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Modeling of liming in acid agricultural soils of Libreville (Gabon)

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Abstract

Soil acidification is an ongoing natural process which can be enhanced by human activities or can be controlled by appropriate soil management practices. Two highly acidified urban garden soils, CHA and NTO, were subjected to single-extraction procedure by water to determine the extractable concentrations of Ca, Mg, K, Na, Al, Cu, Fe, Mn, Pb, Zn and SO_4^{2-}. A modeling of effects of liming on soil solution was carried out from initial pH to pH 8.0 using the PHREEQC-2 code coupled with the PHREEQC.dat thermodynamic database. In NTO soil solution, liming increased the concentration of all cations, exception of Al when in CHA soil solution concentration of Ca, Cu, Fe and Pb increased. The chemical speciation of cations was evaluated in the soil solution. Basic cations Ca, Mg, K and Na were found as free forms (Ca^{2+}, Mg^{2+}, K^+, Na^+) and sometimes complexed by sulfate ($CaSO_4^0$, $MgSO_4^0$). The concentration of the toxic free ion Al^{3+} decreased quickly and was replaced by less toxic hydroxide complexes. For the other metals, relative to the total soluble metal concentrations the amounts of free Cu^{2+} (1%-99%) and Zn^{2+} (74%-97%) were not different in soil solutions when the amounts of free Pb^{2+} (10%-93%) and Fe^{2+} (65%-98%) in NTO soil solution were generally higher than those of CHA soil solution (8%-34% and 43%-84%, respectively). Statistical correlation analysis used to predict the change occurred in the concentration of the free ion in the soil studied showed significant influence of pH, SO_4^{2-} and HCO_3^- on Al^{3+}, Fe^{2+}, Pb^{2+} and Zn^{2+}.

Key-words: tropical acid soils, urban garden, liming, modeling, PHREEQC-2

1. Introduction

Under natural conditions, soils may slowly acidify over time, but agriculture can accelerate acidification. Principal processes of soil acidification are nitrification of ammonium fertilizers to nitric or nitrous acid, production of organic acids from a buildup of soil organic matter and export of organic anions with product removal. Soil acidification can cause their degradation and loss of productivity, aluminum and manganese toxicity, molybdenum, calcium and magnesium deficiencies, and reduced nitrogen fixation. Symptoms of aluminum toxicity include poor root growth, shallow roots and stunted plants (Dalby et al., 2004).

The greatest potential for expanding the world's agricultural frontier lies in the savanna regions of the tropics, which are dominated by Oxisols (Fageria, Baligar, 2008). Tropical soils are believed to be more vulnerable to improper land management practices than soils in temperate region (Zhang et al., 2007). Soil acidity and low native fertility, however, are major constraints for crop production on tropical Oxisols. Soil acidification is an ongoing natural process which can be enhanced by human activities or can be controlled by appropriate soil management practices. Nutrient deficiencies or unavailabilities and aluminum toxicity are considered major chemical constraints that limit plant growth on Oxisols (Fageria, Baligar, 2008).

The appearance of agriculture in urban spaces to Gabon improved the consumption of vegetables and fruits for a healthy diet. A study assessed the fertility level of vegetable soils of Libreville. The results indicated that from ten years of exploitation, soil pH decreased by about 1 unit, fertility, physicochemical soil properties and concentrations of most of metal elements of open field soils decreased significantly (Ondo, 2011). It is consequently urgent to develop strategies for maintaining and enhancing the quality and sustainability of tropical acid soils. Several authors studied the influence of organic and inorganic fertilizers on plant growth and retention capacity of metals in soils and yield of crops (Steiner et al., 2009; Ndakidemi and Semoka, 2006; Ludwig et al., 1999) in order to find a way to stop the process of soil acidification associated with farming. Methods have been developed to fight against the decline in soil fertility. The technologies may include crop rotations, inputs of crop residues, manure, chemical fertilizers, phosphate minerals, carbonate minerals (McClintock and Diop, 2005).

Liming is a dominant and effective practice to overcome acidification and loss of nutrients and improve crop production on acid soils. Lime is called the foundation of crop production or “workhorse” in acid soils (Fageria, Baligar, 2008). The aim of this study was to model the liming to provide information on soil management strategies. An assessment of the concentration of metals and their speciation in soil solution was discussed.

2. Material and methods

Soil samples were collected from two urban gardens in Libreville (9°25’ east longitude and 0°27’ north latitude), Republic of Gabon. The first soil, CHA, was sampled at Charbonnages the second one, NTO, at Ntoum. Detailed information on the studied samples is given in Table 1. The samples were transferred to plastic bags immediately and stored at −4°C. They were air-dried, crushed in a mortar, sieved through a 100 mesh sieve (2 mm), then crushed with a tungsten-carbide blade grinder and subsequently sieved with a 0.2 mm titanium mesh.

Soil properties including CEC were assessed according to the AFNOR protocols (AFNOR, 1994). Metals and sulfate ions were extracted from soil samples by single extraction procedure using deionised water (MilliQ-plus), solid-to-solution ratio of 1/10 (w/v) for 2 hours (Ettler et al., 2007). Ca, Mg, K, Na and SO_4^{2-} concentrations were determined by High Performance Ionic Chromatography (DIONEX ICS 3000) and Al, Cu, Fe, Mn, Pb and Zn concentrations were determined by ICP-AES (Spectra 2000 Jobin Yvon).

The PHREEQC-2 speciation-solubility code (Appelo et Parkhurst, 1999), version for Windows 2.18.3, was used to determine the metal speciation in the extract and at the pH values used in the model. The PHREEQC.dat thermodynamic database was applied to simulate the ion exchange of metals from soil solution and the precipitation of gibbsite $Al(OH)_3$ at pH ranging from pH value of samples soils to 8.0. The modeling was based from measured values of exchangeable cations and the measured values of CEC in the two soils. These values were used to fitting the solution composition at in situ pH. Then, $Ca(OH)_2$ was added in the model in quantities sufficient to attain higher pH values in steps of 0.25 pH units until pH 8. The solutions of each pH step were recorded and are shown in the Figures 1 + 2 and in Table 1. The model used a pε of 4 as starting point. This intermediate value of state in redox conditions is well reflecting the nature of oxisols which can, as a function of rain events, either be quite oxidized or reducing. Due to the lack of data on the temporal data of the evolution of pε with time, this intermediate pε is justified. The model was furthermore based on the assumption that neither $Ca(OH)_2$ nor agricultural fertilizers will bring important metal quantities in soils in the future. The model takes into account metals which adsorption can be influenced by the presence of anionic ligands such as hydroxides, carbonates and sulfates (Gerente et al., 2007). A few model runs were also made using the WATEQ database and using small amounts of dissolved humic acids. These calculations were giving almost identical speciations for all metals, showing that dissolved organic matter was not a major issue in metal speciation in these tropical oxisols.

The XLSTAT (version 2011) software was used for the statistical calculations, in particular for correlation analysis.

3. Results and discussion

The studied heterogeneous reactions were the cation exchange and the solubility of gibbsite, $Al(OH)_3$. The aim of the modeling is to simulate the evolution of the concentration of metals in the soil solution after increasing the pH by the liming with $Ca(OH)_2$.

3.1 Behavior of metal concentration in soil solution

The modeling of lime in the soils CHA and NTO showed different behavior between the metals studied (Table 2, Figures 1 and 2). In soil solution of CHA, the dissolved Al concentration decreased markedly from pH 4 to pH 5, due to precipitation of $Al(OH)_3$ as gibbsite.. At the same time, K, Mg, Na and Zn also decreased in following order: Zn < Na ≈ K < Mg, while concentration of the other metals increased in the following order: Fe <Ca <Pb <Cu. In soil solution of NTO, the concentration of all elements increased after liming, with exception of dissolved Al which precipitated at all pH values above in situ values. Taking into account the ratio between the final and initial concentrations of each element, the concentration increased in order: Na ≈ K < Mg ≈ Ca < Zn < Fe < Pb < Cu (Table 2).

According to the model, liming was able to increase pH, Ca concentration and reduce aluminum concentration in the solution of both soils. Similar results with various means of restoring tropical soils are presented in the literature (Bougnom et al., 2009; Fageria and Baligar, 2008). It also appears that at pH 8, a moderate increase of Fe concentration (from 1.14 to 4.06 times its initial concentration), a strong increase of Pb concentration (from 7.3 to 21 times its initial concentration) and a very strong increase of Cu concentration (from 38 to 139 times its initial concentration). These results are likely to lead to uptake by plants of harmful quantities of metals for human and animal health, or leaching to contaminate groundwater. Similar results are found in literature, but mainly from contaminated soils (Epstein and Bloom, 2005; Hall, 2002).

Between pH 4.5 (pH 5.8, respectively) and pH 8.0, the change is not linear. This result can be understood only after a detailed observation of metal speciation.

3.2 Speciation of metals in soil solution

In order to understand the behavior of metals in soil as a function of pH, the speciation of metals in soil solution is essential. Organic and inorganic metal complexes and free solvated metal ion particularly could be used to predict the phytoavailability of metal. In our soils, dissolved organic matter is at low concentration, and speciation is governed mostly by inorganic chemistry. Liming is able to increasing pH. Our study gives for each metal the concentration of the free ion and inorganic complexes. These inorganic complexes tend to decrease the concentration of free ions and thus reduce the bioavailability of metals to the plant (Morel, 1983, Korfali and Jurdi, 2011). The table 3 shows the percentages of each metal form in the soils studied when they were equal or above 1.

3.2.1 Speciation of basic cations Ca, K, Mg and Na

The model predicts logically an increase in Ca concentration because liming introduces calcium in the soil (Bolan et al., 2003). However, in acid soils, this supply should be monitored because it does not necessarily mean a good plant growth. A high concentration of Ca^{2+} in the soil with high K^+ and H^+ concentrations could decrease the Mg availability and hence its uptake by plants (Marschner, 1995). This is what seems to be observed in CHA soil solution where Ca concentration increased while Mg concentration decreased (Table 2). Still plant growth can be promoted due to the pH increasing and thus a decrease in phytotoxic Al and Mn concentrations (Bolan et al., 2003).

Speciation of basic cations essentially presented free ions (97-98 % for Ca^{2+} and Mg^{2+} and 100% for K^+ and Na^+) and sulfato- complexes (2-3% for $CaSO_4^0$ and $MgSO_4^0$). The presence of ion pairs $CaSO_4^0$ and $MgSO_4^0$ was challenged by Adams (1971) who stated that these ion pairs with anions do not occur or are negligible. But other authors think that the ion pairs between Ca and Mg, and inorganic anions in soil solution are important forms in the Ca and Mg availability in soil (Nogueria and Mozeto, 1990; Zambrosi et al., 2008; Piirainem et al., 2002). In agricultural soils, the K and Na complexes are generally smaller than Ca and Mg complexes (Lindsay, 1979). However, the interaction of potassium and sodium with anions in the soil solution is important for leaching because these cations need support for move along the soil profile (Rosolem et al., 2006).

3.2.2 Speciation of Al, Cu, Fe, Pb and Zn

The dominant chemical forms of Al were free Al^{3+} ion, hydroxo-Al and $Al(SO_4)^+$ (Table 3). Al toxicity to plants qualitatively decreases in this order: polymer Al^{13} (not in a form of phosphates or silicates), Al^{3+}, $Al(OH)_2^+$, $Al(OH)_3^0$, $Al(OH)_4^-$, $Al(OH)^{2+}$ and $Al(SO_4)^+$ (but toxicity of $Al(SO_4)^+$, however, is not always accepted). Aluminum bound in fluoride or organic complexes and $Al(OH)_3$ is supposed to be non-toxic (Drabeck et al., 2005; Gerard et al., 2001). The free form Al^{3+} is therefore the most harmful to plant roots in the present study. The Al^{3+} concentration was low in NTO soil solution (3-9%). In the case of CHA, it was 59% before liming (pH 4.5) and rapidly decreased to stabilize around 1% at pH 6.0, the ionic hydroxide complexes becoming major forms in solution. Under natural conditions, concentrations of Al^{3+} are generally low or moderate in acidic soil solutions (Merino et al., 1998). At low pH, Al is almost completely in the ionic state (Al^{3+}), then when the pH increases it is successively transformed with hydroxide into complexes $Al(OH)_2^+$, $Al(OH)^{2+}$ and $Al(OH)_3^0$. The solubility of Al was almost zero between pH 6 and 7, because under these conditions the mineral Gibbsite would precipitate. In addition, it increased with the formation of the aluminate ion $Al(OH)_4^-$ (Gauthier, 2002). These results indicate that despite the Al^{3+} concentration decreasing, the element is potentially toxic to plants if the concentration is high.

Cu speciation contained the free ion Cu^{2+} and the ion pair $Cu(OH)_2^0$ forms. It is also found forms $Cu(OH)^+$ and $Cu(SO_4)^0$ at concentrations ranging between 1 and 5%. At acidic pH, the prevailing form of copper in the soil solution is Cu^{2+} at pH around 6.75-7 in the both soils studied. From this pH, $Cu(OH)_2^0$ predominates and Cu becomes less available for plants. These results confirm those of Lindsay (1979) and Stumm and Morgan (1996). Indeed, with a pH <6.9, the prevailing species of copper in the soil solution is Cu^{2+}, while $Cu(OH)_2^0$ is the major form of Cu above this pH. Other studies (Barata et al., 1998; Korfali and Jurdi, 2011) found that $Cu(CO_3)^0$ is the prevailing form at alkaline pH. Copper bioavailability therefore decreases above a pH of 6.9. In our tropical oxisols, the copper concentrations are always low and therefore, there is neither a problem of plant toxicity nor one of copper transfer to the food chain. In contrast, it is essential to constrain liming to any pH increase above 7 in order not to cut the supply of the essential metal copper to plants.

Fe speciation in soil solution essentially presented free ion Fe^{2+} in acid medium at pε 4. Total forms of Fe(III) was above 1% from a pH ranged from 6.25 to 6.75. These forms were $Fe(OH)_2^+$, $Fe(OH)_3^0$ and $Fe(OH)_4^-$. Their concentration increased with pH and with Fe^{2+} concentration decreasing. Of course, the variable water content of our soils in rainy and dry seasons will greatly affect soil pε, and therefore our results on Fe speciation are only means of strongly variable conditions.

The important forms of Pb in soil solution were Pb^{2+} (10-93% for CHA and 8-34% for NTO), $Pb(CO_3)^0$ (2-71% for CHA and 51-76% for NTO), $Pb(HCO_3)^+$ (1-4% for CHA and 1-3% for NTO), $Pb(OH)^+$ (3 -17% for CHA and 11-15% for NTO) and $Pb(SO_4)^0$ (1-7% for CHA and 1-5% for NTO). The pH increasing led high concentration of carbonate or hydroxide complex. The free metal ion Pb^{2+} was lower in NTO than in CHA. For pH between 6.0 and 6.5, Pb carbonate ($Pb(CO_3)^0$, $Pb(HCO_3)^+$) complexes represented least 20% of speciation of this element. Experiments performed by Korfali and Jurdi, (2011) also showed the vital role played by carbonate complexes in the reduction of the concentration of the toxic form of lead, Pb^{2+}.

The mobile forms of Zn in soil solution were Zn^{2+}, $Zn(OH)_2^0$, $Zn(CO_3)^0$, $Zn(HCO_3)^0$, $Zn(OH)^0$ and $Zn(SO_4)^0$. Zn^{2+} is dominant throughout the liming process but its concentration decreased with pH. Han and Singer (2007) also observed that Zn^{2+} is the dominant form of zinc in the soil solution as the pH remains below 7.7. Moreover, Ma and Lindsay (1990) found that the concentration of hydroxide forms $Zn(OH)^+$ and $Zn(OH)_2^0$ increased from the pH and became dominant from pH 9.1, particularly in arid areas. Thus, to use the best availability of zinc to the plant, soil pH below 7.7 is required.

3.3 Interactions between metals and anions

Statistical correlation analysis was performed between free ion metals, pH and alkalinity of soil represented by HCO_3^-. Table 4 provides the values of Pearson correlation coefficients. Into both soil solutions, positive significant correlations were showed between (pH and HCO_3^-) and (Fe^{2+}, Pb^{2+} and Zn^{2+}), and SO_4^{2-} had negative significant correlations with the same ions. Al^{3+} had significant correlations with SO_4^{2-} (positive) and HCO_3^- (negative). A multilinear regression analysis carried out in order to bring in a mathematical equation the relationship between the concentration of the free ions (dependent variable) Al^{3+}, Fe^{2+}, Pb^{2+} and Zn^{2+} with pH, HCO_3^- and SO_4^{2-} (independent variables). The results are presented in Table 4. These equations can be used to predict the change occurred in the concentration of the free ion in the soil studied in the case of various environmental conditions (Korfali and Jurdi, 2011).

Conclusion

The free ions of Al, Ca, Mg, K and Na were the dominant form in the soil solution. Exchangeable bases are therefore available to plants in the agricultural soils and the pH increase by liming is a good way to improve the fertility of the soils studied. Likewise, pH correction by liming would reduce the high initial concentration of free ion Al^{3+} in the soil solution, since it tends to complex with hydroxide to form $Al(OH)_3$ which precipitates after pH increasing. On the other hand, the concentration of problematic metals such as Pb increased due to their complexation with hydroxide and carbonate, especially above pH 7. The ideal solution is therefore to provide an intermediate amount of lime to stabilize the pH values between 6 and 7. It is necessary to continue this study by combined laboratory and field experiments in order to validate the model.

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Table 1: Physicochemical properties and metals of soils from two locations, CHA and NTO

Data on soils		CHA	NTO
pH_{water}		4,5	5,8
Kjeldahl nitrogen	g kg^{-1}	1,3	1,2
Organic matter		12,3	23,5
Sand		676	578
Silt		118	276
Clay		206	146
CEC	méq/100g	0,0	26,7
P Olsen	mgkg^{-1}	3,7	4,1
Ca		276,5	1203,7
Mg		31,2	63,6
Na		3,2	3,9
K		57,7	37,6
Al		31054,3	16264,3
Cu		9,4	26,5
Fe		19565,3	12170,3
Mn		167,3	179,1
Pb		6,1	12,8
Zn		15,3	21,9
SO_4^{2-}	mol.L^{-1}	$2.5.10^{-2}$	$1.1.10^{-4}$

Table 2: Ratio between the final total dissolved concentration (at pH = 8) and the initial total dissolved concentration (at pH = 4.5 or 5.8 for CHA and NTO, respectively) of metals in soil solution after liming.

	Al	**Cu**	**Fe**	**Pb**	**Ca**	**Mg**	**Na**	**K**	**Zn**
CHA	0,01	37,80	1,14	7,35	5,45	0,76	0,90	0,88	0,98
NTO	0,02	139,16	4,06	21,11	2,27	1,81	1,27	1,33	2,40

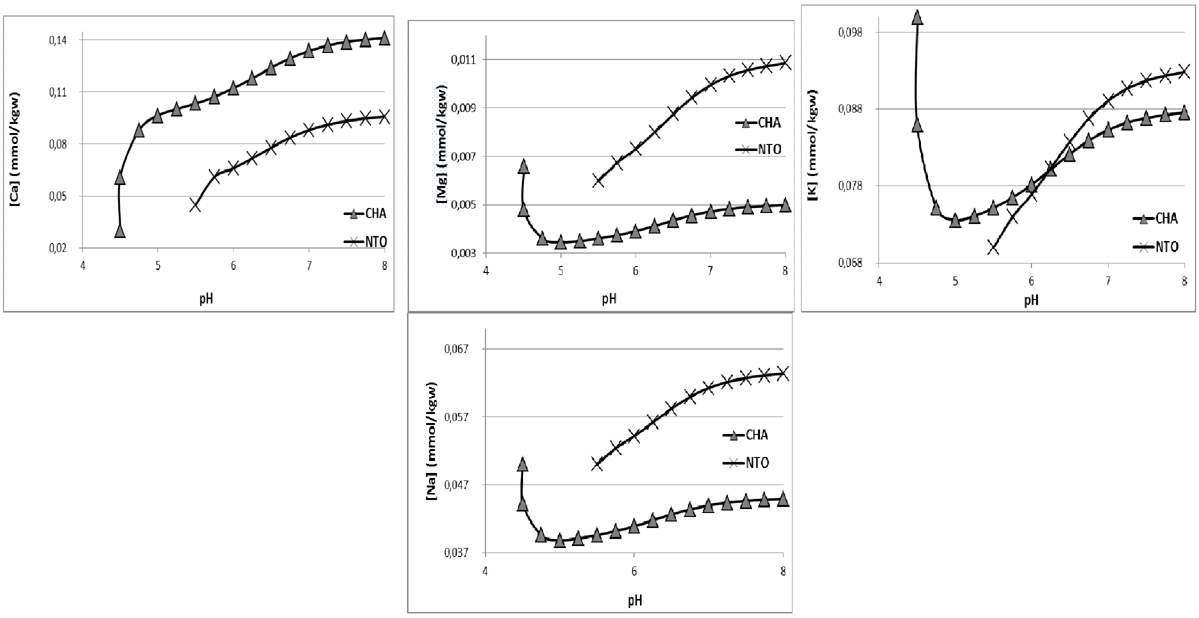

Figure 1: Concentration of basic cations as function of modeled soil pH

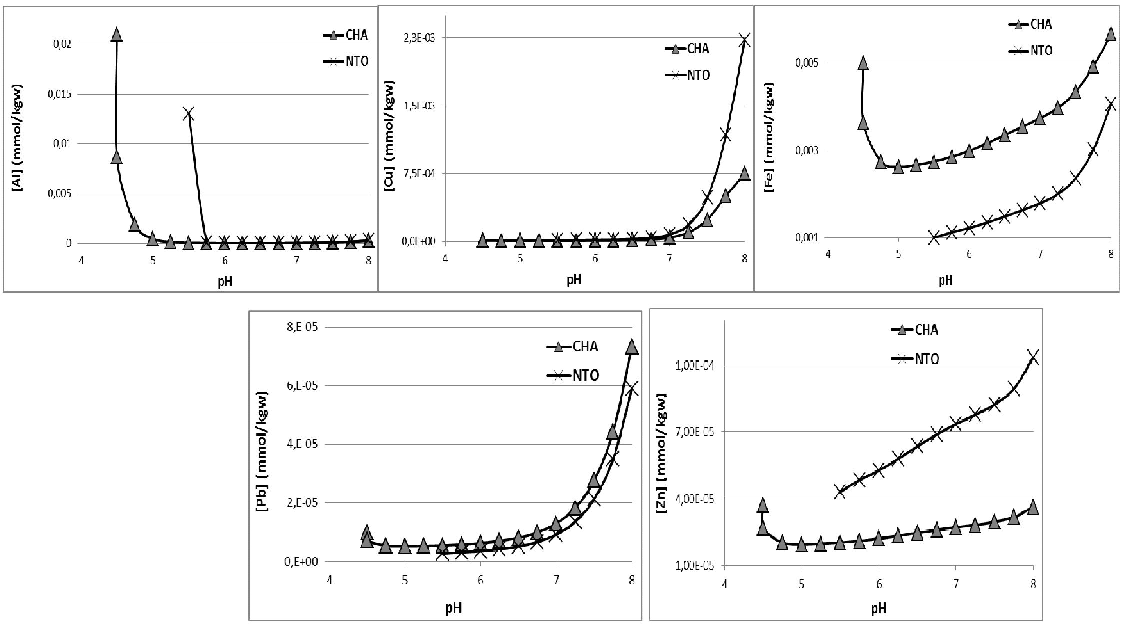

Figure 2: Concentration of metals as function of soil pH.

Table 3: Chemical speciation of metals in solution of CHA and NTO soils according to calculations with PHREEQC.dat database in the pH range of 4.5 to 8.

Metal	Chemical forms	Range of percentage in NTO soil solution	Range of percentage in CHA soil solution
Al	$Al(OH)_2^+$	1-68	1-67
	$Al(OH)_3^0$		1-11
	$Al(OH)_4^-$	6-99	2-99
	Al^{3+}	3-9	1-59
	$Al(OH)^{2+}$	1-17	1-31
	$Al(SO_4)^+$		1-21
Ca	Ca^{2+}	98	97-98
	$CaSO_4^0$	2	2-3
Cu	$Cu(OH)_2$	1-99	2-99

	Cu^{2+} $Cu(OH)^+$ $CuSO_4^0$	2-98 1-3 1-5	2-98 1-3 1-2
Fe	$Fe(OH)^{2+}$ $Fel(OH)_3^0$ $Fe(OH)_4^-$ Fe^{2+} $Fe(OH)^+$ $FeSO_4^0$	4-5 9-46 2-4 43-84 1 1	1-3 2-18 2 65-98 1-2 1-2
K	K+	100	100
Mg	Mg^{2+} $MgSO_4^0$	98 2	97 3
Na	Na^+	100	100
Pb	Pb^{2+} $PbCO_3^0$ $Pb(HCO_3)^+$ $Pb(OH)^+$ $PbSO_4^0$	8-34 51-76 1-3 11-15 1-5	10-93 2-71 1-4 3-17 1-7
Zn	$Zn(OH)_2^0$ Zn^{2+} $ZnCO_3$ $Zn(HCO_3)^+$ $Zn(OH)^+$ $ZnSO_4^0$	1-8 74-93 2-8 1 2-7 2	1-8 75-97 1-6 1 1-7 2-3

Table 4 : Pearson correlation coefficients and mathematical equations between free metal ions and the main soil properties CHA and NTO

	NTO			CHA		
	Pearson correlation coefficients					
	pH	HCO_3^-		pH	HCO_3^-	
Al^{+3}	-0,610	-0,698	Al^{+3}	-0,610	-0,698	Al^{+3}
Cu^{+2}	-0,115	0,132	Cu^{+2}	-0,115	0,132	Cu^{+2}
Fe^{+2}	0,969	1,000	Fe^{+2}	0,969	1,000	Fe^{+2}
Pb^{+2}	0,966	1,000	Pb^{+2}	0,966	1,000	Pb^{+2}
Zn^{+2}	0,972	1,000	Zn^{+2}	0,972	1,000	Zn^{+2}
	Mathematical equations					
	$[Al^{+3}] = 2,296E^{-7} - 2,022E^{-3} * [SO_4^{2-}] - 0,163 * [HCO_3^-] * [SO_4^{2-}]$ for pH > 5.25 and $[Al^{3+}] = f(pH)$ for pH < 5.25 $[Fe^{+2}] = 8,773E^{-7}+9,722E^{-9}*pH+6,133E^{-3}*[HCO_3^-]$ $[Pb^{+2}] = 2,576E^{-9} + 1,781E^{-5} * [HCO_3^-] - 1,640E^{-7} * pH * [SO_4^{2-}]$ $[Zn^{+2}] = 3,425E^{-8} + 2,547E^{-4} * [HCO_3^-] + 9,028E^{-6} * pH * [SO_4^{2-}]$			$[Al^{+3}] = f(pH)$ for pH < 5.75 $[Zn^{+2}] = 4,515E^{-7} - 2,802E^{-3} * [SO_4^{2-}] + 0,358 * [HCO_3^-] * [SO_4^{2-}]$ $[Pb^{+2}] = 1,049E^{-7} - 6,479E^{-4} * [SO_4^{2-}] + 0,100 * [HCO_3^-] * [SO_4^{2-}]$ $[Fe^{+2}] = 6,028E^{-5} - 0,374 * [SO_4^{2-}] + 48,759 * [HCO_3^-] * SO_4^{2-}]$		

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