

SURFACE CHARGE CHARACTERISTICS AND PHOSPHORUS SORPTION CAPACITY OF VARIABLE CHARGE SOILS

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INTRODUCTION

Variable charge soils (VCS) have developed under intensive weathering and leaching conditions in tropical and subtropical regions (Uehara and Keng, 1975). Such soils predominantly contain minerals with variable surface charge density, which are of amphoteric properties and can be protonated or deprotonated to create variable positive or negative charge on their surfaces, respectively (Uehara and Keng, 1975; Qafoku *et al.*, 2004). Therefore, the magnitude and sign of their surface charge changes with alteration of soil pH and ionic strength. In addition, the point of zero charge (PZC) or pH_0 (the pH value at which the number of H^+ and OH^- ions adsorbed on the amphoteric surfaces are equal) is of fundamental significance to the characterisation of VCS because at this pH, net variable charge is zero, so that any residual charge is net permanent charge (Gillman, 1985). Because the charge characteristics of VCS are largely dependent on soil pH, soil acidification often has severe consequences for overall fertility of these soils. They often pose a particular challenge to sustainable management in terms of low CEC at soil pH, rapid reduction in CEC, as soil acidity increases, and their ability to adsorb anionic species, such as P (Gillman and Sumpter, 1986). The majority of the reactions that control nutrient availability of these soils are dependent on the physicochemical processes that occur at soil particle surfaces (Uehara and Gillman, 1981). Therefore, it is essential to determine the charge characteristics of VCS, with a correct determination of the *in situ* CEC and a full understanding of the variation of charge with pH, before establishing strategies for sustainable management of these soils.

MATERIALS AND METHODS

Two Red Ferrosols (Isbell, 1996) were collected in Dorrigo, NSW (Dorrigo Ferrosol) and in Palmerston, north Queensland (Palmerston Ferrosol). These two soil types have similar characteristics, i.e. geric properties, to many upland soils in Vietnam (Moody and Phan, 2008). The other two soil samples were collected from a Redoxic Hydrosol (Hydrosol) and an Aquic Grey Vertisol (Vertisol) (Isbell, 1996) in Ingham, north Queensland. In order to minimise the interference of organic matter on charge determinations, all samples were collected at 20 - 40 cm depth. The soil samples were air-dried and passed through a 2 mm sieve before determining charge characteristics and analysing the physicochemical properties of the soils. The soils are dominated by kaolinite, hematite, goethite and gibbsite, and their clay contents and some chemical properties are given in Table 1.

Charge fingerprint procedure was used to determine the soil pH, pH_0 and the charge characteristics of soils such as the total cation exchange capacity (CEC_T), base cation exchange capacity (CEC_B) and anion exchange capacity (AEC) (Gillman, 2007). Phosphorus buffer index (PBI) was determined using the method described by Burkitt *et al.* (2002).

Table 1. Clay contents and some chemical properties of the studied soils (20-40 cm)

Soils	Clay	¹ TOC	² Al _{Ox}	³ Fe _{Ox}	⁴ Si _{Ox}	⁵ Al _{Cryst.}	⁶ Fe _{Cryst.}
				(%)			
Dorrigo Ferrosol	65	2.50	0.40	0.4	0.01	0.7	6.0
Palmerston Ferrosol	65	1.55	0.30	0.3	0.01	1.8	14.1
Hydrosol	23	0.72	0.05	0.2	0.02	0.0	0.7
Vertosol	61	0.88	0.10	0.2	0.03	0.2	1.8

¹total organic carbon; ²oxalate extractable Al; ³oxalate extractable Fe; ⁴oxalate extractable Si; ⁵crystalline Al; and ⁶crystalline Fe, which are derived from the differences between citrate bicarbonate dithionite extractable Al/Fe and oxalate extractable Al/Fe, respectively

RESULTS AND DISCUSSION

Existing soil pH values of the Hydrosol and Vertosol were significantly higher than those of both Ferrosols (Table 2). The pH₀ value of the Hydrosol was significantly lower than those of the Ferrosols. However, the pH₀ of Vertosol was not estimated from the regression equations for the titration curve. This indicated that the soil predominantly contains minerals with permanent surface charge density.

The CEC_B and CEC_T of the Hydrosol and Vertosol were substantially higher than those of the two Ferrosols (Table 2). Since the Vertosol had the highest soil pH, it also exhibited the highest CEC values, being 4.30 cmol_c kg⁻¹ for CEC_B and 4.34 cmol_c kg⁻¹ for CEC_T. Conversely, the Palmerston Ferrosol had the lowest soil pH, accompanied by the lowest CECs. It should be noted that although the CEC of the Vertosol was not as high as typical alkaline Vertosols (Stace *et al.*, 1968), it is still approximately 20-fold higher than that of the Palmerston Ferrosol. The Palmerston Ferrosol exhibited a significant amount of AEC at soil pH, whereas the other three soils had negligible AECs at their soil pH values (Table 2). This is in agreement with the content of Fe/Al hydrous oxides for these soils (Table 1). Soil positive surface charge mainly originates from the protonation of surface hydroxyl groups of Fe/Al hydrous oxides (Taubaso *et al.*, 2004).

A single-point PBI has been developed to characterise soil P sorption capacity, the higher the value of PBI, the greater the P sorption capacity of a soil. The Hydrosol and Vertosol exhibited very low PBIs in comparison to those of the two Ferrosols, with the Hydrosol having the lowest PBI value (Figure 1). The Hydrosol has low contents of clay and Fe and Al hydrous oxides and this is reflected in its very low PBI. The Vertosol, while having a similar clay content to the Ferrosols, has a much lower content of Fe and Al hydrous oxides than the Ferrosols (Table 1) and therefore a lower PBI than these soils. Wang *et al.* (2009) found that the greater P adsorption by two Oxisols than an Ultisol in China was attributed to the higher content of Fe/Al hydrous oxides in the former soils than in the latter.

Table 2. Comparison of soil pH, pH_0 , CEC_B , CEC_T and AEC between the subsoils (20 - 40 cm) of the Dorrigo Ferrosol, Palmerston Ferrosol, Hydrosol and Vertosol

Soil	Soil pH (1:10)	pH_0	CEC_B , CEC_T , AEC ($cmol_c\ kg^{-1}$)		
			CEC_B	CEC_T	AEC
Dorrigo Ferrosol	4.62 c	3.99 b	1.08 c	1.24 d	-0.07 b
Palmerston Ferrosol	4.26 d	4.63 a	0.23 d	0.24 c	-0.62 c
Hydrosol	4.88 b	3.50 c	1.42 b	1.46 b	0.04 a
Vertosol	5.15 a	*n.e.	4.30 a	4.34 a	0.05 a
LSD _(0.05)	0.02	0.17	0.16	0.15	0.10
CV(%)	0.1	1.8	3.2	3.0	24.5

* Not estimated. Means in the same column followed by different letters are significantly different at $P < 0.05$.

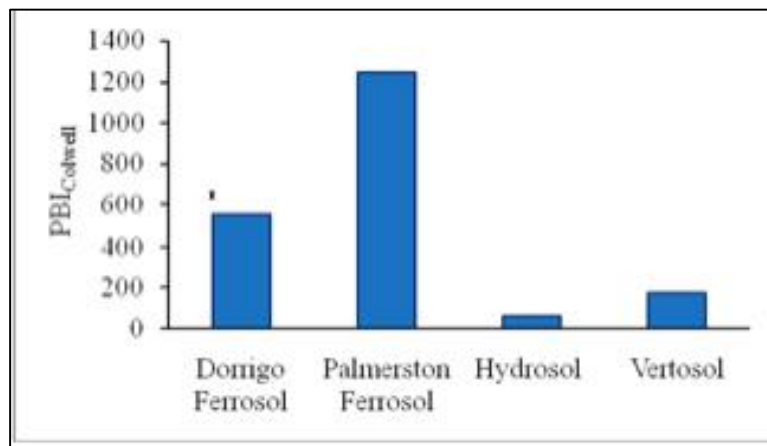


Figure 1. Differences of PBI of the Dorrigo Ferrosol, Palmerston Ferrosol, Hydrosol and Vertosol. The vertical bar is the least significant differences of means at $P = 0.05$

CONCLUSIONS

This study highlights the linkages between the chemical and mineralogical compositions of the VCS, and their surface charge characteristics and P sorption capacities. The results clearly show that charge characteristics and P sorption capacity are significantly different within the studied soils. Particularly, the Palmerston Ferrosol has developed net positive surface charge (a generic property) with its AEC exceeding its CEC. These differences are attributed to variations in the chemical and mineralogical compositions of these soils. In addition, organic matter has a great influence on the pH_0 of variable charge components, and thus on CEC.