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Biogeochemistry of Iron, Aluminium and Silicon in Humid Tropical Mountainous Soils (Bambouto Mountain, West Cameroon)

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Abstract: Humid tropical mountainous soils of the Bambouto volcanic mountain (West Cameroon) have been studied mainly from a chemical view point. The aim of the study was firstly to study the behaviour of iron, aluminium and silicon during pedogenesis, and to determine the forms of the three main elements. Global balance of iron is negative; it is the result of slight illuviation at the base of the profile, and moderate eluviation in the upper horizons. Selective extractions show that iron is mainly in the 'resistant' form, more moderately in the crystallized forms, while the amorphous forms are negligible, with a quasi-absence of organic amorphous forms. Silicon is highly evacuated in all horizons. Aluminium, characterized by high accumulation at the base of the profile and moderate evacuation in the upper part, presents an excess global balance. Otherwise, contrary to iron, organic amorphous forms of aluminium are well represented in these soils, which the occurrence of aluminium permits to assimilate to Aluandosols. Humid tropical mountainous soils show pedological evolution mainly dominated by the behaviour of silicon and aluminium, with iron appearing to have a negligible role. However, contrary to the temperate soils, in which bisiallisation is the predominant process, in mountainous soils, characterized by high evacuation of silica concomitantly to notable accumulations of aluminium, allitisation predominates. This is associated with moderate andosolisation, due to the presence of a volcanic parent rock.

Keywords: Humid tropical mountainous soils, Cameroon, Bambouto Mountain, biogeochemistry, silicon, aluminium, iron, pedoclimatic parameter.

1. INTRODUCTION

Because of their specific environmental conditions, mountainous massifs constitute particular intertropical ecosystems. Generally domains of active volcanic activities, the main geological formations are represented by volcanic rocks. This is the case in the Andes cordillera in South America [1], in New Hebrides in the Pacific Ocean [2, 3] and Kilimandjaro Mountain [4], Cameroon Mountain [5], Manengouba Mountain [6] and Bambouto Mountain [6-8] in Africa. Due to their high altitude and because of the geothermal gradient effect [9], vegetation and the prevalent climate are generally characteristic of temperate zones [10, 11]. The soils which are developed in these mountainous volcanic landscapes are essentially andosolic [12-17].

Many studies have investigated the andosolic soils of tropical mountainous massifs, particularly based on their typology and cartography [14, 16], mineralogy, geochemistry and biogeochemistry [12, 14, 15, 17, 18]. They are thus relatively well known now to consist of three major elements, silicon, aluminium and iron [14, 17]. They are also constituted of mixtures of crystalline minerals such as gibbsite, kaolinite, hematite, goethite, and of paracrystalline to amorphous minerals, such as halloysite, allophane, ferrihydrite and opale [14, 17]. However, the pedological behaviour of the three main constitutive elements (Si, Al and Fe) remains relatively unknown, as well as the various forms (free, combined, amorphous or crystallized) in which they are all along the profiles.

The aim of this study is to determine, the behaviour of each of the three major elements (Si, Al and Fe) and to identify and quantify the main forms in which those three elements exist in the horizons of these mountainous soils. Moreover, because of their influence on the behaviour and on the forms of those elements in soils, pedoclimatic parameters (pH and Eh) will also be characterized.

2. ENVIRONMENTAL SETTING

The study is located in the upper zone of Bambouto Mountain, > 2000 m altitude, in Western Cameroon (Fig. 1). The climate, which is pseudotropical with temperate characteristics due to altitude [11], is fresh and humid, characterized by frequent mists and fogs which impede visibility. Temperatures vary from 10-12°C and mean annual rainfall is 2507 mm. Relief is uneven and natural vegetation is a lawn consisting of *Sporobolus* prairies typical of temperate environments. The rock is a Miocene alkaline trachyte [6], which consists mainly of sanidine. In this study zone, soils are mainly of andosolic nature [16].

3. MATERIALS AND METHODS

3.1. Materials

The studied site is an asymmetrical hill (10°04'16"-10°05'49"E; 5°36'43"-5°38'31"N) with more or less spread summit and steep slopes of unequal lengths. A soil profile located at the summit part of the site has been studied; it is ~ 2 m thick, with three main horizons, from bottom to top (Fig. 2):

75-200 cm: saprolitic horizon constituted by yellow brown (10YR6/8) and whitish grey (7.5YR7/0) domains, porous, loamy and massive, with the

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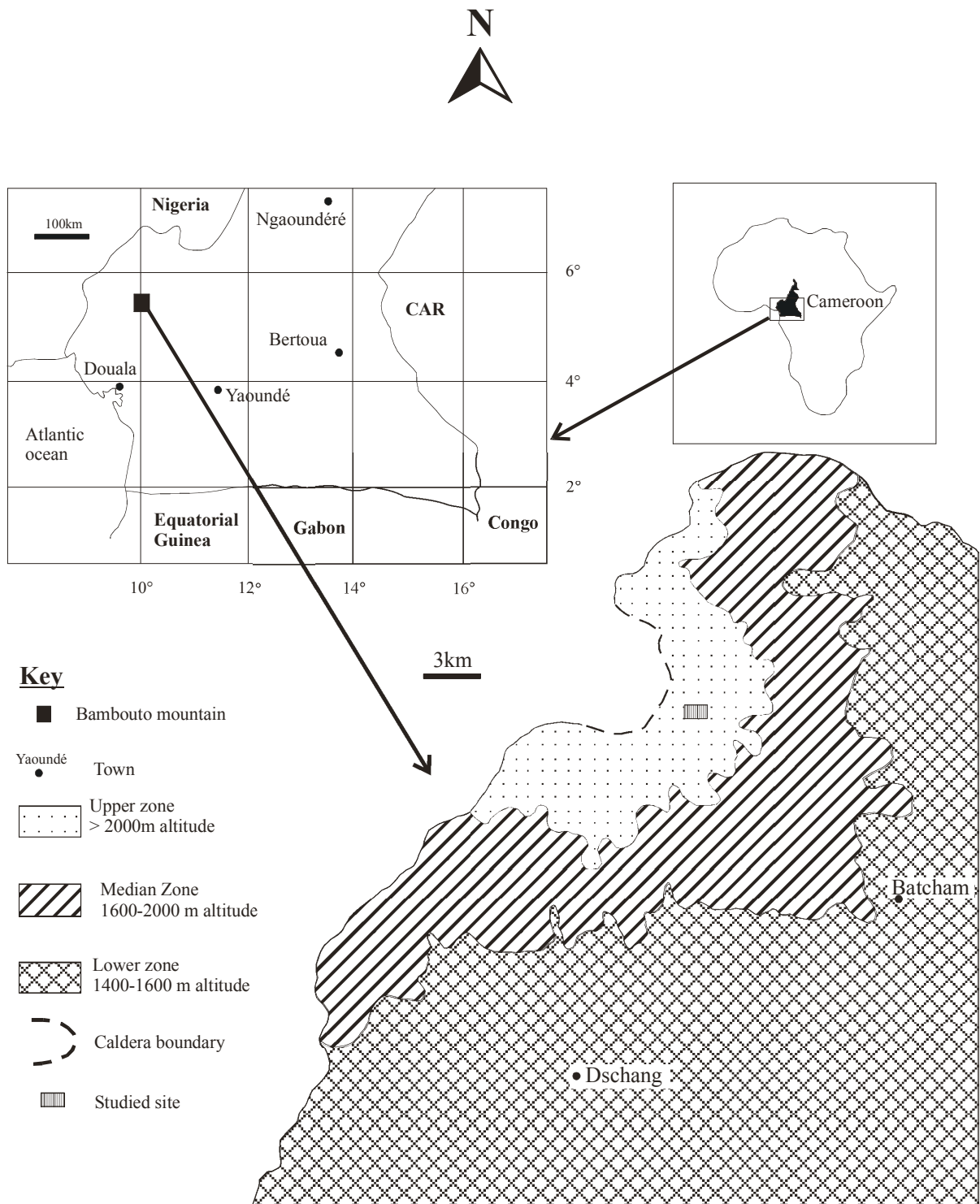


Fig. (1). Location of the studied site in the Bambouto mountain (Western Cameroon).

saccharoidal aspect of the parent rock still preserved. In addition, many blocks of trachyte with rough surfaces are observed in this horizon. Gibbsite is the predominant mineral, associated with allophanes, halloysite, quartz and magnetite, plus goethite and rutile in the yellow brown domains, or small amounts of ferrihydrite, sanidine and ilmenite in the whitish grey ones (Table 1). Geochemically,

the main constituents are Al (41.10-39.10% Al_2O_3), Si (23.50-22.70% SiO_2) and Fe (8.94-6.63% Fe_2O_3) (Table 2). Bases are almost absent. Small amounts of Ti (0.44-0.73 % TiO_2), Mn (0.34-0.14% MnO) and P (0.25-0.29% P_2O_5) are also detected (Table 2);

45-75 cm: yellowish red horizon (5YR4/4) with a clayey texture and fine polyhedral structure. Mineralogically, the horizon differs from the

previous one essentially by the appearance of hematite (Table 1). Geochemically, Al remains the most represented element as at the base of the profile (34.00% Al_2O_3), followed by Si (23.80% SiO_2) and Fe (8.75% Fe_2O_3) (Table 2). The horizon has in addition small quantities of Ti (1.08% TiO_2) and K (0.60% K_2O), associated to more modest quantities of P (0.32% P_2O_5), Mn (0.30% MnO), Mg (0.29% MgO) and Na (0.20% Na_2O); Ca is almost absent (0.08% CaO) (Table 2);

0-45 cm: humiferous horizon, black (2.5YR2.5/0) and porous, with loamy texture and blocky structure. Mineralogical composition remains quite unchanged with gibbsite and allophanes, associated with small amounts of halloysite, ferrihydrite, goethite, hematite, rutile, magnetite and quartz (Table 1). Geochemically, Si and Al are the most important elements (21.50% SiO_2 and 20.30% Al_2O_3), followed by Fe (7.05% Fe_2O_3) (Table 2). In addition to these three main elements, small amounts of Ti (0.97% TiO_2), K (0.48% K_2O), P (0.35% P_2O_5), Mg (0.30% MgO), Ca (0.23% CaO) and Na (0.15% Na_2O) were detected (Table 2).

Finally, the studied soils are characterised by a small thickness ~2 m, a thick humiferous superficial horizon, and a mixture of crystallized, paracrystalline and amorphous minerals, mainly gibbsite, halloysite and allophanes, which are conveyed geochemically by the presence of Al, Si and Fe.

3.2. Methods

The behaviour of Fe, Al, Si, throughout the profile has been approached by calculating elements mass balances

during pedogenesis. These mass balances have been carried out following the calculated ‘mass balance method’ [19-21] by considering titanium as an invariant element [22-24]. It is based on the residual enrichment in closed systems and supergene enrichment in open systems, which previously need the determination of horizon deformation rates. Horizon deformation rate (ϵ), element mobilization rate (τ) and total mass of mobilized elements (m) in each horizon are calculated according to the following formulae:

$$\epsilon_a = \frac{C_{i,p} \cdot d_p}{C_{i,a} \cdot d_a} - 1; \tau_{j,a} = \frac{d_a}{d_p} \frac{C_{j,a}}{C_{j,p}} (\epsilon_a + 1) - 1$$

$$m_{j,a} = \left(\frac{C_{j,p}}{100} d_p \cdot V_p \right) \tau_{j,a} \quad \text{in g/cm}^3; v_p = 1 \text{ cm}^3 [19]$$

In these formulae, $C_{i,p}$ and $C_{i,a}$ are the concentrations of an invariant element i (here, Ti) respectively in the parent rock p and the horizon a ; $C_{j,p}$ and $C_{j,a}$ are concentrations of any common element j , respectively, in the parent rock p and the horizon a ; d_p and d_a are, respectively, the bulk density of the parent rock p and the horizon a ; V_p is the parent rock volume which corresponds to 1 cm^3 [19].

The identification and the quantification of Fe forms have been achieved through selective extractions by citrate-bicarbonate with or without dithionite (CBD or CB) and by oxalic acid (Tamm, 1922 in Temgoua, 2001 [24]). CBD, oxalic acid and CB reagents, respectively, extract total free Fe forms (Fe_{CBD}), amorphous forms (Fe_{Ox}) and organic amorphous forms (Fe_{CB}). Non-extractable Fe forms ($\text{Fe}_{\text{total}} - \text{Fe}_{\text{CBD}}$), commonly attributed to iron included into silicate crystalline structure, will be considered here as ‘resistant’ iron forms according to Gaviria (1993) [25]. The fifth Fe form that can be identified is the well crystallized one; it is

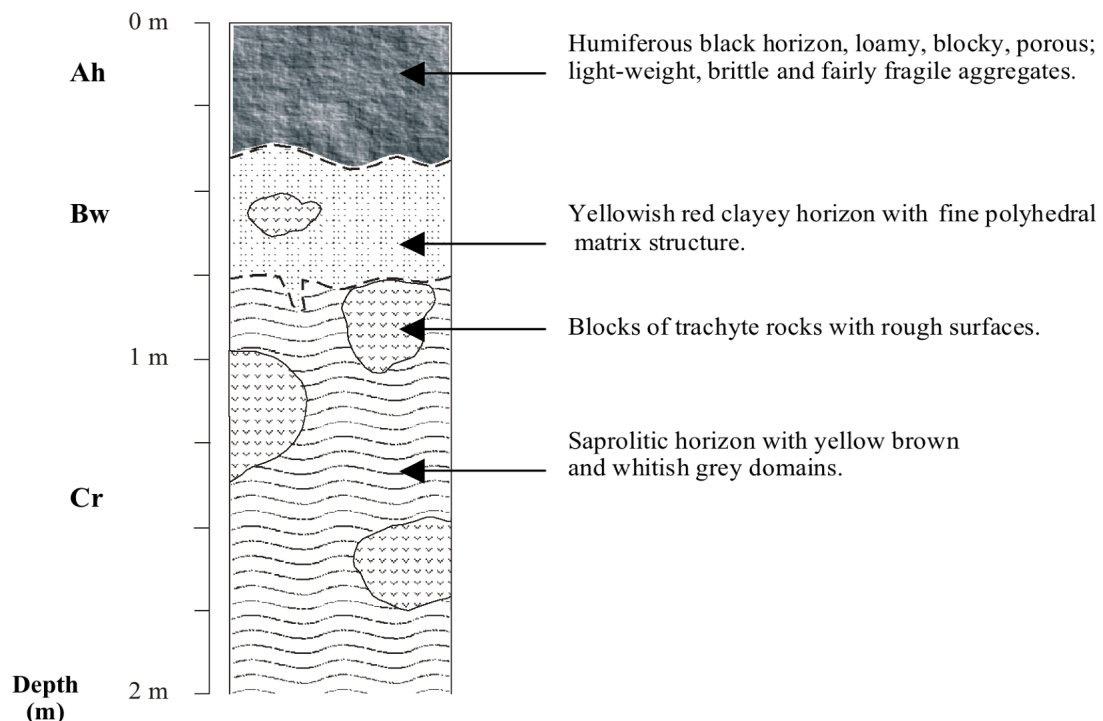


Fig. (2). Macroscopic organization of the studied Andosolic soil profile.

Table 1. Mineralogical Composition of Soils

Horizons		Minerals	Sa	Ma	Ha	All	Gi	Goe	He	Feh	Ru	Ilm	Q
Black humiferous horizon (0 – 0.45 m)		Ah	/	+	+	++	+++	+	+	+	+	/	+
Yellowish red clayey and loose horizon (0.45 – 0.75 m)		Bw	/	+	+	++	++++	+	+	/	+	/	+
Saprolitic horizon (0.75 – 2 m)	Cr	Yellow brown domain	/	+	++	++	++++	++	/	/	+	/	+
		Whitish grey domain	+	+	++	+	++++	/	/	+	/	+	+

/: non identified; +: traces; ++: very deficient; +++: deficient; ++++: abundant; ++++: very abundant

Gi: gibbsite; Goe: goethite; Q: quartz; He: Hematite; Ha: halloysite; Ilm: ilmenite; Sa: sanidine; Ma: magnetite; Ru: rutile; All: allophanes; Feh: ferrihydrite.

Table 2. Chemical Composition of Soils and Parent Rock

Horizons		Oxides (%)											Total
		SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	K ₂ O	Na ₂ O	CaO	MgO	MnO	P ₂ O ₅	PF	
Black humiferous horizon (0 – 0.45 m)		21.50	20.30	7.05	0.97	0.48	0.15	0.23	0.30	0.05	0.35	48.10	99.48
Yellowish red clayey and loose horizon (0.45 – 0.75 m)		23.80	34.00	8.75	1.08	0.60	0.20	0.08	0.29	0.30	0.32	30.20	99.62
Saprolitic horizon (0.75 – 2 m)	Yellow brown domain	23.50	39.10	8.94	0.73	0.12	0.00	0.00	0.13	0.14	0.29	28.00	100.95
	Whitish grey domain	22.70	41.10	6.63	0.44	0.08	0.00	0.01	0.09	0.34	0.25	26.20	97.84
Alkaline trachyte		58.00	18.40	5.63	0.44	5.23	6.56	2.10	0.41	0.30	0.14	2.01	99.22

obtained by subtracting amorphous forms (Fe_{ox}) from total free forms (Fe_{CBD}). Note that total iron (Fe_{Total}) represents the whole amounts of Fe of a sample, including all Fe forms. It has been obtained by X-ray fluorescence on pressed powder pellets, using a Philips PW 2400 instrument with a rhodium anode end window tube, in the Mineral Analysis Centre at the Polytechnic Institute of Lausanne in Switzerland. The Fe_{Total} values of all the studied samples are presented in Table 2.

The three reagents, CBD, CB and oxalic acid, which are specific of soil iron forms, can be extended to the study of Al forms, but only on the amorphous ones which they dissolved [26, 27]. In consequence, total free Al does not include crystallized forms like gibbsite or boehmite. The previous chemical extractants are ineffective on Si [28], and the difference between Si extracted with CBD and Si extracted with oxalic acid is generally negative [28, 29]. For these reasons, the notion of extracting forms of Si has not been approached here. Supernatants from chemical extractions obtained by CBD (1 g of soil + 50 ml of CB solution + 1 g of dithionite), CB (1 g of soil + 50 ml of CB solution) and oxalic acid (1 g + 40 ml of oxalic acid solution) were decanted and analysed by atomic absorption spectrometer. Those selective extractions have been carried out in the "Laboratoire d'Analyses des Sols, Plantes, Engrais et Eaux (LASPEE)" of the Institute of Agricultural Research for Development (IRAD) of Yaoundé (Cameroon).

Soil mineralogy was investigated with a Philips X-ray diffractometer, using a copper anode with a characteristic wavelength of 1.54×10^{-10} m (40 kV source) and a xenon X-ray detector, in the Mineral Analysis Centre at the Polytechnic Institute of Lausanne in Switzerland. Amorphous and paracrystalline minerals have been identified by IR spectroscopy in the "Laboratoire de Minéralogie Cristallographie de Paris Jussieu" in France.

The determination of pH and potential redox (Eh) has been done in the same solution (soil/solution ratio $\frac{1}{2.5}$) using a direct reading pH meter HQ11D in the Wastewater Research Unit of the Faculty of Science (University of Yaoundé I, Cameroon). The redox level rH₂ has been calculated using the formula $rH_2 = \frac{Eh + 0.06pH}{0.03}$ [30].

4. RESULTS

4.1. Behaviour of Iron, Aluminium and Silicon in the Studied Soils

In the saprolitic horizon, Si is highly depleted out of the profile. Its mobilisation rate varies between -61% in the whitish grey domain and -75% in the yellow brown domain (Table 3), thus mean value of -68% (Fig. 3a), which corresponds to a mobilized mass of ~ 1.89 g/cm³ (Fig. 4a). Al and Fe on the other hand are imported in the weathering horizons. Their importation rates fluctuate respectively, from 123-29% and from 18 to -4% (Table 3), thus mean values of 76% for Al and 7% for Fe (Fig. 3a), which correspond, respectively, to a mobilized mass of 0.67 and 0.02 g/cm³ (Fig. 4a).

In the yellowish red clayey horizon, Si, Al and Fe are all depleted out of the profile. Their depletion rates are, respectively, -83, -35 and -37% (Table 3 and Fig. 3b), corresponding, respectively, to a mobilized mass of -1.15, -0.11 and -0.05 g/cm³ (Table 4 and Fig. 4b). Si is equitably depleted in the loose yellowish red clayey horizon and in the black humiferous horizon (Table 3; Fig. 3b, 3c). Al and Fe, although their negative rate, are most highly depleted in the humiferous horizon than in the loose yellowish red clayey horizon (-50% and -43%, respectively) (Table 3 and Fig. 3c).

Table 3. Bulk Density and Element Mobilization Ratios in the Horizons

Horizons	Db, ϵ , τ	Db (g/cm ³)	ϵ -Ti	τ Si	τ Al	τ Fe
Black humiferous horizon (0 – 0.45 m)		0.64	0.70	-0.83	-0.50	-0.43
Yellowish red clayey and loose horizon (0.45 – 0.75 m)		1.00	-0.02	-0.83	-0.35	-0.37
Saprolitic horizon (0.75 – 2 m)	Yellow brown domain	1.10	0.32	-0.75	0.29	-0.04
	Whitish grey domain	1.7	0.41	-0.61	1.23	0.18
Alkaline trachyte		2.4	0	0	0	0

Db: bulk density; ϵ -Ti: deformation ratio at Ti constant; τ : relative enrichment ratio of an element in comparison with the parent rock.

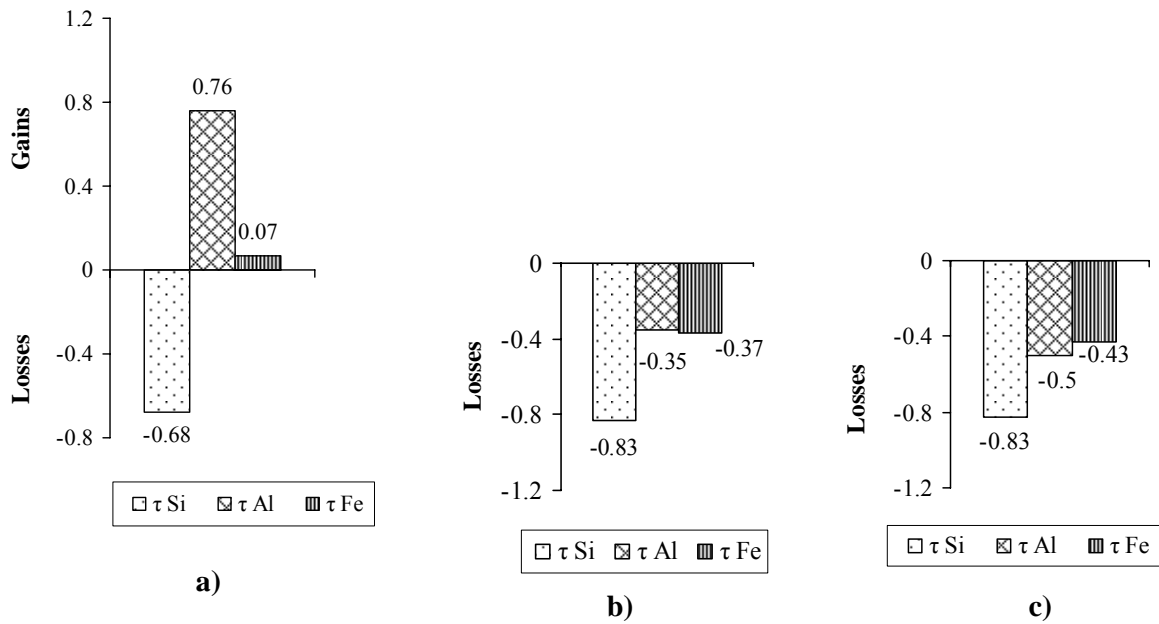


Fig. (3). Mobilization rate of silicon, aluminium and iron in the saprolitic horizons (a), in the yellowish red clayey and loose horizon (b), in the black humiferous horizon (c) of studied soils.

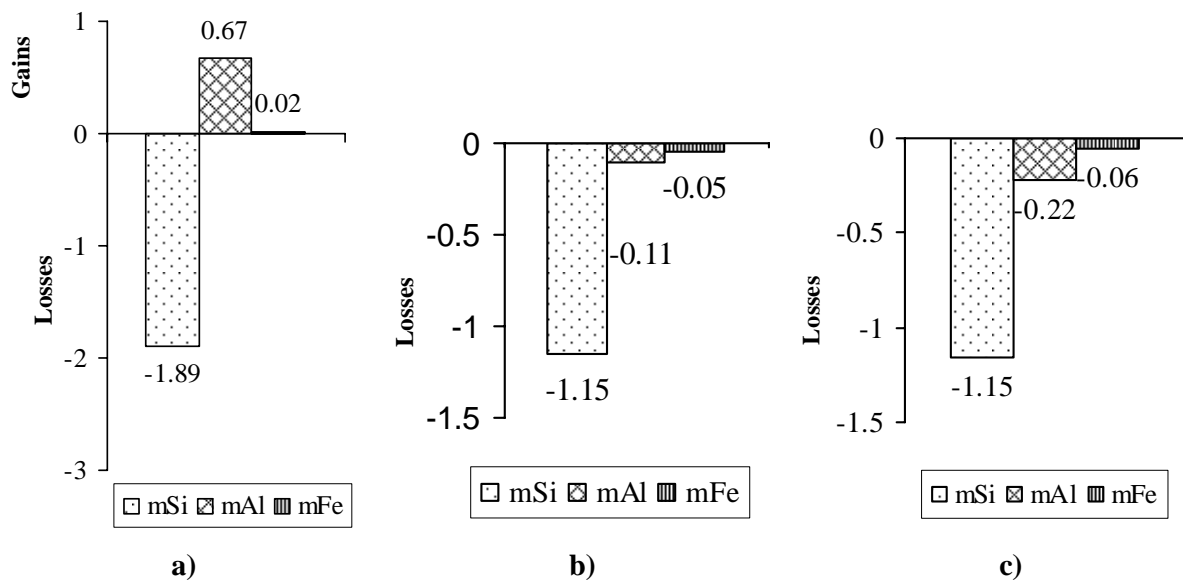


Fig. (4). Total mass of silicon, aluminium and iron in the saprolitic horizons (a), in the yellowish red clayey and loose horizon (b), in the black humiferous horizon (c) of studied soils.

Table 4. Mobilized Mass (m) of Elements in the Horizons (g/cm³)

Horizons	Elements	mSi	mAl	mFe
Black humiferous horizon (0 – 0.45 m)		-1.155	-0.221	-0.058
Yellowish red clayey and loose horizon (0.45 – 0.75 m)		-1.155	-0.110	-0.050
Saprolitic horizon (0.75 – 2 m)	Yellow brown domain	-1.044	0.128	-0.005
	Whitish grey domain	-0.849	0.543	0.024
Sum		-4.203	0.340	-0.089

Total mass of exported elements: -5.52 g/cm³ (include Ca, Mg, K, Na and Mn which are also depleted from the profile); Total mass of imported elements: 0.344 g/cm³ (include P which is also imported into the profile).

Fe and Al are then imported at the base of the profile, but depleted in the upper part, while Si is depleted throughout the profile. The global balance of Fe is however negative and its value is -16%; that value corresponds to a total mobilized mass of -0.089 g/cm³ (Table 4 and Fig. 5b) and represents 1.61% of the total mass of elements exported from the profile. Because Al is more highly enriched in the weathering horizon at the base of the profile, its global balance is in excess (17%) (Fig. 5a) and its total mass mobilized is 0.34 g/cm³ (Table 4 and Fig. 5b); this value represents 98.84% of the total elements imported in the whole profile. The global balance of Si is negative, with mean value of -75% (Fig. 5a), that corresponds to a total mobilized mass of -4.203 g/cm³ (Table 4 and Fig. 5b), representing 76.14% of the total mass of elements exported from the profile.

4.2. Identification and Quantification of the Main Forms of Iron and Aluminium in the Studied Soils

The different forms of Fe and Al identified are free, amorphous, crystallized and ‘resistant’ forms.

4.2.1. ‘Resistant’ Forms

The ‘resistant’ forms have only been identified for Fe. Their contents are high and fluctuate between 2.74-4.38% Fe₂O₃ (Table 5), and represent 59.03-69.96% of the total Fe (Table 6). The highest value (4.38% Fe₂O₃) is observed in the yellow brown domain, while the lowest one (2.74% Fe₂O₃) is noted in the whitish grey domain of the saprolitic horizon (Table 5). However, a slight decrease is noted towards the surface (Table 5).

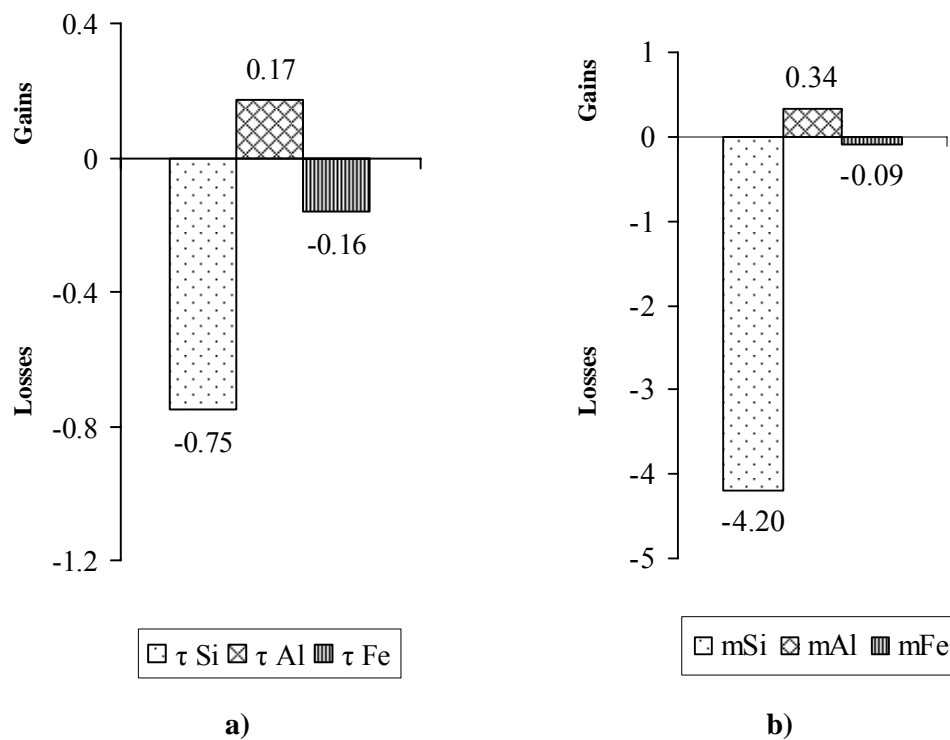


Fig. (5). Mobilization rate (a) and total mobilized mass (b) of silicon, aluminium and iron in the studied soils.

Table 5. Forms of Iron and Aluminium in the Studied Soils and their Contents

Horizons	Total Fe (%Fe ₂ O ₃)	Total Al (%Al ₂ O ₃)	CBD mg/g		CB mg/g		Oxalate mg/g		'Resistant' iron % Fe ₂ O ₃	Crystallized Iron mg/g	$\frac{Fe_{Ox}}{Fe_{CBD}}$ %	$\frac{Al_{Ox}}{Al_{CBD}}$ %	Al _{ox} +1/2Fe _{ox} %
			Fe _{CBD}	Al _{CBD}	Fe _{CB}	Al _{CB}	Fe _{Ox}	Al _{Ox}					
			Fe _{total} -Fe _{CBD}	Fe _{CBD} -Fe _{Ox}									
Black humiferous horizon (0 – 0.45 m)	4.94	10.75	17.20	6.88	0.01	1.72	0.40	1.95	3.22	16.80	2.33	28.34	0.22
Yellowish red clayey and loose horizon (0.45 – 0.75 m)	6.13	18.00	18.80	4.70	0.02	1.20	0.41	1.81	4.25	18.39	2.18	38.51	0.21
Saprolitic horizon (0.75 – 2 m)													
Yellow brown domain	6.26	20.70	18.80	5.87	0.01	1.54	0.43	2.34	4.38	18.37	2.29	39.86	0.26
Whitish grey domain	4.64	21.76	19.01	6.33	0.03	1.71	0.40	2.14	2.74	18.61	2.10	33.81	0.24

Ox: Oxalate.

4.2.2. Total Free Forms

Total Free Iron

Total free Fe (Fe_{CBD}) contents fluctuate between 17.20-19.01 mg/g (Table 5), representing 30.67-40.97% of total Fe. The extractible iron forms are more important at the base of the profile (19.01 mg/g) than at the top of the profile (17.20 mg/g) (Table 5).

Total Free Aluminium

Total free Al (Al_{CBD}) includes only amorphous Al forms. It globally presents low contents; they vary between 4.70-6.88 mg/g (Table 5) and represents ~2.61-6.33% of total Al. The highest value is obtained in the humiferous horizon (6.88 mg/g), while the lower one is noted in the loose yellowish red clayey horizon (4.70 mg/g) (Table 5).

4.2.3. Crystallized Forms

Crystallized Iron Forms

Crystallized Fe forms contents range between 16.80-18.61 mg/g (Table 5). The higher value, 18.61 mg/g, is observed in the saprolitic horizon at the base of the profile, while the lower one is noted in the humiferous horizon at the upper part. Those contents represent 29.35-40.11% of total Fe (Table 6), and 97.67-97.90% of the total Fe free form extracted by CBD.

Crystallized Aluminium Forms

'Crystallized Al', by analogy to crystallized Fe, corresponds to the difference between Al_{CBD} and Al_{Ox}; it constitutes 1.61-4.59% of the total Al and 60-71% of the total Al free form extracted by CBD (Table 6). These forms of Al are considered as Al included into iron in hematite or goethite networks [24, 25, 27].

4.2.4. Amorphous Forms

Amorphous Iron Forms

The amorphous iron forms (Fe_{ox}) are very poorly represented in the profile (Fig. 7). Their contents vary

between 0.40-0.43 mg/g (Table 5 and Fig. 7), and represent 0.67-0.86% of total iron (Table 6), or 2.10-2.33% of the total free forms Fe_{CBD} (Table 5). The amounts of Fe associated with organic matter (organic amorphous iron forms) are negligible (0.01-0.03 mg/g) (Table 5), compared to the mineral amorphous forms (Fig. 8a); it represents 2.50-7.50% of the total amorphous Fe, while mineral amorphous Fe on the other hand, represents 92.50-97.50% of total amorphous Fe (Table 6).

Amorphous Aluminium Forms

Amorphous Al is the best represented amorphous form in the studied soils (Table 5 and Fig. 6). Its contents oscillate between 1.81-2.34 mg/g (Table 5 and Fig. 6), representing 81.53-84.48% of total amorphous forms (Fe and Al) extracted by the oxalate reagent, or 0.98-1.81% of total alumina (Table 6). However, the form of Al linked to organic matter (organic amorphous Al forms), in the form of Al-humus complexes (Al_{CB}), is better expressed than the mineral forms (Fig. 8b), contrary to Fe (Fig. 8a). Its contents vary slightly along the profile, between 1.20-1.72 mg/g (Table 5 and Fig. 8b), which represent ~ 65.81-88.21% of the total amorphous Al forms, while the mineral fraction on the opposite only represents 11.79-34.19% (Table 6). The proportion of amorphous Al compared to the total free Al extracted by CBD is somewhat high and varies between 28.34-39.86% (Table 5).

Al_{ox}+1/2Fe_{ox} Ratio

The Al_{ox}+1/2Fe_{ox} ratio values are globally low. They vary between 0.21-0.26 (Table 5).

4.3. Physical and Chemical Soil Parameters

The soil pH values, which vary between 3.9-5.4 (Table 7), reveal an acidic nature with pronounced acidity in the black humiferous horizon (3.9). One can note that those values regularly decrease from the base to the upper profile. The redox potential values, contrary to the pH ones, increase

Table 6. Forms of Iron and Aluminium in the Studied Soils and their Relative Contents

Horizons	Total Fe (%Fe ₂ O ₃)	Total Al (%Al ₂ O ₃)	Amorphous Iron		Al _{ox} (%Al _{total})	Amorphous aluminium		Crystallized Iron (%Fe _{total})	'Resistant' Iron (%Fe _{total})		
			Fe _{ox} (%Fe _{total})	Mineral Amorphous Iron (%Fe _{ox})		Organic Amorphous Iron (%Fe _{ox})	Mineral Amorphous Aluminium (%Al _{ox})			Organic Amorphous Aluminium (%Al _{ox})	
Black humiferous horizon (0 – 0.45 m)	4.94	10.75	0.81	97.50	2.50	1.81	11.79	88.21	34.01	65.18	
Yellowish red clayey and loose horizon (0.45 – 0.75 m)	6.13	18.00	0.67	95.12	4.88	1.01	33.70	66.30	30.00	63.33	
Saprolitic horizon (0.75 – 2 m)	Yellow brown domain	6.26	20.70	0.69	97.67	2.33	1.13	34.19	65.81	29.35	69.96
	Whitish grey domain	4.64	21.76	0.86	92.50	7.50	0.98	20.09	79.91	40.11	59.03

Ox: Oxalate.

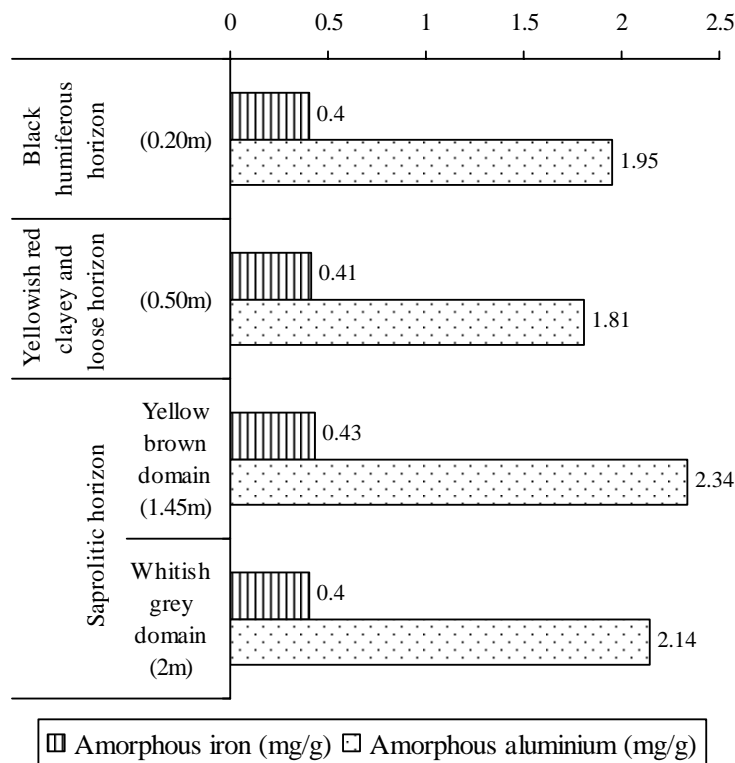


Fig. (6). Comparison of amorphous forms of iron and aluminium extracted by oxalic acid in studied soils.

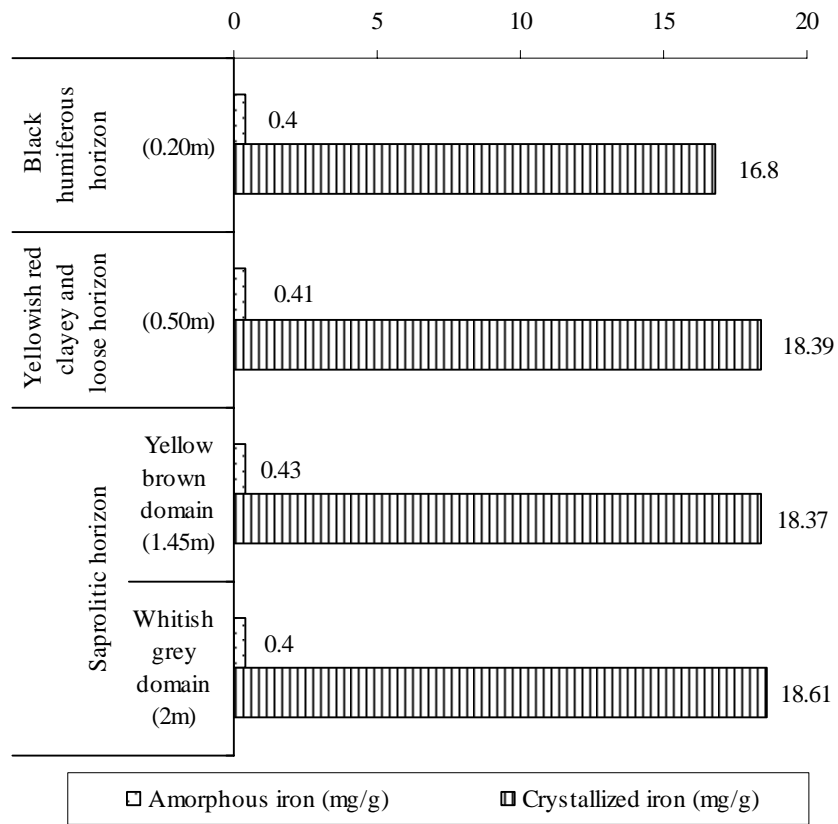


Fig. (7). Variation of amorphous and crystallized iron in studied soils.

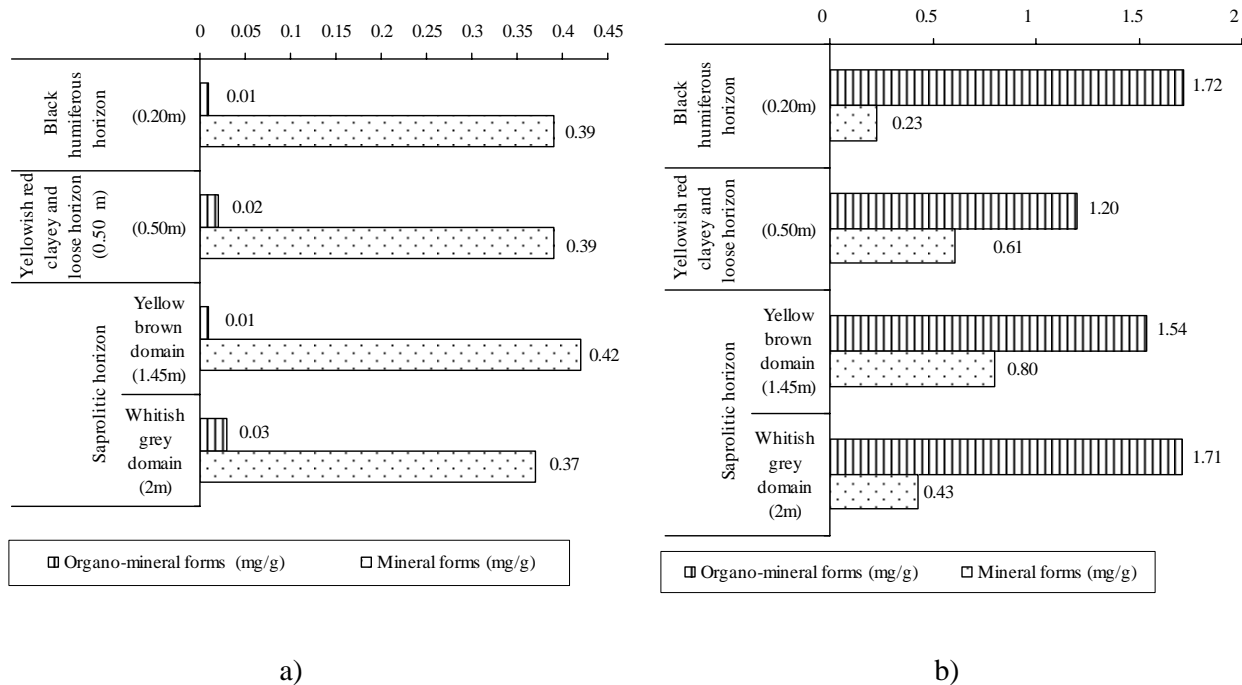


Fig. (8). Variation of organo-mineral and mineral forms of amorphous iron (a) and amorphous aluminium (b) in the soil profile.

Table 7. Physico-Chemical Characteristics of Soils

Horizons	pH	Eh (Volt)	rH ₂
Black humiferous horizon (0 – 0.45 m)	3.9	0.18	13.8
Yellowish red clayey and loose horizon (0.45 – 0.75 m)	5.0	0.12	14.0
Yellow brown domain (1.45m)	5.3	0.10	13.9
Saprolitic horizon (0.75 – 2 m)			
Whitish grey domain (2m)	5.4	0.09	13.8

from bottom to top, varying between 0.09-0.18V (Table 7). The highest value, 0.18V, is recorded in the black humiferous horizon which is the most acidic one. The redox level, rH₂, shows values ranging between 13.8-14.0 (Table 7).

5. DISCUSSION AND INTERPRETATION

The studied soils are mainly constituted by Al (20.30-41.10% Al₂O₃), Si (21.50-23.80% SiO₂) and Fe (6.63-8.94% Fe₂O₃), present essentially in the form of gibbsite, halloysite, allophane, goethite, hematite and ferrihydrite. Among these three elements, only Si is strongly leached in all horizons. Its leaching might have been accelerated by the incorporation of soil organic matter (SOM) [31], as confirmed by the high mobilization rate of Si obtained in the upper profile. This evacuation of Si is, however, contrary to the phenomenon which is observed in temperate zones, characterized by high accumulation of Si in the form of clay minerals, leading to bisiallitisatation [32].

Fe, despite its non-negligible contents (6.63-8.94% Fe₂O₃), is enriched in the weathering horizon at the base of the profile (18%), but depleted in the half upper part (-37 to -43%). Its mobilization rate increases from bottom to top. It presents a negative global balance and a total mobilized mass of -0.089 g/cm³, which globally remains relatively low. The evacuation of Fe from the profile agrees with the Eh and rH₂ values (respectively, < 0.20 V and 20), which are favourable to its reduction [30]. This reduction is favoured by the presence of micro-organisms that cause SOM oxidation and maintain reducing conditions [33, 34]. Fe is widely dominated by non-extractible Fe forms or resistant forms, which represent ~ 60-70% of the total Fe in the studied soil. These high values are similar to those obtained in andosolic soils in the Nilgiri Highlands of India [15] and podzolic soils of Brazil [28]. It is represented in the studied soils mainly by magnetite and ilmenite which are clearly identified in those soils and well known as non-extractible minerals [35]. Those 'resistant' iron minerals, which are fairly inert, are mostly inherited from the parent rock. Fe seems to be indifferent to the soil evolution processes, contrary to its well known role in ferrallitic soils for example [24, 35]. This might mainly be the result of the high presence of 'resistant' Fe forms. Among the extractible forms, crystallized ones are the most important fraction (29-40%), represented mainly by hematite and goethite. The amorphous Fe contents are low and constant throughout the profile, 0.40-0.43 mg/g, values which correspond to 0.67-0.86% of the total Fe and 2.10-2.33 of total extractible Fe. The amorphous Fe associated with SOM extracted by CB reagent is almost negligible (2.50-7.50 of total amorphous Fe), indicating that most

amorphous Fe is in mineral form (Fig. 6a), probably in the form of ferrihydrite, as identified in the studied soils.

Al, as with Fe, is enriched in the weathering horizon (29-123%), but depleted in the upper part profile (-35 to -50%). Its mobilization rate increases from bottom to top, a behaviour similar to Fe. The global balance of this element is in excess and the total mass mobilized in the studied soils is 0.34 g/cm³. The depletion of Al in the upper profile might be attributed to acid pH (3.9) which is unfavourable to the stability of Al oxide [36]. Amorphous Al forms are 4-5 times higher than amorphous Fe forms (Fig. 6a). The amorphous Al fraction associated with SOM (Al_{CB}) is equally remarkable in its amounts (66-88% of total amorphous Al), contrary to mineral amorphous forms, which are weakly represented. This amorphous mineral is probably in the form of allophane, as identified in mineralogical analyses. The presence of allophane characterizes the processes of andosolisation which occur in this volcanic environment. However, this process is weakly expressed as testified by the low Al amorphous mineral form contents and the Alox+1/2Feox ratio, which values vary between 0.21-0.26% (Table 5), and are characteristic of very weakly allophanic soils [37]. The low pH in the upper profile (3.9) and the high SOM content might inhibit allophanes formation [15]. The decreasing gradient of relative Al enrichment towards the surface (123% at the bottom of the profile and -50% Al₂O₃ in the humiferous surface horizon) might be partly attributed to the acido-complexolysis of gibbsite and the production of Al organo-metallic forms [15]. Amorphous Al contracts then close links with organic matter and causes its insolubilization by the formation of compounds which are resistant to biodegradation [38-43, 15], leading to the high residence time, up to several thousand years even values approaching 30000 years [44-46] and then the persistence of a thick black surface humiferous horizon.

Generally, the acidic pH and weakly redox potential cause strong mobilization of Si and Fe, concomitantly with high accumulation of Al in the soils [31, 25]. The strong occurrence of Al could permit describing these soils as Aluandosols using the "Référentiel de Pédologie Français" [47]. Globally, two zones can be distinguished in the profile. Firstly, the two upper horizons considered as an eluviation zone (loss of Si, Al and Fe), in which pH, Eh and rH₂ are, respectively, 3.9-5.0, 0.12-0.18 and 13.8-14. Secondly, the weathering horizon at the base of the profile, considered as an illuviation zone (accumulation of Al and Fe), in which pH, Eh and rH₂ are, respectively, 5.3-5.4, 0.09-0.10 and 13.8-13.9 (Table 7). Despite the environmental conditions of the mountainous massifs which are similar to those of high latitudes temperate zones, the crystallochemistry processes

are very different, with a clear general tendency to bisiallisation in the second case, but monosiallisation associated to high allitisation [32] in these tropical mountainous environments, as testified by the high evacuation of Si and bases, and the strong accumulation of Al in the profile. This might be attributed to high rainfall volume and uneven relief which promote excellent drainage [31].

6. CONCLUSIONS

The soils of the upper part of Bambouto Mountain are characterized by a high evacuation of Si and a moderate evacuation of Fe out of the profile, a high accumulation of Al and a strong occurrence of Al-humus complexes. 'Resistant' Fe forms are strongly represented. Extractible Fe fraction is dominated by crystallized Fe forms, which is associated with small quantities of mineral amorphous form identified mainly as ferrihydrite. Fe links to SOM are negligible. Extractible Al fraction on the opposite is dominated by organic amorphous in the form of Al-humus complexes, associated with small quantities of mineral amorphous fraction, mainly in the form of allophane. The behaviour of the three elements and the forms in which they are present in the studied soil are globally controlled by pH and Eh values, which are favourable to their movement and stabilisation. Although the environmental conditions (climate, vegetation,...) are similar to those of the temperate zone, the biogeochemical functioning of the tropical mountainous soils remains very different. There is a high allitisation associated to andosolisation on volcanic rocks in the mountainous zone, but bisiallisation on all rock types associated with podzolisation, andosolisation or brunification in the temperate zone.

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