation of their mineral grains and their low porosity present a small surface area for P sorption. The results have important agroecological implications since laterite soils are abundant in sub and tropical regions and commonly are ascribed as high P-sorbing materials.

Key words: Weathering, tropical soils, plinthite, free Fe.

Los suelos con lateritas endurecidas: ¿Son realmente altamente adsorbentes de P?

Abstract

En los ambientes tropicales muy meteorizados, es común encontrar lateritas en el perfil del suelo. Los suelos con lateritas en general se consideran pobres debido a problemas asociados con su manejo, tales como endurecimiento de la costra laterítica una vez que son expuestas a la superficie y su alta fijación de fosforo. En estos suelos, las formas amorfas y cristalinas de Fe y Al son las principales responsables de los sitios de adsorción de P; sin embargo la adsorción tiende a decrecer a medida que los compuestos amorfos envejecen y se hacen cristalinos. En esta contribución, catorce series de suelos tropicales que difieren, de acuerdo a la presencia (o ausencia) de lateritas endurecidas en el perfil, fueron comparadas en sus valores de adsorción de P y parámetros relacionados. La adsorción de P fue menor en el caso de los suelos lateríticos, no obstante que las lateritas presentes en el subsuelo tenían un mayor contenido de hierro libre.

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Básicamente, los suelos lateríticos adsorben menos P que los no lateríticos probablemente porque la fracción arcilla es diluida por fragmentos de laterita, así se presenta una menor área superficial para la adsorción de P inducida por la cementación y baja porosidad de los granos de laterita. Los resultados tienen importantes implicaciones agroecológicas ya que las lateritas son abundantes en las regiones subtropicales y tropicales donde comúnmente se asocian como materiales con alta capacidad para adsorber P.

Palabras clave: Meteorización, suelos tropicales, plintita, Fe libre.

Introduction

One of the most studied topics in soil and environmental sciences is the chemistry of phosphorus (P), particularly the phenomenon of P adsorption in soils and sediments. P-sorption have been characterised as a process of great complexity involving in greater extent the chemistry of iron (Fe) and aluminium (Al) in acidic environments, whereas calcium (Ca) chemistry dominates in calcareous environments (1,2,3,4). In acid soils, amorphous and crystalline forms of Fe and Al are the main responsible for P-sorbing sites, however adsorption of P tends to decrease as long as the amorphous forms of Al and Fe are aged and transformed in more arranged crystalline forms. Temperature and moisture content are factors which can induce marked changes in the degree of crystallinity of Fe and Al compounds including their phosphate forms (5,6). Since crystallinity is favoured by high temperature Fe and Al compounds, particularly oxi-hydr(oxides) exist in a highly crystalline form in tropical environments (5). When amorphous iron and aluminium oxi-hydr(oxides) are transformed into a crystalline form, the specific surface area is lowered and consequently the reactivity and capacity to retain phosphate also decreases (7,8,9).

In well weathered tropical soils (Ultisols and Oxisols), a common feature of the environment is the presence of laterites within the soil profiles (this old term have been replaced by plinthite and/or petroplinthite (10), those Fe and Al enriched materials present very low amounts of basic cations and primary silicates, but conversely, may be enriched in quartz and kaolinite (10,11,12). The soils with presence of laterites cover important part of the humid tropics and they are considered agriculturally poor or practically useless because of many major agro-management-related problems in which the most notorious are the irreversibility hardening upon exposure, the restriction to water flow and root development, and phosphorus fixation (10). However, it must be noted that the expected high P-sorption of the lateritic material due to the abundance of hydrous oxides is partially reduced by the incorporation in the laterite structure of gravels and other non P-sorbing quartz materials; moreover, the hardness of the material is associated with a higher degree of crystallinity of the sorbing materials, an aging phenomenon, which in turn decrease P-fixation processes.

Although the literature is abundant in research concerning P-sorption in tropical soils, there is little or no report known to the author about a comparison of P adsorption in well weathered soils with and without the presence of hardened (or concretionary) laterite in the profile. It can be hypothesised that soils with laterite in the profile are lower P-adsorptive than well weathered soils where the laterite is not present.

Since the higher degree of crystallinity of the hydr(oxides) in the former affect the amount of sorption sites, beside lateritic soils, in general, may present lower clay content in the subsoil.

Therefore, in this contribution, fourteen different soil series represented by matched tropical sub- and topsoil were compared for P-sorption and some associated soil properties.

Materials and methods

Soils

The soil samples used represent fourteen chosen soil series (or sites) from moderately humid to very humid tropical environments with and without the presence of hardened (or concretionary) laterite in the profile, ten Oxisols and two Utisols from Malaysia, and two Oxisols from Venezuela. The soils from Malaysia correspond from moderate humid to very humid tropical climate and the Venezuelan soils correspond to dry savannas. The soils were taken from landscapes where Oxisols or Oxisol:Ultisols intergrades are predominant.

The soils present contrasting levels of amorphous and crystalline Al and Fe hydr(oxides), seven with concretionary or hardened laterite in the subsoil, hereafter called L, and seven without laterite, hereafter called NL. In each chosen soil profile, matched pairs of topsoil and subsoil (40-100 cm) were used in the investigation. All the samples were acid in reaction.

Determination of soil properties

Following air-drying, free iron was removed with dithionite-citrate solution (DC extraction method) (13) and the iron released to the solution was determined by atomic absorption in a Varian Techtron AA6. Extractable aluminium was obtained using ammonium acetate solution (1) and determined by colorimetric technique in a Spectronic, Bausch and Lomb (14). Clay content was determined by the pipette method, pre-treating with hydrogen peroxide but not with hydrochloric acid because of the acid reaction of the soils. Per cent of carbon was determined by chromic acid digestion (15).

Phosphate adsorption index of soils

The adsorption isotherm has provided excellent means of characterising soil P-sorption, but it involves a considerable amount of analytical work. Single-point isotherms have consequently proposed to determine adsorption characteristics. Bache and Williams (16) suggested using 155 mg P/100 g soil (1550 mg kg^{-1}) as an adsorption point of the isotherm to determine the P sorption index because 100 mg P/100g soil was too low and there were potential analytical problems at 200 mg P/100g or greater.

P sorption determination

The sorption value was obtained by shaking 2.5 g air dry soil ground to < 30 mesh with 50 mL of a solution 0.025 M KH_2PO_4 and 0.02 M KCl. All determinations were carried out at 20±1°C for 18 hours. After the shaken period, the suspension was filtered and centrifuged and the final phosphorus concentration was determined by Murphy and Riley´s method (17) in a Spectronic, Bausch and Lomb. All sorption experiments were run in triplicates. No problems of analytical precision were observed in our P analyses.

Calculation of the sorption index

A single point in the soil isotherm was used as a simple phosphate sorption index (Bache and Williams' index) calculated as follow:

$$IBW = x/\log C$$

Where IBW is the sorption index, x is the sorption (mgP/100g soil) from one initial addition of 155 mgP/100g soil, and C (µmol/L) is the phosphate equilibrium concentration.

Statistical analysis

For comparisons of mean the t-test was used. Analyses were performed using the statistical package SPSS 13.0 with a level of significance $p < 0.05$ and 0.01. Pearson's correlation coefficients between the P-sorption and the various parameters studied were performed using the computer program STATISTICA version 3.1.

Results

Rating Bache and Williams' indices

The overall mean IBW index of laterite soils was 20.6 (Table 1), whereas in the non-laterite soils the mean index was 30.0 (Table 1), so it is convenient to consider 25 as an average value. In the following sections, verbal descriptions, according to Burnham and López-Hernández (18) use the following arbitrary conventions: 0 to 10 very low, 10 to 20 low, 20-30 medium, 30-50 high and over 50 very high.

Table 1. Mean values and standard deviations (in brackets) of the soils (top +subsoil samples) with laterite (L) and without laterite (NL). Different letters indicate significant difference ($p< 0.05$) between each soil type (L and NL)

Soils	P-sorption	Free Fe cmol/kg	Extractable Al cmol/kg	% Clay	%C
Laterite soils L	20.6(11.5)a	95(91)a	0.70(0.32)a	23.9(12.0)a	1.53(1.06)a
Non-laterite soils NL	30.0(13.7)b	101(69)a	0.69(0.29)a	45.0(19.4)b	1.61(1.10)a

Comparative studies between the soils with and without laterites

The values of the phosphate sorption, free iron oxides, extractable aluminium, clay content and per cent of carbon of the L and NL soils are given in Tables 2a, b, respectively. Also in the same tables in italics are presented the range (highest and lowest values) of the soil properties.

The soils with laterite (Table 2a) ranged from a very low P-sorption value (7.5, corresponding to Calabozo 1 and Calabozo 2, Venezuela topsoils) to a high value (46.6, Munchong, Malaysia topsoil), whereas for the non-laterite (Table 2b) soils P-sorption ranged from low (17.1, corresponding to Rengam and Sungei Mas, Malaysia topsoils) to a very high value (62.6, Langkawi, Malaysia subsoil).

Table 2a. Phosphate sorption and soil properties of the soils with laterite (L). T and S correspond to topsoils and subsoils, respectively.

Soils Location	P-sorption	Free Fe cmol/kg	Extractable Al cmol/kg	%Clay	%C
Chungloon, Malaysia T	36.1	130	0.71	17.8	1.72
Chungloon, Malaysia S	20.6	*287*	0.44	26.0	0.56
Munchong, Malaysia T	*46.6*	154	*1.20*	31.2	1.80
Munchong, Malaysia S	33.5	229	0.82	13.5	*0.52*
Durian, Malaysia T	13.1	13	0.68	32.8	*4.44*
Durian, Malaysia S	13.9	13	1.01	40.1	1.10
Batu Anam, Malaysia T	13.9	36	1.17	30.6	2.56
Batu Anam, Malaysia S	19.2	50	1.01	40.5	1.19
Calabozo1, Venezuela T	*7.5*	*5*	0.29	19.5	1.30
Calabozo 1, Venezuela S	20.6	197	0.36	7.2	0.76
Calabozo 2, Venezuela T	*7.5*	39	0.36	*4.3*	1.21
Calabozo 2, Venezuela S	9.4	97	*0.27*	13.7	0.72
Tavy, Malaysia T	22.7	47	0.82	33.9	2.60
Tavy, Malaysia S	24.1	30	0.67	*45.4*	1.00

The lateritic soils (L) present a medium value of IBW (20.6) that is significantly lower than the higher mean values (30.0) corresponding to the non-lateritic (NL) soils (Table 1), a similar result was found for the content of clay (23.9% and 45.0 % for L soils and NL, respectively). Concerning the other soil properties, mean values for free iron content, extractable aluminium, and percent of carbon in both soil populations were almost the same, therefore the comparison of means did not reach significances (Table 1).

Table 2b. Phosphate sorption and soil properties of the non-laterite soils (NL).T and S

Soils without laterite	P-sorption	Free Fe cmol/kg	Extractable Al cmol/kg	% Clay	% C
Rengam, Malaysia T	*17.1*	*21*	0.83	20.8	1.82
Rengam, Malaysia S	26.3	25	0.95	29.6	1.16
Langkawi, Malaysia T	30.2	*208*	0.43	*13.6*	*4.13*
Langkawi, Malaysia S	*62.6*	143	*1.07*	*70.9*	0.54
Munchong, Malaysia T	18.5	65	1.02	65.6	1.70
Munchong, Malaysia S	50.6	69	*1.07*	70.5	1.08
Segamat, Malaysia T	22.7	165	0.68	46.8	2.06
Segamat, Malaysia S	38.9	165	0.58	66.9	1.12
Sungei Mas, Malaysia T	*17.1*	149	0.18	38.7	2.68
Sungei Mas, Malaysia S	40.8	197	0.29	57.5	*0.47*
Kampong Kolem , Malaysia T	24.1	54	0.82	34.8	3.23
Kampong Kolem, Malaysia S	28.6	97	0.51	54.7	0.62
Kampong Kubor, Malaysia T	17.8	22	0,47	30.0	1.49
Kampong Kubor, Malaysia S	24.8	30	0.72	29.2	0.48

Comparative studies of topsoils and subsoils in L and NL

Soils with laterite in the profile

In the case of the L soils, there was no difference in the sorption index between the topsoils and subsoils (Table 3) similar information was found for the extractable aluminium and the clay content which were almost the same in both soil depths. Although the content of free iron was much higher in the subsoils (129 cmol Fe kg^{-1}) compared with the topsoils (61 cmol Fe kg^{-1}) (Table 3) there was not significance between means, a result which was ascribed to the high variability of the data. On the contrary, the mean value of the content of carbon in the topsoil (2.23 %) was significantly higher respect the C content in the subsoil (0.84 %).

Soils without laterite in the profile

The subsoils of the NL soils contain significantly higher amounts of clay (% 54.2), and higher P retention values (IBW 38.9) than the topsoils (35.8 and 21.1 for clay and P-sorption, respectively), while the extractable aluminium and the free iron oxides, although higher in the subsoils, did not reach significance respect the topsoils (Table 3), on the contrary, as expected, per cent of carbon was significantly lower in the subsoils.

Discussion

Validity of the Bache and Williams' index

Single-point isotherms were initially introduced by Bache and Williams (16) to determine phosphate sorption capacity of a wide range of British soils, and since then, the Bache and Williams' index has been extensively used in the soil literature (1,18,19,20,21). The approach assumes that single point addition of phosphate at high concentration is adequate to saturate all available P sorption sites. In fact the IBW uses a P concentration of 1550 mg kg^{-1}, which is enough to saturate the sorption sites of even well-weathered soils such as the ones here studied. Moreover, it has been shown that phosphate sorption values for various soils at this high phosphorus concentration were well correlated with the maximum adsorption estimated from Langmuir sorption model (16,22) and have a wide range according with soil characteristics. The universe of soils here studied presented IBW indexes which ranged from 7.5 to 62.6 (Tables 2a,b). Other authors also have found a wide variability in P-sorption values measured with the IBW index; thus, Indiati *et al.,* (23) reported for Typic Xerorthents of Italy values ranging from 9.6 for a sandy soil with low content of free Fe, and 51.6 for a clay soil with important amounts of free Fe.

Soils with hardened laterites are they really high P-sorbing?

As previously hypothesised results show that well weathered Oxisols and Ultisols presenting hardened laterite nodules (L) have a significant lower P adsorption capacity than similar well weathered soils without laterite (Table 1); a result that could be a little bit surprising because of the higher amounts of free iron oxides present in the laterite nodules (10,11,18). In contrast, P-sorption was much higher in the weathered, non-laterite soils studied (NL) which also contain important clay contents enriched with a great proportion of amorphous iron (and aluminium) hydrous oxides. Laterites (e.g. plinthite and petroplinthite) are formed under a large supply of iron, with a later process of cementation and hardening due to packing of the crystal that reduce the surface area and consequently the P-sorption sites (8,10,18).

It appears that the general difference in P sorption, between lateritic and non-lateritic soils studied in this work is mainly due to the latter having more clay than the lateritic soils. Basically, other conditions being the same, lateritic soils sorb less P than the non-lateritic probably because the clay fraction is diluted by coarse laterite fragments that, because of the cementation of their mineral grains and their low porosity, present a small surface area for P sorption. These fragments are rich in Fe oxides, which were extracted by the DC reagent after grinding; however these Fe oxides contributes little to P sorption. The dithionite method generally extracts both crystalline and amorphous forms.

P-sorption and soil properties within the soil profile and factors related to phosphate adsorption

The amount and form of sorbing materials differ according with their place in the profile. When analysing together all the topsoils and subsoils corresponding to L and NL, P-sorption and clay content were significantly higher in the subsoil respect the surficial topsoil (L+NL, Table 3). Similarly, free iron was higher in the subsoil, although significance was not reached between depths due to the high variability of the results, also extractable Al was the same at both soil depths, whereas, as expected, the mean organic carbon was significant lower in subsoil. López-Hernández and Burnham (1) analysed a large population of different tropical soil series and also reported that subsoils tend to have higher amounts of free iron oxides and clay contents than the topsoils, whereas the mean value of per cent C, as expected, decrease with depth. Contrary, they found phosphate sorption did not differ significantly at both soil depths, because of the variability of the soil properties; moreover, the higher organic matter contents in the superficial soils contribute to decrease or block the potential sites of sorbing (1,24,25).

When comparing the top- and subsoil of the non-laterite soils, a significant difference was found for P-sorption in the profile, which is ascribed to the higher clay contents present in the subsoil compared with the superficial soil (Table 3). Contrary, the laterite soils did not differ in P retention capacities within the soil profile and so occurred with other soil properties, except per cent C, which in all cases was superior in the surficial soil compared with the subsoil. In L, the presence of the laterite accounted for a reduction in the clay content in the subsoil, which in turn contributes to decrease the P-sorption sites (Table 3).

The interrelationships among the different soil properties were evaluated by simple correlation (Table 4). In L soils, the most important factor related to phosphate adsorption is free iron followed by extractable aluminium, whereas, per cent C was not related to P-sorption; similar information for tropical environments have already presented in many studies (18,26). Contrary to the general finding, P adsorption in L soils did not show a significant correlation with the clay content; no doubt the gravel content in those soils affected the result. A different situation was found in the NL soils where the effect of clay content on P sorption is particularly important (0.639**) and superior to values found for the free iron (0.378^{ns}) and extractable aluminium (0.331^{ns}). The negative correlation between per cent C and P adsorption (-418^{ns}) in NL is well related to the competition between organic anions and phosphate for sorbing places (18,24,25,26).

Table 3. Mean values and standard deviations (in brackets) of the topsoils and subsoils of the soils with laterite (L) and without laterite (NL). Different letters indicate significant difference ($p< 0.05$) between top and subsoils within each soil type (NL and L) and between soil depth (Top and Sub) of all the top and subsoils analysed (L+NL).

	P-sorption	Free Fe cmol/kg	Extractable Al cmol/kg	%Clay	%C
L Top	21.1(15.1)a	61(58)a	0.75(0.35)a	24.3(10.1)a	2.23(1.11)b
L Sub	20.2(7.6)a	129(108)a	0.65(0.31)a	23.5(14.4)a	0.84(0.26)a
NL Top	21.1(4.9)a	98(75)a	0.63(0.29)a	35.8(17.2)a	2.44(0.96)b
NL Sub	38.9(13.9)b	104(67)a	0.74(0.30)a	54.2(18.0)b	0.78(0.32)a
L+NL Top	21.1(10.8)a	79(67)a	0.69(0.32)a	30.0(15.1)a	2.34(1.00)b
L+NL Sub	30.0(14.5)b	116(87)a	0.70(0.29)a	40.0(24.0)b	0.81(0.28)a

Table 4. Pearson's correlation coefficients between P-sorption (IBW) and soil properties. *and ** significant at P<0.05 and 0.01, respectively

Soil	Free iron	Extractable Al	% Clay	% C
L	0.517*	0.499*	0.100^{ns}	0.074^{ns}
NL	0.378^{ns}	0.331^{ns}	0.639**	-0.418^{ns}

Conclusions

In a population of Oxisols and Ultisols with and without hardened laterite, phosphate sorption was lower in the case of the soil with hardened or concretionary laterite, none-the-less, the laterite soil presented a higher amount of free iron in the subsoil. The results from the present study have important agroecological implications since laterite soils are abundant in sub- and tropical regions and commonly are ascribed as high P-sorbing materials, therefore a major agricultural constrain in those lateritic soils is a physical impediment to root growth and penetration.

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