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Mineralogical, chemical and charge properties of Geric Ferralsols from New Caledonia

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Abstract

The mineralogical, chemical and surface charge properties of Geric Ferralsols of New Caledonia were examined. These soils, which corresponded to two soil mantles formed either on ultramafic rocks or volcanic ejecta and ashes, were respectively dominated by iron and aluminium oxides. The electric charge characteristics were studied by measuring retention of Ca^{2+} and Cl^{-} at different pH values ranging from 3 to 7. The cation exchange capacity (CEC_T) increased with soil organic carbon and pH and varied from 0 to $35 \text{ cmol}_c \text{ kg}^{-1}$ soil. The anion exchange capacity (AEC) reached $4.25 \text{ cmol}_c \text{ kg}^{-1}$ soil in Bo horizons at pH 4. The magnitude of the CEC_T and AEC variations was modelled according to $\text{CEC}_T = 10^{a_1 \text{pH}} * 10^{B_1}$ and $\text{AEC} = -10^{a_2 \text{pH}} * 10^{B_2}$. Parameters a_1 and a_2 were low for samples with high organic carbon (from 0.10 to 0.19 and from

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–0.44 to –0.66, respectively) and could increase to 1.25 and –0.39, respectively, when organic carbon content decreased. The parameters a_1 and a_2 could be also useful to regroup soil types according to the nature of the properties that can be manipulated for their management. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Iron and aluminium oxides; Organic matter; pH-dependent charge; Ion adsorption; Cation exchange capacity; Anion exchange capacity

1. Introduction

Highly weathered Ferralsols occur extensively in New Caledonia (Latham et al., 1978). Two types of soil very rich in iron and aluminium oxides are present. The first type is derived from ultramafic rocks and represents a third of the surface of the main island (Grande Terre). The second one, derived from volcanic ejecta and ashes, covers 19% of the surface area of the Loyalty Islands.

These soils are generally deficient in most plant nutrients. In the Grande Terre, the lack of land and the increasing demand for food and vegetables lead to the use of these rather infertile soils. They had never been cultivated before the beginning of the 1980s, when vegetable and fruit started to be produced. In the Loyalty Islands, Ferralsols are the main cultivated soils because they are the deepest. The agricultural production was mainly traditional, with long fallow periods that maintained the soil fertility. However, the development of a cash-cropping sector since a few years is leading to a breakdown in the traditional strategies of soil fertility maintenance.

Appropriate management of these soils requires detailed information on their properties. Little is known about their mineralogical and physico-chemical characteristics. A few mineralogical studies (Tercinier, 1971; Schwertmann and Latham, 1986) indicates that iron and aluminium oxides and oxyhydroxides are their main constituents, while silicates are present in small amounts. A pH-dependent cation exchange capacity (CEC) and anion exchange capacity (AEC) result from the presence of Fe and Al oxides and organic matter. Variable charges in these soils should have a major incidence on the bioavailability and movement of nutrients as well as toxic metals (Ni, Cr...). Phosphorus is highly sorbed on the two types of soils (Dubus et al., 1998) and nitrate sorption also occurs on the soils of the Loyalty Islands (Duwig et al., 1999). The high levels of bioavailable Ni found in some soils of the Grande Terre (Becquer et al., 1995) can reach toxic levels for crops (L'Huillier and Edighoffer, 1996).

Changes in management practices can affect environmental factors, such as pH or organic matter content, and the sorption characteristics of the soils. The aims of the study were therefore: (i) to characterise the mineralogy and the chemistry of these soils, and (ii) to study the influence of organic matter, Fe and Al oxides, and pH on their charge characteristics.

2. Materials and methods

2.1. Study area and soils

Two sets of soil profiles corresponding to the two types of oxide-rich soils of New Caledonia (Fig. 1) were studied.

The first set, located in Ouénarou (E 166°44'–S 22°8') in the south of the main island, came from a highly weathered mantle derived from peridotite. Three different profiles under natural vegetation situated along a soil toposequence were selected (Table 1). They correspond to a piedmont soil (OUE 1), a colluvio-alluvial soil (OUE 3) and an alluvio-colluvial soil with temporary reducing conditions (OUE 4), respectively. OUE 1 was a very compact soil with a loamy sand texture and a poorly developed fine sub-angular polyhedral structure. Profiles OUE 3 and OUE 4 were constituted by colluvio-alluvial materials with variable texture occurring in successive horizons of irregular thickness. OUE 4 contained a lot of ferro-manganese coatings suggesting the existence of reducing conditions at the base of the toposequence. These soils were poorly structured except in the topsoil where roots and organic matter were quite abundant.

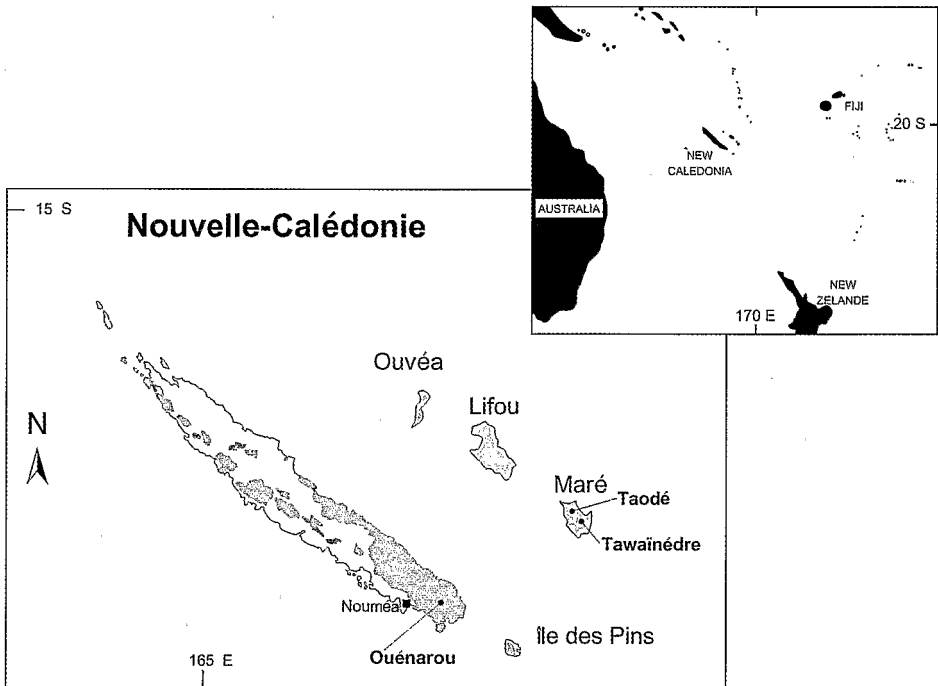


Fig. 1. Map of the two types of highly weathered Ferralsols in New Caledonia (in dark grey on peridotite and in light grey on uplifted coral atolls) and location of the study areas.

Table 1
Soil profile descriptions

Soil profile	Horizon	Depth (cm)	Color (moist)	Texture	Structure	Cohesion	Roots	Boundary
<i>OUE 1</i>								
OUE 1-1	A	0–5	10 R 3/3	LAS	sgs/fcr	1	1	s
OUE 1-2	ABo	5–20	2.5 YR 3/4	LAS	fsap/fap	3	3	s
OUE 1-3	Bo1	20–35	10 R 3/2	LS	fap	4	4	d
OUE 1-4	Bo2	35–65	10 R 3/2	LAS	fap	5	5	d
OUE 1-5	Bo3	65–100	10 R 3/4	LSa	fap	4	5	
<i>OUE 3</i>								
OUE 3-1	Ah	0–4	5 YR 3/4	La	fcr/fap	1	1	s
OUE 3-2	ABo	4–15	2.5 YR 4/4	La	fsap/fcr	2	1	s
OUE 3-3	Bo	15–30	2.5 YR 3/6	LSa	m	3	3	s
OUE 3-4	2Bo1	30–55	5 YR 3/2	Lsa	m	3	3	s
OUE 3-5	2Bo2	55–80	2.5 YR 4/6	Lsa	m	1	4	s
OUE 3-6	3Bo	80–100	2.5 YR 3/2	LSa	m	3	4	
<i>OUE 4</i>								
OUE 4-1	Ah	0–4	2.5 YR 3/4	La	fcr/fap	1	1	s
OUE 4-2	A	4–12	2.5 YR 4/6	A	fsap/fcr	2	1	s
OUE 4-3	2Bog	12–42	2.5 YR 3/6	Sa	sgs	3	3	s
OUE 4-4	3Bog	42–70	2.5 YR 4/6	S1	sgs	1	3	s
OUE 4-5	4Boc	70–90	10 YR 3/2	S	sgs	1	5	
<i>MAR 3</i>								
MAR 3-1	Ap	0–12	7.5 YR 3/2	L	fcr/sgs	1	1	s
MAR 3-2	Bo1	12–35	5 YR 3/3	L	mic	1	2	d
MAR 3-3	Bo2	35–70	5 YR 3/4	L	mic	3	3	s
	R							
<i>MAR 5</i>								
MAR 5-1	Ap	0–12	7.5 YR 3/4	L	fcr/sgs	1	1	s
MAR 5-2	Bo1	12–25	5 YR 3/4	L	mic	1	2	d
MAR 5-3	Bo2	25–40	5 YR 3/4	L	mic	3	4	d
MAR 5-4	Bo3	40–60	5 YR 3/4	L	mic	1	3	s
	R							

Horizon: according to FAO (1994).

Color: according to the Munsell color chart.

Texture: S (s) = sandy; L (l) = silty; A (a) = clayed.

Structure: fcr = fine crumb; fsap = fine subangular polyhedral; fap = fine angular polyhedral; m = massive; mic = microaggregated; sgs = single-grain structure.

Cohesion: 1 = very loose; 2 = loose; 3 = quite compact; 4 = compact; 5 = very compact.

Roots: 1 = abundant; 2 = quite abundant medium and fine; 3 = present; 4 = few; 5 = very few.

Boundary: d = diffuse; s = sharp.

The second set of profiles was located in the Loyalty Islands. These islands are uplifted coral atolls built upon an underlying volcanic structure. The soils derive probably from volcanic ejecta and ashes (Tercinier, 1971) deposited on

the coral rocks. The soil studied belonged to the deepest type, with depths ranging from 0.3 to 1 m. Two profiles located on the island of Maré, at Tawainèdre (E 168°4'–S 21°30') (MAR 3) and Taodé (E 167°55'–S 21°27') (MAR 5), were selected. The first site was covered by a regularly burnt bush fallow with 1–4 m shrubs; the second one was an older fallow with re-growing forest of 10–15 m. These profiles were located on the level surface of the former lagoon. They were characterised by little horizon differentiation (Table 1). The surface horizons showed a fine crumb to sub-angular polyhedral structure related to their high organic matter content, whereas the deepest ones were micro-aggregated. Root density decreased sharply with depth and with decreasing carbon content and increasing soil cohesion.

Two samples were selected and analysed in each profile. The first one corresponded to a surface or sub-surface horizon (A) generally rich in organic matter and the second one was a Bo horizon poorer in organic matter.

2.2. Soil analysis

The soil samples were dried at 40°C and sieved at 2 mm. Particle size was determined by wet sieving (2000–50 μm) and pipetting (< 50 μm) following treatment with 35% H_2O_2 and dispersion through overnight shaking with Na-resin (Bartoli et al., 1991). The pH was measured in water and in 1 M KCl suspensions using 1:2.5 (w/v) soil:solution ratio. Total organic carbon and nitrogen were analysed by dry combustion in a Carlo Erba 1108 chromatograph. Phosphate retention (P_{ret}) was determined according to Blakemore et al. (1987). Effective cation exchange capacity (ECEC), exchangeable bases (EB) and exchangeable acidity (EA) were assessed according to the methods described by Rouiller et al. (1994). Total elements were measured by atomic absorption spectrometry (AAS) (Varian AA300) after a nitro-perchloric acid attack.

Selective dissolutions of aluminium and iron compounds were carried out using two chemical reactants. The oxalate extraction was performed by shaking 2 g of soil in 80 ml of a 0.2 M ammonium oxalate buffered at pH 3 solution in the dark at 20°C for 4 h (McKeague and Day, 1966). The dithionite–citrate–bicarbonate (DCB) extraction is a modification of the Holmgren's (1967) method. Two sets of extractions were performed, the first one with only citrate–bicarbonate (CB), the second one with the addition of dithionite (CBD) (Jeanroy et al., 1991). Centrifuge tubes containing 75 mg of soil with (or without) 250 mg of dithionite and 25 ml of citrate–bicarbonate solution (CB) were placed in an end-over-end shaker at 25°C for 5 days. Then, the samples were centrifuged at $7300 \times g$ for 10 min and the supernatant analysed for Fe, Al and Si by ICP. The Fe, Al and Si extracted by oxalate were referred to as Fe_o , Al_o , and Si_o and those extracted by DCB as Fe_d , Al_d , and Si_d . The aluminium substitution ratio in iron oxides was calculated from the composition of the DCB minus CB extracts according to Jeanroy et al. (1991).

X-ray diffraction (XRD) analyses were performed (i) on total powder, (ii) on silt + sand and clay fractions after deferrification. The clay samples were also X-rayed after solvation with ethylene glycol or heating at 550°C.

The AEC and the CEC were determined according to the method described by Gillman and Sumpter (1986). The soil was first saturated with 0.1 M CaCl₂ and washed with 0.002 M CaCl₂ to remove the excess of salt. Then, 0.002 M CaCl₂ solutions with pH ranging from 3 to 7 were added to the soil in a 1:5 (w/v) soil:solution ratio and the suspension was gently shaken in an horizontal roller–shaker. After a week of shaking at 25°C, the pH was recorded and the suspension centrifuged at 2000 × *g*. The supernatant solution was retained for Ca²⁺, Al³⁺ and Cl[−] analysis and the tubes were weighed to estimate the volume of entrained solution. Ca²⁺, Al³⁺ and Cl[−] were extracted with a 1 M NH₄NO₃ solution and analysed after centrifugation. Ca²⁺ and Al³⁺ were measured by ICP and Cl[−] was determined by titrimetry. The basic exchange capacity (CEC_B) referred only to the amount of Ca²⁺ adsorbed, the total exchange capacity (CEC_T) to the sum of Ca²⁺ and Al³⁺ adsorbed and the anion exchange capacity (AEC) to Cl[−] adsorbed.

The relationship between ion adsorption and pH were fitted according to the models of Wada and Okamura (1980) and Okamura and Wada (1983):

$$\log \text{CEC}_T = a_1 \text{pH} + b_1 \log C + c_1$$

$$\log(-\text{AEC}) = a_2 \text{pH} + b_2 \log C + c_2$$

where pH is the pH of the soil suspension, *C* is the concentration of the electrolyte and *a*₁, *a*₂, *b*₁, *b*₂, *c*₁, *c*₂ are constants adjusted for each soil.

However, in our experiments, only one concentration (*C* = 0.002 mol l^{−1}) was used and the term of the model related to the concentration was integrated into a constant term *B*, where *B* = *b* log *C* + *c*. The equations became:

$$\log \text{CEC}_T = a_1 \text{pH} + B_1 \quad \text{or, } \text{CEC}_T = 10^{a_1 \text{pH}} * 10^{B_1} \quad (1)$$

$$\log(-\text{AEC}) = a_2 \text{pH} + B_2 \quad \text{or, } \text{AEC} = -10^{a_2 \text{pH}} * 10^{B_2} \quad (2)$$

3. Results and discussion

3.1. Chemical properties

The main chemical properties of the soils are shown in Table 2.

The soils from Ouénarou were acidic with the lowest pH in the topsoils. The ΔpH (pH_{KCl}–pH_{H₂O}) were close to zero or slightly positive in the upper horizons but they could be over one unit in the deep ones. Positive ΔpH indicates that positive charges prevail in these horizons (Parfitt, 1980). The organic carbon content decreased sharply with depth. The C/N ratios were close

Table 2
Main physical and chemical properties of the soils

Horizon	Depth of sampling (cm)	Particle size distribution				pH		Δ pH	Organic matter		P_{ret} (%)	EB				EA	ECEC
		CL (%)	FS (%)	CS (%)	S (%)	H ₂ O	KCl		C (g kg ⁻¹)	N (g kg ⁻¹)		Ca ²⁺ (cmol _c kg ⁻¹)	Mg ²⁺ (cmol _c kg ⁻¹)	K ⁺ (cmol _c kg ⁻¹)	Na ⁺ (cmol _c kg ⁻¹)		
<i>Ouéñarou</i>																	
OUE 1-1	0–5	52.7	27.3	6.9	13.0	4.6	5.1	0.47	36.2	1.62	54.7	0.5	0.4	0.1	0.1	0.05	1.7
OUE 1-4	38–57	18.9	35.8	27.4	17.9	4.8	5.8	1.06	2.4	0.16	93.8	0.1	0.1	0.0	0.0	0.04	0.2
OUE 3-1	0–4	40.0	45.6	9.0	5.4	5.1	5.1	-0.01	76.3	2.37	50.5	9.9	2.4	0.5	0.2	0.07	14.4
OUE 3-4	40–51	42.2	40.8	12.9	4.1	5.0	6.1	1.10	11.9	0.71	69.1	0.2	0.6	0.1	0.0	0.03	1.1
OUE 4-2	4–9	52.9	34.6	6.5	5.9	4.6	4.7	0.10	25.4	1.35	71.0	0.2	0.5	0.1	0.0	0.03	1.4
OUE 4-3	26–39	39.4	36.9	16.5	7.2	5.0	6.2	1.24	9.6	0.51	78.1	0.1	0.2	0.0	0.0	0.05	0.5
<i>Maré</i>																	
MAR 3-1	0–12	62.4	26.5	8.8	2.4	6.8	6.3	-0.43	72.3	6.84	82.2	17.8	10.5	0.3	0.2	0.05	28.8
MAR 3-3	35–60	85.6	8.8	5.1	0.5	5.8	6.0	0.17	10.1	0.90	93.8	0.7	0.8	0.0	0.1	0.02	1.7
MAR 5-1	0–12	60.9	32.4	4.8	1.9	6.3	5.9	-0.37	117.3	8.75	75.2	23.6	11.5	0.4	0.3	0.1	36.0
MAR 5-4	40–50	83.1	12.3	3.8	0.9	5.4	5.6	0.27	9.8	0.86	91.6	1.0	1.2	0.0	0.1	0.02	2.4

CL = clay (< 2 μm); FS = fine silt (2–20 μm); CS = coarse silt (20–50 μm); S = sand (50–2000 μm)
 P_{ret} = phosphate retention; EB = exchangeable bases; EA = exchangeable acidity ($Al^{3+} + H^+$); ECEC = effective cation exchange capacity measured in 0.5 M NH_4Cl

	Mineral fine earth composition														K_r	K_i	
	LOI	residual	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	MnO ₂ (g kg ⁻¹)	NiO	Cr ₂ O ₃	CoO	CaO	MgO	K ₂ O	Na ₂ O			TRB (cmol _c kg ⁻¹)
<i>Ouéñarou</i>																	
OUE 1-1	174	37	22	107	623	2	6	8	31	1	0	4	0	0	18.0	0.05	0.20
OUE 1-4	145	31	17	103	648	3	9	9	30	1	0	3	0	0	17.3	0.04	0.16
OUE 3-1	166	85	91	70	539	1	8	12	27	1	1	8	0	0	41.6	0.26	1.25
OUE 3-4	138	144	75	72	521	2	7	11	28	1	0	8	0	0	41.1	0.22	0.99
OUE 4-2	197	64	73	63	563	1	7	12	20	1	0	4	0	0	19.6	0.21	1.12
OUE 4-3	146	87	42	95	579	2	9	10	32	1	0	6	0	0	31.1	0.11	0.43
<i>Maré</i>																	
MAR 3-1	329	19	8	376	210	11	13	n.d.	n.d.	n.d.	1.2	0.6	0	0	75.7	0.02	0.02
MAR 3-3	248	6	15	440	251	8	8	n.d.	n.d.	n.d.	0.2	0.3	0	0	19.2	0.02	0.03
MAR 5-1	391	6	10	321	186	11	8	n.d.	n.d.	n.d.	1.8	0.5	0	0	92.1	0.02	0.03
MAR 5-4	252	9	13	427	241	13	6	n.d.	n.d.	n.d.	0.6	0.3	0	0	35.9	0.02	0.03

n.d. = not determined.
 LOI = loss on ignition.
 TRB = total reserve in bases; $K_r = SiO_2/Al_2O_3 + Fe_2O_3$; $K_i = SiO_2/Al_2O_3$.

to 20, indicating a low degree of N incorporation in the humic components. The ECEC were very low except in the upper horizon of OUE 3.

The soils from Maré were slightly acid in the topsoil with a decrease of pH with depth. The ΔpH were negative in the surface horizons but were over 0.1 in the deeper ones. The organic matter was well humified with a C/N ratio close to 10. Carbon contents reached 12% in the upper horizons and decreased sharply with depth. These high amount of organic matter in surface horizons could be attributed to the strong binding of aluminium and iron compounds by organic substances and to the low mobility of the humic acid or humate complexes at soil pH (Schnitzer, 1986). The phosphate retentions (P_{ret}) exceeded 75% and 90% in the A and Bo horizons, respectively. In these soils, the CEC_{T} is highly correlated to organic carbon ($r^2 = 0.96$) and exchangeable bases are dominated by calcium and magnesium.

3.2. Mineralogy

The oxidic nature of these soils was evident from the total elements analysis of the fine earth (Table 2), from the extraction by DCB and from the XRD results (Table 3).

In the samples from Ouénarou, total Fe_2O_3 content was always higher than 50% of the mineral fine earth composition and could reach 65% in OUE 1 (Table 2). The mineralogy was dominated by goethite, whereas hematite and maybe magnetite (which was not distinguishable from chromite with XRD as there are both spinels) were present at lower levels (Table 3). The dark red colour of some horizons (Table 1) was rather unexpected as hematite content was low. The amounts of Fe_0 and Al_0 were very low (Table 3) indicating that Fe and Al oxides were mainly crystalline. Generally, more than 95% of the total iron content of the samples were dissolved by the DCB extraction (Table 3). The Al-substitution ratios of iron oxides varied from 0.1 to 0.17 mol mol⁻¹ (Table 3). In our study, we used a 5-day DCB extraction as the dissolution rates were low (results not shown). Jeanroy et al. (1991) explained that the low DCB solubility of different iron oxide-rich tropical soils is related to the high levels of Al substitution. Moreover, chromium, which was also present in the Fe-oxides in these soils (result not shown), reduces their dissolution rate much more (Cornell and Schwertmann, 1996).

The amounts of silica were very low. Total SiO_2 contents were close to 2% and 4–9% in the piedmont (OUE 1) and alluvio-colluvial soils (OUE 3 and OUE 4), respectively. The XRD analysis, after deferification, showed little differences between samples. The main silicate mineral was talc and traces of quartz and chlorite (OUE 3 and OUE 4) or mica (OUE 1) were also detected (Table 3). The extent of the weathering of the soils can be estimated by the K_r and K_i ratios [$K_r = \text{SiO}_2 / (\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3)$; $K_i = \text{SiO}_2 / \text{Al}_2\text{O}_3$] and by the total reserve in bases (TRB) (Table 2). These parameters showed that the

Table 3
Selective extractions of Al, Fe and Si and mineralogy of the soil samples

	Oxalate extraction			DCB extraction			Fe _o * 10 ³ / Fe _d	Fe _d / Fe _{tot}	Al substitution (mol mol ⁻¹)	Mineralogy
	Al _o (g kg ⁻¹)	Fe _o (g kg ⁻¹)	Si _o (g kg ⁻¹)	Al _d (g kg ⁻¹)	Fe _d (g kg ⁻¹)	Si _d (g kg ⁻¹)				
<i>Ouénaou</i>										
OUE 1-1	0.97	2.11	0.03	43	420	4.1	5.0	0.96	0.171	Go, He, Ta, Sp, Q
OUE 1-4	1.87	1.57	0.03	47	447	4.0	3.5	0.99	0.179	Go, He, Ta, Sp, Q, Mi
OUE 3-1	1.44	3.08	0.22	20	327	6.4	9.4	0.87	0.105	Go, He, Ta, Sp, Ch, Q
OUE 3-4	1.13	1.9	0.27	26	347	6.1	5.5	0.95	0.131	Go, He, Ta, Sp, Ch, Q
OUE 4-2	1.03	7.31	0.24	32	427	6.3	17.1	1.08	0.132	Go, He, Ta, Sp, Ch, Q
OUE 4-3	1.35	2.97	0.20	37	393	5.4	7.6	0.97	0.160	Go, He, Ta, Sp, Ch, Q
<i>Maré</i>										
MAR 3-1	11.34	4.41	0.11	45	138	0.0	32.0	0.94	0.371	Gb, Bo, Go, Q, Ma, Ch, Fe
MAR 3-3	4.59	4.07	0.08	46	162	0.0	25.1	0.92	0.359	Gb, Go, Bo, Q, Ma, Fe
MAR 5-1	12.43	3.76	0.04	46	118	0.0	31.9	0.91	0.401	Gb, Go, Bo, Q, Ma, Ch, Fe
MAR 5-4	7.21	3.15	0.02	50	162	0.0	19.4	0.96	0.375	Gb, Go, Bo, Q, Ma, Ka, Fe

Bo, boehmite; Ch, chlorite; Fe, feldspar; Gb, gibbsite; Go, goethite; He, hematite; Ka, kaolinite; Ma, magnetite; Mi, mica; Q, quartz; Sp, spinelle; Ta, talc.

piedmont soil (OUE 1) is the most weathered one. In the colluvio-alluvial soils (OUE 3 and OUE 4) talc was likely more abundant and the TRB, which was close to 30–40 $\text{cmol}_c \text{ kg}^{-1}$ in Bo horizons, was mainly due to magnesium. However, Si_d varied from 4 to 6 g kg^{-1} , whereas Si extracted with CB was close to zero (except for OUE 3-1). Si_d represented 40–50% of the total Si content for OUE 1 and 15–30% for OUE 3 and OUE 4. Therefore, a substantial part of Si seemed to be associated with iron oxides.

In the soils of the Loyalty Islands, the crystalline fraction is mostly present as gibbsite and boehmite for aluminium oxides and goethite for iron oxides. These results are in agreement with those of Tercinier (1971). A few primary silicates such as quartz and feldspar remained in the soil. As for Ouénarou soils, a 5-day extraction with DCB was necessary to solubilize up to 90% of total Fe (Table 3). The amount of Al_d was 45–50 g kg^{-1} , corresponding to Al-substitution ratios of the iron oxide fractions of about 0.35 mol mol^{-1} . This high Al-substitution in goethite, which is generally observed in highly desilicified, gibbsitic soils (Cornell and Schwertmann, 1996), explained the slow dissolution rates of the iron oxides. The intense weathering of this soil led to total SiO_2 contents close to 1% and thus to very low K_r and K_i ratios (Table 2). The TRB in the deepest horizons is relatively high probably due to carbonate particles contamination from the underlying coral rocks. Chemical extractions of Si showed that $\text{Si}_o > \text{Si}_d$. This result might indicate the presence of allophanic products, but the levels of Si_o were too low to account for the presence of substantial amount of allophane.

3.3. Surface charge properties

The ion adsorption method has been used extensively to determine the negative and positive surface charges of soils with pH-dependent charges (Wada and Okamura, 1980; Okamura and Wada, 1983; Wada and Wada, 1985; Gillman and Sumpster, 1986; Parfitt, 1992; Van Ranst et al., 1998).

The CEC_T varied between 0.3–36 and 0–3.8 $\text{cmol}_c \text{ kg}^{-1}$ in A and Bo horizons, respectively, in the range of pH 4–7 (Fig. 2). It was mainly related to the organic matter content, as the mineralogical composition of A and Bo horizons were similar. The dissociation of carboxyl groups of the organic matter is strongly pH-dependent and increases progressively with pH (Tate and Theng, 1980). However, some differences exist between the two types of soils. For similar levels of organic carbon, the CEC_T was higher in the soil from Maré than in those from Ouénarou. The CEC_T per unit of organic carbon calculated at pH 7 from A horizons was 281 $\text{cmol}_c \text{ kg}^{-1} \text{ C}$ in Ouénarou soils, whereas in Maréan soils it was 360 $\text{cmol}_c \text{ kg}^{-1} \text{ C}$. This could be related to differences of organic matter qualities as expected from their different C/N ratios. The oxidic compounds could also have consequences on the CEC_T . OUE 1–4 was very poor in organic carbon (2 g kg^{-1}) and exhibited a particular shape of its

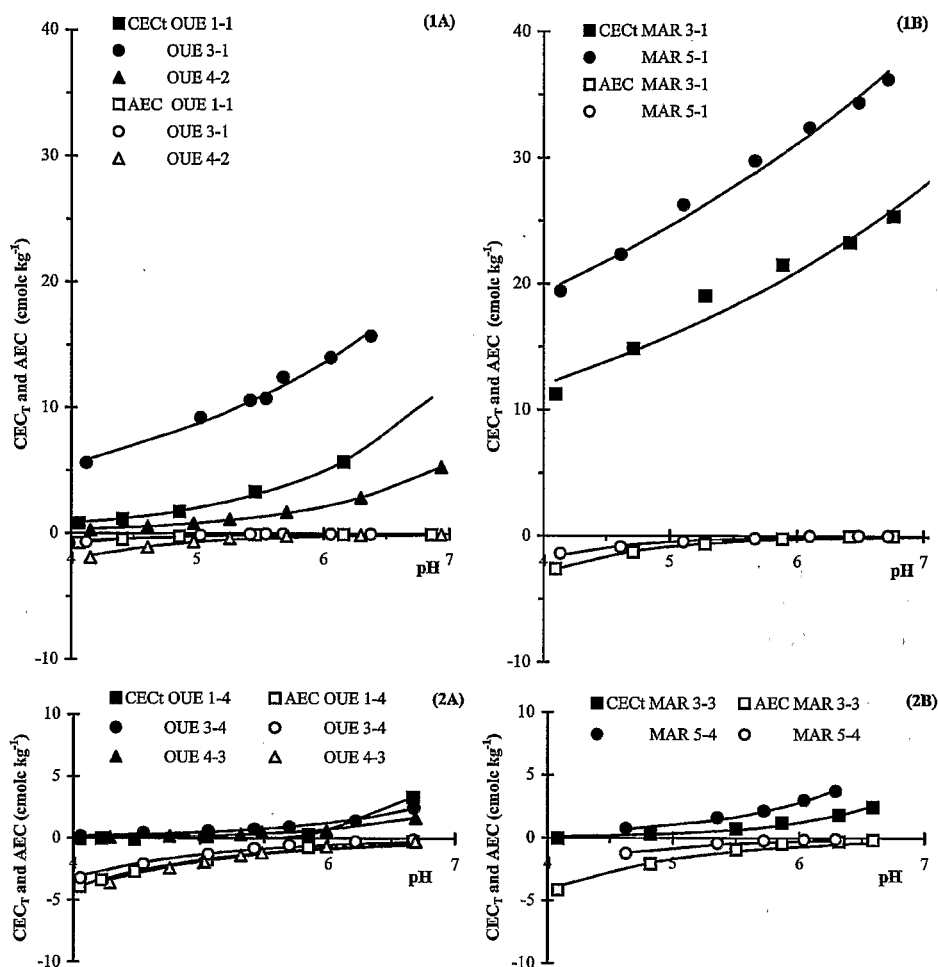


Fig. 2. Variation of CEC_T and AEC with pH for the surface (1A, 1B) and deep (2A, 2B) horizons of Ouénarou (A) and Maré (B). Measurements and modelling.

CEC_T-pH curve (Fig. 2A). The CEC_T was nil below pH 5.5 and increased sharply above. An increase of pH causes a decrease of the electric potentials of oxides and the increase of the dissociation of bivalent cations (Barrow, 1987). These two phenomena are favourable to cation sorption on the surface of the oxides and result in a sudden increase in adsorption with increasing pH (Barrow, 1987).

The CEC_B was close to CEC_T except at pH below 4. Aluminium oxides were solubilised at lower pH during the equilibrium phase with 0.002 M CaCl₂. During the subsequent extraction with 1 M NH₄NO₃, leading to an increase of 1–2 pH units, the Al³⁺ previously solubilised was either sorbed on negative surface charge, if present, or precipitated as Al-oxides leading to some artefacts. Therefore, the CEC_T below pH 4 were not taken into account.

The AEC was lower in A than in Bo horizons (Fig. 2) with values ranging between 0.63–2.99 and 2.38–4.25 $\text{cmol}_c \text{kg}^{-1}$ at pH 4, respectively. The differences between samples could be related to the types of oxides, to the particle size distribution as well as to the organic matter content, the latter being probably the most important. A close association of Fe and Al compounds with organic anions at the surface of the oxides could reduce the sites available for Cl^- sorption and therefore decrease the AEC. The values found here were higher than those observed in other studies on Ferralsols (Okamura and Wada, 1983; Gillman and Sumpter, 1986; Parfitt, 1992; Van Ranst et al., 1998) and are of the same magnitude as those generally found on Andosols (Okamura and Wada, 1983; Parfitt, 1992). In those studies, the soils exhibit permanent negative charges and the negatively charged surfaces repel anions from the double layer (Gillman and Sumpter, 1986). Therefore, AEC does not represent the total amount of positive surface charges. In our conditions, the permanent negative charges were practically nil and the AEC measured was equal to the total positive surface charge of the soil.

CEC_T and AEC were modelled according to Eqs. (1) and (2), respectively, and the values of adjustable parameters a_1 , B_1 , a_2 , B_2 and the coefficient of determination (r^2) are given in Table 4. The agreement between the calculated and measured values was good ($r^2 = 0.971$ to 1.000). The values of a_1 and a_2 describe the effect of pH on the variation of charge of the soils. The values of a_1 were low in organic matter-rich samples; they increased when carbon contents decrease. The a_1 values (0.10–0.19) obtained for the samples with C > 5% were of the same magnitude as those reported by Wada and Okamura (1980), Okamura and Wada (1983) and Wada and Wada (1985). They reported values in

Table 4
Coefficients a_1 , a_2 , B_1 , B_2 and coefficients of determination r^2 for regression Eqs. (1) and (2)

	Negative charge			Positive charge		
	a_1	B_1	r^2	a_2	B_2	r^2
<i>Ouéarou</i>						
OUE 1-1	0.391	-1.647	0.996	-0.597	2.312	0.996
OUE 1-4	1.246	-7.786	0.999	-0.389	2.177	0.996
OUE 3-1	0.189	-0.004	0.987	-0.721	2.814	0.996
OUE 3-4	0.421	-2.430	0.989	-0.440	2.304	0.993
OUE 4-2	0.420	-2.189	1.000	-0.571	2.662	0.998
OUE 4-3	0.508	-3.182	0.990	-0.412	2.331	0.995
<i>Maré</i>						
MAR 3-1	0.116	0.631	0.971	-0.547	2.665	0.996
MAR 3-3	0.502	-2.909	0.988	-0.473	2.560	0.993
MAR 5-1	0.100	0.896	0.987	-0.553	2.447	0.983
MAR 5-4	0.409	-1.997	0.988	-0.655	3.131	1.000

the range of 0.11–0.34 for Andosols and 0.04–0.23 for Alfisols, Oxisols and Ultisols. The different kinds of functional groups of the organic matter and/or the different mineral compounds (clay minerals, oxides, allophane...) present in those soils led to a slight increase in CEC_T with pH. For the samples in the deepest horizon, the narrow range of points of zero charge of Fe and Al oxides, ranging from 7 to 9.5, led to a sharp increase of the CEC_T with pH. In the same way, the absence of repulsion of anions by permanent negative charge at low pH as described above led to a sharp increase of the AEC. The a_2 values ranged from -0.55 to -0.72 and from -0.39 to -0.66 in A and Bo horizons, respectively. These values were lower than those reported by Okamura and Wada (1983), which are between -0.05 and -0.36 .

3.4. Soil classification

The two types of soils were classified according to FAO (1998). They resulted from an intense weathering and were highly desilicified. Their mineralogy was dominated by iron and aluminium oxides. Different field observations and chemical characteristics, such as their loamy to loamy-sandy texture, their strong microaggregation, and their low ECEC led to classify these soils as Ferralsols. However, the TRB was sometimes over $25 \text{ cmol}_c \text{ kg}^{-1}$ in the Bo horizons. For the Loyalty Islands, this could be related to traces of calcium carbonate originating from the underlying coral rocks. At Ouénarou, the colluvio-alluvial soils (OUE 3 and OUE 4) have been rejuvenated by the input of traces of Mg-rich phyllosilicates (talc and chlorite). Accordingly, the TRB of their Bo horizons are somewhat larger than $25 \text{ cmol}_c \text{ kg}^{-1}$ and are similar in this respect to those found in other ferralsols deriving from Mg-bearing parent materials (Herbillon, 1986).

According to their ΔpH higher than 0.1 and to their low ECEC in the Bo horizons, the soils were classified as Geric Ferralsols.

The soils from Maré indicated some Andic properties such as a bulk density less than 0.9 Mg m^{-3} (result not shown) and a phosphate retention of more than 70% in A and Bo horizons. However, the $Al_o + 0.5Fe_o$ values close to 1.5% in the A horizons or 1% in the Bo horizons (Table 3) were too low to use the Andic qualifier. The Al oxide content above 25% of the fine earth fraction led to the use of the Gibbsic qualifier. The Humic qualifier could also be used as there was an average carbon content of 2.6–3.8% in the fine earth fraction on the whole profile. Therefore, the soil of Maré can be classified as a Geri-Gibbsic Ferralsol (Humic).

For Ouénarou soils, none of the qualifiers of the Ferralsols could be used to describe these soils except the Geric one. For OUE 4, reducing conditions could occur leading to some iron and manganese oxide coatings. However, the gleyic colour pattern was too weak to use this qualifier. Therefore, these soils were simply classified as Geric Ferralsol.

These soils were previously classified by Latham (1980–1981) according to their dominant oxide types: the “ferritiques” soils, rich in Fe-oxides, developed on the ultramafic rocks; the “allitiques” soils, rich in Al and Fe-oxides, on the coral rocks. According to FAO (1998), the Gibb'sic qualifier can be used for the soils from the Loyalty Islands. However, the Ferric qualifier cannot be used for the soils on ultramafic rocks as segregation of iron has not taken place in these soils. In order to take into account the high level of iron oxide and in agreement with the regional classification system in use in New Caledonia, a Ferritic qualifier could be suggested for Ferralsols with more than 25% of iron oxide in the fine earth fraction. In this way, the two types of Ferralsols could be easily separated in the FAO classification scheme on the basis of their differences in oxide composition.

3.5. *Agronomic and environmental consequences*

Geric Ferralsols with high levels of Fe and Al oxides are known to adsorb anions. On the soil of New Caledonia, a very high fixation of phosphorus occurs (Dubus et al., 1998) and leads to yield limitations for crops (L'Huillier et al., 1998). The adsorption of non-specifically adsorbed anions such as nitrate is also observed on the soil of the Loyalty Islands (Duwig et al., 1999). The reduction of the movement of nitrate through the soil limits the contamination of underlying groundwater (Duwig et al., 2000).

The two types of soils varied mainly according to their surface horizons. In the soil from Maré, the organic matter content was larger and better humified. CEC_T and AEC varied to a lesser extent in this soil as shown by the lower values of parameters a_1 and a_2 . The CEC_T that was mainly related to the organic matter was greater and saturated by Ca and Mg owing to the underlying coral rocks. In the soils from Ouénarou, exchangeable trace metals (Ni, Mn...), which are often pointed out to explain the infertility of soils derived from ultramafic rocks (Proctor and Woodell, 1975), are also present (Becquer et al., 1995). In both soil types, exchangeable potassium was very low. Thus, the fertility of Maré Ferralsol is certainly higher than that of Ouénarou Ferralsol.

The CEC_T and AEC act on the retention of major nutrient cations or anions and on the availability of toxic metals like Ni, Cr, Mn and Co. Both CEC and AEC are affected by factors such as the pH, the soil solution concentration and the nature of the surface charge of the different compounds of the soils. As the development of negatively charged sites will enhance cation retention on the one hand and anion leaching on the other (and the opposite for positively charged surfaces), management strategies (inputs of fertilizers, organic matter or lime...) could have major agronomic and environmental consequences. The shapes of the curves giving the surface charge variations with pH, or the parameters a_1 and a_2 describing these shapes, could be useful tools to separate different soil types into management groups.

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