Assessment of Fe(II), Fe(III) and Al(III) in a mineralogical profile of Gabonese soil

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Abstract

Four depths of a soil were sampled, extracted successively with water, 1 N KCl and aqua regia and analyzed. The soil displays a lithogenic discontinuity with a soil profile which was loam, sandy loam or clay. It was from slightly acid to strongly acid. Data showed significant correlations between soil properties and antagonist effects between Fe ions in the iron oxide formation. Metal speciation by a three extraction scheme showed that the total concentration of Fe(II) in the four soil horizons decreased as function of depth when the concentration of Al(III) and Fe(III) increased in the same time. The mineralogical fraction, the bigger fraction, decreased for all elements studied. This change led to increase significatively the water-soluble and exchangeable fractions of Fe(II) and exchangeable fraction of Al(III) and Fe(III). Significant correlations indicated inter-dependence of fractions and showed the influence of soil properties on the solubility and mobility of aluminum and iron.

Keywords: acid soils; metals; sequential extraction

1. Introduction

Metal species identification is used by researchers studying soil fertility, water quality, soil genesis and geomorphology, environmental quality, soil ecology, and soil remediation. The ubiquity of metals combined with the complexity of soils makes the study of metals one of the most important disciplines of soil chemistry (Walna et al., 2010). Iron and aluminum are the two most essential elements for understanding various soil forming processes. Distribution of different forms of iron and aluminum in soil is important to understand Fe and Al soil chemistry and the physicochemical properties of soil. The Fe and Al released during the weathering of Fe and Al bearing parent materials are reprecipitated in the soils as oxides or hydroxide and oxihydroxide of iron and aluminum. The amount and distribution of extractable Fe and Al oxides in soil profiles indicate the stage and degree of soil development. However, very meager information is available on the degree of soil development and the direction of pedogenic processes of Fe and Al in these soils. The present study was intended to investigate the different forms of Fe and Al and the interrelationship among themselves as well as with some important soil characteristics. (Bera et al., 2005).

The aim of the present research was to determine the fractionation of aluminum and iron in different depths of soil and their dependence to the soil properties.

2. Material and methods

This study was conducted from a hand dug well to Bikele (0°24′N, 9°34′E) near Libreville, the capital of Gabon. The climate is equatorial type. The annual rainfall varies from 1,600 to 1,800 mm. Average temperatures oscillate between 25 and 28°C with minima (18°C) in July and maxima (35°C) in April, and a hygrometry of 80 to 100%. The soil is strongly altered and desaturated (Delhumeau, 1969).

The soil samples were randomly collected with a stainless steel shovel at 0 (H0), 2 (H2), 4 (H4) and 6 (H6) meters of depth. The samples were put in plastic bags immediately and stored at −4°C. They were air-dried, crushed in a mortar, sifted through a 100 mesh sieve (250 µm).

Soil physicochemical properties have been assessed according to the ISO standard (AFNOR, 1994). They include: Particle size (three fractions), pH (water and 1 N KCl), and cation exchange capacity (CEC).

The sequential extraction method used aims to separate the studied elements in three fractions:

- Water-soluble fraction: 10 g of soil sample and 25 mL of deionised water were added into 100 mL plastic centrifuge tubes. The tubes were shaken for 2 h, and then allowed to stand for 24 h. The solutions were separated from the soil by centrifugation and filtered through a 0.43 µm filter paper.

- Exchangeable fraction: 100 mL of 1 M KCl solution were added to the soil sample into 100 mL plastic centrifuge tubes. The tubes were shaken for 2 h, and then allowed to stand for 24 h. The solutions were separated from the soil by centrifugation and filtered through a 0.43 µm filter paper.
- Mineralogical fraction: The soil sample was mineralized at 200°C for 5 hours using aqua regia (1/3 HNO_3+2/3 HCl)

Total Al^{3+}, Fe^{2+} and Fe^{3+} were also mineralized from soil samples. Al^{3+} and Fe^{2+} concentration were determined by titrating with standard NaOH solution in an N_2 atmosphere (Pansu and Gautheyrou, 2006). The concentration of iron in the ferric form was determined colorimetrically by the reaction of Fe^{3+} with thiocyanate forming under acidic conditions a red-colored complex (Furman, 1962). The complex was determined by UV-visible spectrophotometry at 480 nm. The experiments were conducted in triplicate.

3. Results and discussion

The particle-size distribution, pH, cationic exchange capacity (CEC), exchange acidity and concentration of major metal oxides of soils under study are shown in Table 1.

In terms of grain size, the soil displays a lithogenic discontinuity. The silt and clay fractions of H2 differed substantially compared to those of the other horizons. The soil profile is loam or sandy loam exception of H2 where it is clay. However, this difference was not significant in CEC level. This is probably due to the presence of kaolinite as main clay in soils of the region (Ondo, 2011). But, it is known that the CEC of kaolinite is 3-15 cmol/kg (Wilson, 1994), which does not affect the overall soil CEC. The conducted pH determinations put them in the class of slightly acidic soil for H2 and strongly acidic soils for the others. The lowest pH_{KCl} is characteristic of the topsoil which displays the humus accumulation and the highest organic C content (Walna et al., 2010).

The mineralogical composition influenced the concentrations of the metals examined in the soil horizons and had been studied earlier onto soils near this site (Ondo, 2011). It showed a dominance of quartz and clay minerals such as kaolinite, illite and chlorite. These clay minerals could be the main source of aluminium, iron and silica.

Significant positive correlations between clay fraction and pH_{water} ($r = 0,815$), pH_{KCl} ($r = 0,684$) and exchange acidity ($r = 0,882$), and between pH_{water} and exchange acidity ($r = 0.738$) were found indicating that a increase in the clay fraction level would allow to increase the pH and exchange acidity. On the other hand, the negative correlation between FeO and (Al_2O_3 and Fe_2O_3) ($r = -0,773$ and $r = -0.921$) and the positive correlation between Al_2O_3 and Fe_2O_3 ($r = 0,736$) would indicated an antagonism between Fe(II) and Fe(III) which benefits Fe(III) when the concentration of Al oxides increases.

Metal speciation by three extraction scheme was performed on all samples. Aqueous extract simulates metal release to soil solution under common conditions. In the case of Al, it implicates actual Al toxicity. Extraction by KCl releases exchangeable metals. The major pool of these metals is soil sorption complex. Thus extraction by KCl solution describes potential threat for a case of strong disturbance of soil conditions (Dlouha et al., 2009). The metal mineralogical fraction is strongly bounded to soil minerals. The analyte concentrations and percentages in the three fractions are shown in Table 2 and Figure 1.

The total concentration of Fe(II) in the four soil horizons decreased as function of depth from 20,491 mg/kg (H0) to 5,409 mg/kg (H6), since the concentration of Al(III) and Fe(III) increased in the same time from 30,142 mg/kg (H0) to 41,567 mg/kg (H6) and 12,656 mg/kg (H0) to 20,258 mg/kg (H6), respectively. The data show that the studied metals were mainly in mineralogical form. However, this fraction decreased between topsoil and subsoils. So, mineralogical fraction decreased from 91.3% to 79.4% (H2) for Al(III), 94.8% to 71.8 (H6) for Fe(II) and 93.9 to 86.3% (H6) for Fe(III) . In the case of Fe(II), this change led to increase significatively the water-soluble and exchangeable fractions from 0.8% to 8.8% and 4.4% to 19.4%, respectively. In opposite, the mineralogical fraction decrease allowed to increase only significatively exchangeable fraction, from 7.8% to 15.6% for Al(III) and 5.5% to 13.4% for Fe(III). The majority of studied metals exist in the residual fraction of all the samples. XRD analysis of soils this zone (Ondo, 2011) showed that the soils profile mainly consisted of kaolinite, anatase, rutile, gibbsite and goethite. The main source of Al in the soil samples is the weathering of aluminosilicates. Thus, Al is present in the samples mainly in the form of primary and secondary silicate minerals such as kaolinite and gibbsite (Favas et al., 2011) since Fe should be present in the form of goethite and other minerals.

Highly significant correlations (Table 3) were found between the water-soluble fraction and (exchangeable and mineralogical) fractions of Al(III) ($r = 0.626$ and $r = 0.708$), which indicates influence of last fractions on the water-soluble fraction.

There was a good correlation between the pH_{KCl} and (water-soluble and KCl-extractable) Al(III) ($r = 0.521$ and r

= 0.791; Table 3). This suggests that the vertical distribution of the water-soluble and exchangeable Al was regulated by soil acidity. Furthermore, the topsoil generally contained the highest organic matter, the exchangeable Al concentration was the lowest in the soil profile. This result suggests that the organic colloids had a weak role to play in holding exchangeable Al, possibly because of the low density of negative charge on the colloid surfaces under acidic conditions (Lu et al., 2011).

The positive correlation between the Fe(II) concentration in the exchangeable Fe(II) fraction and the pH value of the soil (r = 0.798; Table 3) indicates that the solubility of Fe(II) in this fraction increases with soil pH increasing. In soils saturated with water as soils of Libreville, the iron reduction is accompanied by an increase of the solubility of Fe(II) characterized by a lower redox potential, an increase in pH to acidic soils, rapid growth reduced iron contents in the soil and in the liquid phase (Vizier, 1988).

The negative correlations between the exchangeable Fe(II) and the sand and silt contents(r = 0.797 and r = 0.747) and the positive correlation between exchangeable Fe(II) and the clay content(r = 0.830) indicate this Fe(II) fraction stably bound with the clay particles, since increasing particle size led to decreasing solubility of the Fe(II) in this fraction. In the same time, the negative correlation between mineralogical Fe(III) and sand content (r = -0.538) indicates the similar behavior even if the other correlations (with silt and clay) were low. But the important quantity of negative correlations between (total and mineralogical fraction) Fe(II) and (total and mineralogical fraction) Al(III) and Fe(III), positive correlations between (total and mineralogical fraction) Fe(III) and Al(III) indicate that Al(III) and Fe(III) are often committed in the same minerals and that the increase of Fe(II)-minerals decreased the content of Fe(III)- and/or Al(III) minerals. This decrease is probably due because substitution of Al(III) and Fe(III) by Fe(II). Indeed, Taylor and Mckenzie (1980) indicated foir example that in the absence of oxygen, Fe(II) solutions react with aluminum hydroxide suspensions to form new Fe(II)-AI(III) hydroxy anion compounds. The positive correlations between pH_{KCl} and most fractions of studied metals indicate the participation of these metals in the exchange acidity of soils.

4. Conclusion

Fractionation of soil Al(III), Fe(II) and Fe(III) by sequential extraction stays suitable in defining various forms of these elements in soils. Solubility and mobility of Al and Fe in soils is related to the different physicochemical soil properties such as pH which was low. Aluminum and iron are major soil elements occurring in several soil minerals. They are in mineral composition or adsorbed in surface of other minerals. From now, the extractable elements in soil depths could serve to assess availability or toxicity of these elements in soils.

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Table 1. Physicochemical soil properties of Bikele

Echantillon	H0	H2	H4	H6
% Sand	51,7a	20,7b	29,2b	43,9a
% Silt	34,5ab	7,6c	39,6a	29,6b
% Clay	12,0c	69,2a	28,4b	27,0bc
C.E.C.	12,7a	13,1a	11,8a	12,6a
pH_{water}	4,1b	5,6a	4,9ab	4,3b
pH_{KCl}	3,3b	4,9a	4,6a	4,5ab
Al_2O_3 (%)	11,4a	12,2a	15,3a	14,9a
FeO (%)	7,6a	4,3b	2,5c	2,0c
Fe_2O_3 (%)	4,6b	7,0a	7,4a	7,7a

Table 2: Concentrations of Al^{3+}, Fe^{2+} and Fe^{3+} in different fractions and depths.

		H0	H2	H4	H6
Al^{3+} (mg/kg)	F1	250	371	419	675
	F2	2363	6075	6345	6480
	F3	27529	24882	33353	34412
Fe^{2+} (mg/kg)	F1	168	461	489	475
	F2	894	1439	1118	1048
	F3	19429	9326	5440	3886
Fe^{3+} (mg/kg)	F1	70	63	59	66
	F2	699	1677	2096	2711
	F3	11887	16782	17481	17481

F1: water-soluble fraction; **F2**: Exchangeable fraction; **F3**: mineralogical fraction

Table 3: Pearson correlation matrix of physicochemical properties and metal fractions of soils

		Sand	Silt	Clay	C.E.C.	pH_{water}	pH_{KCl}	Al_2O_3	FeO	Fe_2O_3
Sand		1								
Silt		0,554	1							
Clay		-0,85	-0,892	1						
C.E.C.		-0,085	-0,375	0,344	1					
pH_{water}		-0,849	-0,597	0,815	0,256	1				
pH_{KCl}		-0,778	-0,454	0,684	-0,095	0,422	1			
Al_2O_3		-0,236	0,292	-0,04	-0,358	-0,146	0,659	1		
FeO		0,432	-0,02	-0,253	0,178	-0,172	-0,75	-0,773	1	
Fe_2O_3		-0,595	-0,126	0,435	0,036	0,366	0,804	0,736	-0,921	1
Al^{3+}	F1	-0,037	0,039	0,041	-0,087	-0,151	0,521	0,681	-0,864	0,772
	F2	-0,648	-0,26	0,527	-0,079	0,468	0,791	0,541	-0,925	0,872
	F3	0,298	0,62	-0,491	-0,365	-0,388	0,027	0,492	-0,619	0,335
Fe^{2+}	F1	-0,637	-0,149	0,423	-0,134	0,372	0,784	0,601	-0,906	0,891
	F2	-0,797	-0,747	0,83	-0,102	0,798	0,575	-0,089	-0,248	0,336
	F3	0,449	0,053	-0,301	0,194	-0,233	-0,72	-0,662	0,981	-0,869
Fe^{3+}	F1	0,442	-0,2	-0,112	0,298	-0,514	-0,192	-0,316	0,26	-0,412
	F2	-0,209	-0,011	0,183	0,004	0,13	0,494	0,494	-0,897	0,777
	F3	-0,538	-0,082	0,399	0,146	0,344	0,72	0,621	-0,926	0,939

F1: water-soluble fraction; **F2**: Exchangeable fraction; **F3**: mineralogical fraction

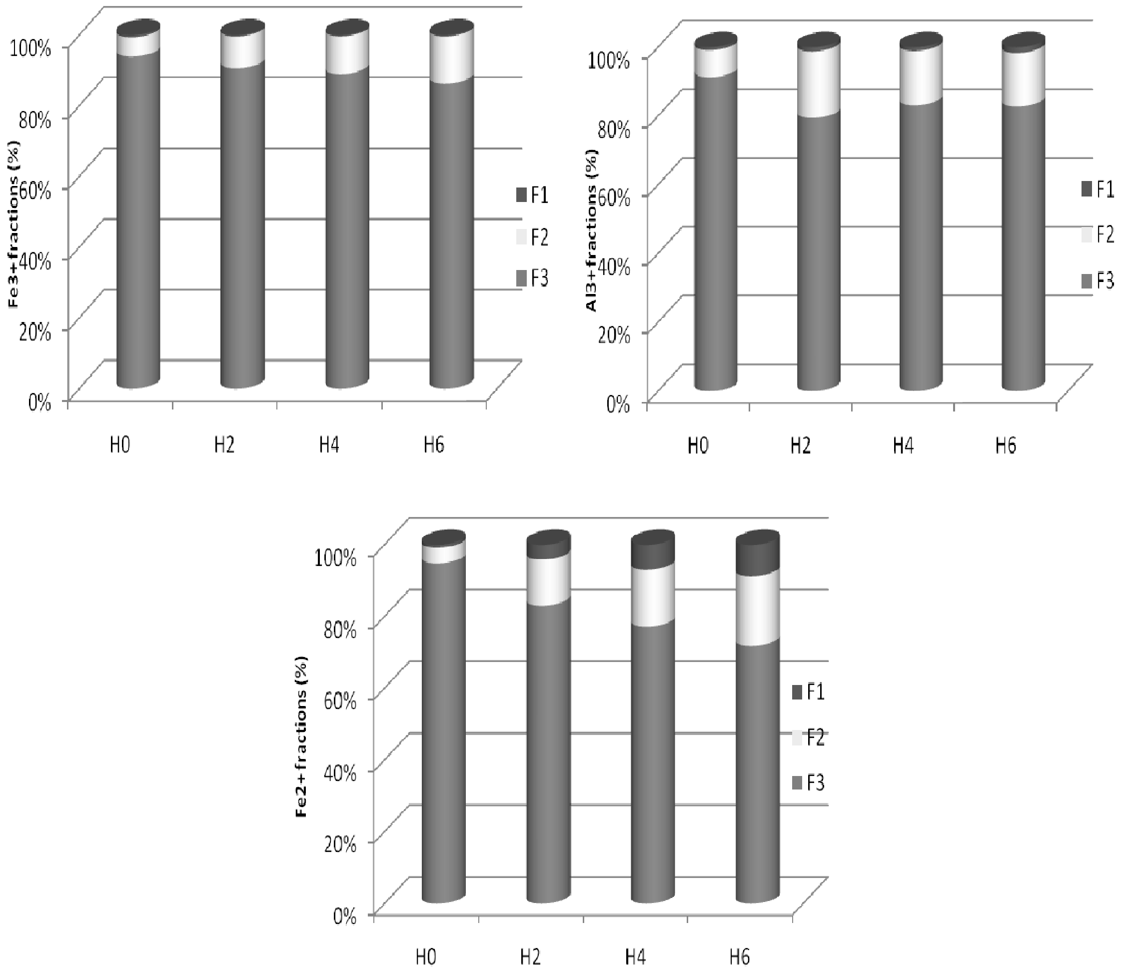

Figure 1: Sequential extractions as percent of total Al(III), Fe(II) and Fe(III) in soil with **F1**: water-soluble fraction; **F2**: Exchangeable fraction; **F3**: mineralogical fraction

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