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Research Article

Extractable Al and Soil Solution Ionic Concentrations in Strongly Leached Soils from Northwest Iberia: Effects of Liming

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Strongly leached soils occurring in Northwest Iberia contain high concentration of Al which may affect crop growth. Information regarding the extractability of Al and lime required to eliminate toxic Al species in the soil solution is scarce. In this context, the extractability of Al on these soils was determined using 1 M KCl, 0.33 M $LaCl_3$ and 0.5 M $CuCl_2$. The effects of lime on the concentration and activity of Al species in soil solution, using the GEOCHEM program was also evaluated. Extractability of Al was in the order: 1 M KCl < 0.33 M $LaCl_3$ < 0.5 M $CuCl_2$, with ranges from 0.7–3.3, 1.3–4.4, and 1.8–13.5 $\text{cmol}_c\ \text{kg}^{-1}$, respectively. These values were positively correlated with cation exchange capacity and organic C, clay, Alo and Feo contents. Application of 6 t $CaCO_3$ ha^{-1} increased the total concentrations of Ca^{+2}, Mg^{+2}, K^{+}, and Na^{+} ions in soil solution, whereas, application of 2 t $CaCO_3$ ha^{-1} reduced the concentration and activity of Fe^{+3}, Al^{+3}, Mn^{+2}, Zn^{+2}, Cu^{+2}, $SO_4{}^{-2}$, and $PO_4{}^{-3}$ ions,and eliminated toxicity threshold of free Al^{+3} and Al soluble complexes in the soil solution. Application of low amounts of lime may prevent the negative effects of soluble Al on crops.

1. Introduction

Soils developed under Mediterranean-type climate conditions show a wide range of geochemical characteristics associated with differences in total soil organic C (SOC) content [1, 2] and clay mineralogical composition [3]. This trend is observed in Portugal for soils developed on granites, which cover about 35% of the north-west and central parts of the country [4, 5]. In fact, soils developed in wetter areas (above 1500 mm precipitation) are strongly leached and show organic C-rich superficial horizons (30–80 C g kg^{-1}) and variable contents of gibbsite in the clay fraction along soil profile: negligible in the surface and larger (up to 80%) in deeper horizons [6, 7]. In drier areas, soils are less leached and show low SOC content and gibbsite is absent.

Soil acidity originating from the hydrolysis of Al is one of the major constraints for crop growth [8]. Several chemical and biological reactions relating plant nutrient toxicity due to low pH conditions of the aqueous system (pH 5 and below) have been reported by Kamprath [9] and Dietzel et al. [10]. Such system may contain hydrolytic by-products, for instance, high concentrations of Al species of varied bioavailability and biotoxicity characteristics [11, 12]. At such acidic conditions, the monomeric species, mainly Al^{+3}, $Al(OH)^{+2}$, and $Al(OH)_2{}^{+}$, may predominantly form in soil solution, limiting crop growth [13, 14]. Their abundance (especially Al^{+3}) may also be phytotoxic to several crops [15–18] and forage species [19]. However, the yield-limiting effects of Al^{+3} for most crops may be alleviated or eliminated by liming [20, 21]. Liming the soil to a pH above 5.5 may lower the concentration of monomeric Al ions [22–24]. Although lime application has been advocated in many acidic soils to reduce Al concentration in soil solution, information regarding the adequate rate of liming is scarce for strongly leached soils developed under humid Mediterranean climate.

Several studies have also reported the contribution of SOC content to the formation of stable complexes of Al with humic and aliphatic organic acids to suppress detrimental effects of Al in soil solution on plants [25–27]. The evaluation of extractable Al using suitable methods is crucial to discriminate the inorganic and organically complexed forms of Al in soil. The extraction with 1 M KCl has been used as conventional method of estimating readily exchangeable Al in acid soils [28–30]. Nevertheless, other extractants (e.g., 0.33 M $LaCl_3$ and 0.5 M $CuCl_2$) have also been successfully used to determine Al associated with organic matter via ligand exchange reactions [31–33]. However, information regarding organic and inorganic forms of Al as well as on the use of extractants other than 1 M KCl is still scarce for strongly leached soils that contain high amounts of Al and SOC.

The information on the concentration and distribution of Al species and other ions in free, complex, pair, and chelate states in soil solution is crucial to assess the detrimental effects of Al in soil systems [34–37]. The modified version by Parker et al. [38] of the GEOCHEM program developed by Sposito and Mattigod [39] has been widely used to predict equilibrium concentration and activities of ions in solution of many acid soils. However, it has not yet been used to differentiate Al species in strongly leached soils under humid Mediterranean conditions.

Having this in view, a study was conducted to gain deeper understanding regarding extractability Al and lime effects on its solubility in soils developed on granites, occurring under a wide range of mean annual precipitation. The specific objectives were (1) to determine the contents of extractable Al using 1 M KCl, 0.33 M $LaCl_3$, and 0.5 M $CuCl_2$ extractants and evaluate their relationships with soil properties; (2) to assess the concentration of Al species and other ions in soil solution following lime application and speciate and calculate their respective activities in solution using the GEOCHEM program.

2. Materials and Methods

2.1. Study Soils. Twenty-two surface and subsurface horizons from acidic soils developed on granite, situated at different sites from the north-west and central of Portugal, taking into account the mean annual precipitation (MAP), were used in the present study (Table 1). According to the World Reference Soil Data Base System [40], selected pedons correspond to several major soil groups: Umbrisols, Cambisols, Regosols, and Luvisols. The Umbrisols (pedons 1, 2, 3, and 4), Cambisols (pedons 5 and 6) and Regosols (pedons 9, 10, and 11) are located between 530 and 1520 m above sea level, having high MAP (1600–2800 mm), at slopes between 2 to 30% under forest, shrubland/forest, or shrubland/pasture. The Luvisols (Pedons 7 and 8) are under lower MAP (500–800 mm) than other soils and occur at low elevation (300–720 m) under cereal production. The mean annual temperature of the chosen sites varies between 10 and 16°C. The site description and some chemical and mineralogical properties of selected horizons have been detailed elsewhere [3, 6].

2.2. Chemical Analyses. Soil samples were air dried, homogenized, and sieved (<2 mm) prior to laboratory determinations. Soil pH was determined on suspension of soil in water and 1 M KCl (1 : 2.5 ratio) after 1 h of intermittent shaking, using a pH meter (Metrohm 632). Soil total organic C content was determined by wet oxidation following the Springer and Klee method [41]. Clay content of the soil was determined by pipette analysis following dispersion method with sodium hexametaphosphate [42]. Cation exchange capacity was determined using continuous leaching of 5 g soil with 100 mL of 1 M NH_4OAc buffered at pH 7 [43]. Basic cations (Ca^{+2}, Mg^{+2}, K^+, and Na^+) from the leachate were measured using atomic absorption spectrophotometer (AAS).

Amorphous or poorly crystalline inorganic forms of aluminium (Al_o) and iron (Fe_o) were extracted by the acid ammonium oxalate and were determined using the methodology described by Blakemore et al. [44]. Crystalline forms of Fe (Fe_d) were extracted using dithionite-citrate-bicarbonate and were determined following the procedures described by Mehra and Jackson [45]. Organically complexed Al (Al_p) and Fe (Fe_p) were extracted by 0.1 M sodium pyrophosphate and were determined following the methods described by Blakemore et al. [44]. Al and Fe in the filtered extracts were measured using the AAS (Perkin Elmer Analyst 300) at 309 and 302 nm, respectively.

Readily exchangeable Al in the soil was extracted with 1 M KCl. This was performed by adding 50 mL of 1 M KCl to 5 g of soil in 100 mL plastic centrifuge tubes, and suspensions were shaken for 1 h, using a reciprocal shaker [46]. In addition, 0.33 M $LaCl_3$ and 0.5 M $CuCl_2$ were also used as alternative extractants for forms of Al associated with soil organic matter. This was done by adding 50 mL of 0.5 M $CuCl_2$ and 0.33 M $LaCl_3$ extractants to 5 g of soil in 100 mL plastic centrifuge tubes, and each suspension was shaken for 30 min. Suspensions were then centrifuged at 3,000 ×g for 10 min and filtered using a Whatman number 42 filter paper. Extractions were performed in triplicate for each soil sample. Al in the extracts was measured using AAS at 309 nm.

2.3. Lime Incubation. Of the 22 studied soil horizons, nine surface horizons (of pedons 1, 3, 4, 5, 6, 7, 8, 10, and 11) yielded a pH of 4.5–5.3 and a wide range of total organic C content (4–73 $g\,kg^{-1}$) were selected for the lime incubation experiment in order to study its effects on the concentration and activity of Al and of other ions. For each soil, 100 g of air dried, 2 mm crushed soil (in duplicate) were placed in plastic bags. Reagent-grade $CaCO_3$ was added at 0, 1, 2, and 3 $g\,kg^{-1}$ soil (equivalent to 0, 2, 4, and 6 $t\,ha^{-1}$), which is the range commonly required for enhancing crop growth in many acid soils [20, 47]. The soil was rewetted to field capacity by adding the predetermined volume of distilled water, twice weekly [48], within the incubation period of three months at laboratory room conditions. After three months of incubation, soils were air dried in the laboratory room for three days and then pulverized gently using mortar and pestle.

Table 1: Location and environmental conditions of study pedons. Alt: altitude; MAT: mean annual temperature; MAP: mean annual precipitation.

Pedons	Location	Alt (m)	MAT (°C)	MAP (mm)	Slope (%)	Vegetation
			Umbrisols			
1 (Sapateiro)	41°51′07′′N, 7°53′17′′W	1250	10	1800	3	Forest/shrubland
2 (Tribelo)	41°43′06′′N, 8°06′24′′W	730	12	2800	15	Pine forest
3 (Montemuro)	40°58′00′′N, 8°00′36′′W	1250	10	2000	10	Shrubland/forest
4 (Serra da Estrela)	40°18′30′′N, 7°33′10′′W	1520	10	2400	20	Shrubland/forest
			Cambisols			
5 (Gontim)	42°04′18′′N, 8°10′06′′W	1180	11	2400	2	Shrubland/pasture
6 (Roçadas)	42°04′25′′N, 8°08′43′′W	1150	11	2400	4	Shrubland/pasture
			Luvisols			
7 (Niza)	39°30′20′′N, 7°37′15′′W	300	16	800	2	Cereal crops
8 (Almeida)	40°43′30′′N, 6°59′55′′W	720	13	500	<2	Cereal crops
			Regosols			
9 (Cando)	41°58′40′′N, 7°54′19′′W	100	11	2400	30	Pine forest
10 (Cabeças)	42°00′24′′N, 8°16′39′′W	810	11	2400	10–15	Forest/shrubland
11 (Castro-Daire)	40°46′20′′N, 7°54′20′′W	530	13	1600	10	Pine forest

2.4. Extraction of Soil Solution and Chemical Speciation. Unlimed (control) and limed soils were rewetted with predetermined volume of distilled water at field capacity. Soil solution was extracted by packing the soil uniformly in a complex funnel containing Whatman number 542 filter paper. The solution was displaced slowly into Erlenmeyer flask, using a mechanical vacuum extractor [49]. Extracted solutions were then filtered by a 0.22 μm pore membrane. A subsample solution of 5 mL from the filtered extract was immediately taken and analyzed for pH and electrical conductivity (EC) using an pH (Metrohm 632) and conductivity (Metrohm 712) meters. The total concentration of Ca^{+2}, Mg^{+2}, K^{+}, Na^{+}, Fe^{+3}, Al^{+3}, Zn^{+2}, Mn^{+2}, and Cu^{+2} ions in the filtered extracts from unlimed and limed soils was measured using the inductively coupled plasma atomic emission spectrometry (ICPAES). Phosphate ($PO_4{}^{-2}$) was determined by the molybdenum blue method [50, 51] and measured using a spectrophotometer (Unicam Spectronic) at 882 nm. Water soluble sulfate ($SO_4{}^{-2}$) was also determined from unlimed and limed filtered extracts, using the turbidimetric method [52]. This was done by adding 5 mL of 2.5% $BaCl_2$ and 0.5% polyvinyl alcohol mixture to an aliquot of filtered extract in 20 mL glass tube and shaken mechanically (2 rpm) for 30 min. $SO_4{}^{-2}$ in filtered extract was measured using a spectrophotometer (Unicam Spectronic) at 420 nm.

The values of pH and total concentration of Ca^{+2}, Mg^{+2}, K^{+}, Na^{+}, Fe^{+3}, Al^{+3}, Zn^{+2}, Mn^{+2}, and Cu^{+2} ions in unlimed and limed soil solutions were entered into the modified geochemical speciation model by Parker et al. [38] of the GEOCHEM program [39] to calculate the activities of different free ions and soluble complexes.

2.5. Statistical Analysis. Analyses of variance were done using Statistica 9 software [53]. The Tukey multiple range test was used to test differences between contents of extractable Al by various tests, concentrations, and activities of ions in the soil solution. The relationships between the amounts of Al in soil determined by different extractants and soil constituents were determined using correlation analysis.

3. Results and Discussion

3.1. Soil Characteristics. The relevant chemical properties of studied soils are shown in the Table 2. The soil organic C (SOC) content in the surface horizons of Umbrisols (pedons 1, 2, 3, and 4), Cambisols (pedons 5 and 6), and Regosols (pedons 9, 10, and 11) was 43–70, 56–64 and 27–73 $g\,kg^{-1}$, respectively. In both surface and subsurface horizons, the values of cation exchange capacity (CEC)

Table 2: Values of pH, sum of bases (SB), and cation exchange capacity (CEC), and contents of clay, total organic carbon (SOC), amounts of aluminium and iron extracted by acidified ammonium oxalate (Alo and Feo), by sodium pyrophosphate (Alp and Fep), and extractable iron by dithionite-citrate-bicarbonate (Fed), and values of the Alo/Alp and SOC/Alp molar ratios in studied soils.

Pedon	Hor	Depth (cm)	pH		SB	CEC	Clay	SOC	Alo	Feo	Fed	Alp	Fep	Alo/Alp	SOC/Alp
			H_2O	1 M KCl	(cmol$_c$ kg^{-1})					(g kg^{-1})					
								Umbrisols							
1	Ah1	0–20	4.6	3.8	0.75	28.70	160	63	5.28	9.60	17.21	5.17	5.40	1.02	27.42
	Ah2	20–45	4.9	4.0	0.37	31.14	130	56	6.70	8.15	17.91	6.97	5.25	0.96	18.08
2	Ah1	0–15	4.7	3.8	0.42	15.61	160	43	3.74	6.89	12.31	4.00	6.12	0.94	24.19
	Ah2	15–35	4.8	4.1	0.25	19.54	110	41	6.60	3.47	7.21	5.10	2.70	1.29	18.09
3	Ah1	0–20	4.9	3.4	0.65	20.25	140	70	4.53	2.78	4.74	4.57	2.61	0.99	34.46
	Ah2	20–40	5.0	3.9	0.47	21.92	150	65	6.06	2.81	9.50	4.90	2.67	1.24	29.85
4	Ah1	0–20	4.8	3.7	0.45	12.41	70	50	1.57	0.81	2.44	1.83	0.86	0.86	61.48
	Ah2	20–45	5.1	3.8	0.24	12.08	80	36	4.60	0.71	2.94	3.60	0.82	1.28	22.50
								Cambisols							
5	Ah	0–15	4.7	4.0	0.28	15.74	160	64	5.63	5.50	15.95	4.99	3.27	1.13	28.86
	A/B	15–30	4.7	4.1	0.18	25.09	180	52	5.37	7.05	18.42	5.36	4.38	1.00	21.83
6	Ah1	0–15	4.6	3.8	0.24	23.31	140	56	7.45	6.38	18.53	5.31	3.44	1.40	23.73
	A/B	15–30	4.7	4.2	0.15	27.73	140	50	6.88	5.96	16.45	6.01	4.79	1.14	18.72
								Luvisols							
7	Ah	0–15	5.2	4.0	1.31	5.60	150	8	0.35	0.65	3.90	0.51	0.60	0.69	35.29
	Bt	15–30	4.9	4.1	0.57	5.88	230	3	0.49	0.77	7.81	0.53	0.58	0.85	12.74
8	Ah	0–20	5.0	3.7	0.77	4.42	50	4	0.24	0.97	12.32	0.34	0.24	0.71	26.47
	Bt	20–35	5.3	3.8	3.18	8.75	140	3	0.41	1.71	12.47	0.59	0.40	0.69	11.44
								Regosols							
9	Ah1	0–15	4.8	4.0	0.14	9.70	80	37	5.45	2.36	11.06	4.36	1.56	1.25	19.09
	Ah2	15–30	5.0	4.2	0.18	30.48	210	80	12.42	5.52	18.34	10.09	4.03	1.23	17.84
10	Ah	0–20	4.5	3.8	0.31	17.47	140	73	6.86	3.40	10.22	5.61	2.57	1.22	29.28
	C1	20–40	5.0	4.7	0.15	13.27	80	22	4.20	0.65	5.53	3.96	0.56	1.06	12.50
11	Ah	0–20	5.1	4.0	0.42	6.95	120	27	2.44	1.08	5.91	2.22	0.68	1.10	27.36
	A/C	20–45	5.1	4.3	0.07	4.58	130	6	1.85	0.41	5.64	1.20	0.41	1.54	11.25

and content of base cations ranged 2.4–31.1 and 0.14–0.75 $\text{cmol}_c\,\text{kg}^{-1}$, respectively; the base saturation degree was very low (0.6–6.0%), reflecting strong leaching conditions associated with high precipitation. In contrast, SOC content (3–8 g kg^{-1}), values of CEC (4.4–8.7 $\text{cmol}_c\,\text{kg}^{-1}$), and base cations (0.57–3.18 $\text{cmol}_c\,\text{kg}^{-1}$) were low in the horizons of Luvisols (pedons 7 and 8), but with somewhat high base saturation degree (10–36%) compared to other study soils. The former soil major groups showed Alp content (1.2–10.2 g kg^{-1}) similar to that of Alo (1.9–12.4 g kg^{-1}), indicating that extractable Al by the ammonium oxalate may be mostly associated with organic matter.

3.2. Extractable Al. The content of Al extracted by the 1 M KCl, 0.33 M $LaCl_3$, and 0.5 M $CuCl_2$ in studied pedons is shown in Table 3. The content of Al extracted by KCl was the lowest (0.7–3.3 $\text{cmol}_c\,\text{kg}^{-1}$) followed by that of $LaCl_3$ (1.3–4.4 $\text{cmol}_c\,\text{kg}^{-1}$). The content of Al extracted by $CuCl_2$ (1.8–13.5 $\text{cmol}_c\,\text{kg}^{-1}$) was significantly higher than the others.

The content of Al extracted by KCl was positively correlated with that of $LaCl_3$ and $CuCl_2$ ($r = 0.76$ and 0.88, $P < 0.001$, resp.), with correlation between the content of Al extracted by $LaCl_3$ and that of $CuCl_2$, being weaker ($r = 0.54$, $P < 0.01$). In the surface horizons, correlations between the content of Al extracted by KCl with those of $LaCl_3$ and of $CuCl_2$ were $r = 0.89$ and 0.93, $P < 0.001$, respectively, and between the content of $LaCl_3$ and of $CuCl_2$ ($r = 0.83$, $P < 0.01$) being stronger than for whole horizons. In the subsurface horizons, significant correlation was only noted between the content of Al extracted by KCl and by $CuCl_2$ ($r = 0.85$, $P < 0.001$). This trend was in agreement with results reported by Barra et al. [54] for surface and subsurface horizons from a wide range of Brazilian soils of the Rio de Janeiro State.

The content of Al extracted by $LaCl_3$ was about one to three times more than that of KCl (see Table 3), indicating higher ability of $LaCl_3$ to extract Al than KCl, following trends reported by García-Rodeja et al. [33] for a wide range of European volcanic soils. This trend may be associated with the fact that the content of Al extracted by 0.33 M $LaCl_3$ presumably includes the portions of readily exchangeable Al and less hydroxylated as well as polymerized Al bound to the organic matter [24, 55]. Ritchie [31] also reported that the 0.33 M $LaCl_3$ may not only extract exchangeable form of Al but also interlayer Al and some organically bound forms of Al. In contrast, the lower contents of Al extracted by the 1 M KCl may be attributed to limited ability of this extractant to only extract readily exchangeable form of Al and not the reactive Al which is associated with organic matter [9, 56, 57]. The content of Al extracted by $CuCl_2$ was about two to five times more than that obtained by KCl and one to four times than that obtained by $LaCl_3$. The values of Al extracted by $CuCl_2$ (3.5–11.8 $\text{cmol}_c\,\text{kg}^{-1}$), the differences between Al extracted by $CuCl_2$ and by KCl and between Al extracted by $CuCl_2$ and by $LaCl_3$ in soils containing high contents of SOC (27–80 g kg^{-1}) were high compared to other soils. Such association suggests strong ability of 0.5 M $CuCl_2$ to extract Al associated with the portions of potentially reactive nonreadily exchangeable Al and Al associated with organic matter, interlayer Al, and hydroxyl-Al polymers than by 1 M KCl and by 0.33 M $LaCl_3$ extractants as reported by Oates and Kamprath [58] Kaiser and Zech [59]. This agrees with the fact that both Al extracted by $CuCl_2$ and difference between Al extracted by $CuCl_2$ and the KCl were strongly correlated with Alp content ($r = 0.89$ and 0.90, $P < 0.001$, resp.). High contents of Al extracted by $CuCl_2$ determined in organic C rich horizons were in agreement with the data reported by Barra et al. [54] for acidic Brazilian soils from Rio Janeiro State and by Matus et al. [60] for soils rich in organic C from Chile.

The strong ability of 0.5 M $CuCl_2$ to extract Al relative to that of 1 M KCl and 0.33 M $LaCl_3$ may also be associated with its acidic nature which may facilitate the depolymerization of Al-hydroxides [59, 60]. The strong complexing power of Cu^{+2} ion and its high affinity with the functional groups of soil organic matter as reported by Matus et al. [60] may also enhance the dissolution of Al from organo-Al complexes and from interlayer silicate minerals [56, 58]. In general, soils or horizons with low SOC content showed low amounts of Al extracted by $CuCl_2$ (1.8–4.1 $\text{cmol}_c\,\text{kg}^{-1}$). This behaviour was observed in the Ah and Bt horizons of pedons 7 and 8, and A/C horizon of pedon 11, where the lowest SOC content (3–8 g kg^{-1}) and low values of $CuCl_2$-$LaCl_3$/$CuCl_2$ molar ratio (18.2–97.6) were observed (Table 2). However, in these horizons differences between the Al extracted by $CuCl_2$ and KCl were also marked, as the ratio between the Al extracted by $CuCl_2$ and KCl was within the range of other soils. This pattern suggests that the smaller amounts of Al extracted from these soils were also associated with either organically bound Al or some precipitated Al in the soil as reported by Ritchie [31] for acidic soils.

3.3. Extractable Al and Soil Properties. The correlation coefficients between the content of Al determined by studied extractants and soil properties are shown in Table 4. The contents of Al extracted by 1 M KCl and 0.5 M $CuCl_2$ were positively correlated with the values of CEC ($r = 0.80$ and 0.85, $P < 0.001$, resp.), correlation being stronger in the subsurface ($r = 0.83$, $P < 0.01$ and 0.96, $P < 0.001$, resp.) than in the surface ($r = 0.80$, $P < 0.01$ and 0.68, $P < 0.05$, resp.) horizons. The correlation observed between the content of Al extracted by 0.33 M $LaCl_3$ and values of CEC in the surface horizon was weaker ($r = 0.66$, $P < 0.05$). The positive correlation between the contents of Al determined by studied extractants and the CEC values suggest that the extracted Al in the study soils was strongly associated with the components responsible for the development of charge, particularly originating from Al-organo complexes [33]. For instance, the highest content of Al extracted by the KCl and $CuCl_2$ (3.3 and 13.50 $\text{cmol}_c\,\text{kg}^{-1}$, resp.) obtained in the Ah2 horizon of pedon 1 coincided with the high CEC value (31.1 $\text{cmol}_c\,\text{kg}^{-1}$). This may be associated with the fact that a strong positive correlation between the values of CEC and SOC content ($r = 0.81$, $P < 0.001$) was observed, suggesting that high proportion of dissolved Al was associated with the organic matter. The contents of Al extracted by 1 M

TABLE 3: Content of Al ($\text{cmol}_c\ \text{kg}-1$) extracted by 1 M KCl (A), 0.33 M $LaCl_3$ (B), and 0.5 M $CuCl_2$ (C), values of the differences and ratios between extractants in studied soils. Symbols: D ($LaCl_3$-KCl), E ($CuCl_2$-KCl), F ($CuCl_2$-$LaCl_3$), G ($LaCl_3$/KCl), H ($CuCl_2$/KCl), I ($CuCl_2$/$LaCl_3$), and J ($CuCl_2$-$LaCl_3$)/$CuCl_2$. Means in the same horizon followed by different letters are significant at $P < 0.05$ by the Tukey test.

Pedons	Hor	Depth	A	B	C	D	E	F	G	H	I	J
						Umbrisols						
1	Ah1	0–20	2.79a	3.59b	7.63c	0.80	4.84	4.04	1.29	2.73	2.13	206.42
	Ah2	20–45	3.32a	3.49b	13.50c	0.17	10.18	10.01	1.05	4.07	3.87	103.70
2	Ah1	0–15	2.63a	4.44b	8.78c	1.81	6.15	4.34	1.69	3.34	1.98	122.44
	Ah2	15–35	2.02a	2.89b	9.69c	0.87	7.67	6.80	1.43	4.80	3.35	105.78
3	Ah1	0–20	2.04a	3.31b	5.14c	1.27	3.10	1.83	1.62	2.52	1.55	340.47
	Ah2	20–40	2.50a	4.06b	8.22c	1.56	5.72	4.16	1.62	3.29	2.02	197.69
4	Ah1	0–20	1.30a	2.09b	3.52c	0.79	2.22	1.43	1.61	2.71	1.68	355.11
	Ah2	20–45	1.86a	2.91b	6.35c	1.05	4.49	3.44	1.56	3.41	2.18	141.73
						Cambisols						
5	Ah	0–15	2.31a	2.76a	8.76b	0.45	6.45	6.00	1.19	3.79	3.17	182.65
	A/B	15–30	2.17a	2.92a	9.48b	0.75	7.31	6.56	1.35	4.37	3.25	137.13
6	Ah1	0–15	1.92a	2.68a	7.84b	0.76	5.92	5.16	1.40	4.08	2.93	178.57
	A/B	15–30	2.59a	3.15a	10.89b	0.56	8.30	7.74	1.22	4.20	3.46	114.78
						Luvisols						
7	Ah	0–15	0.86a	1.32b	2.05b	0.46	1.19	0.73	1.53	2.38	1.55	97.56
	Bt	15–30	1.64a	3.78b	4.05b	2.14	2.41	0.27	2.30	2.47	1.07	18.52
8	Ah	0–20	0.67a	1.34b	1.77b	0.67	1.10	0.43	2.00	2.64	1.32	56.50
	Bt	20–35	1.74a	3.72b	4.13b	1.98	2.39	0.41	2.14	2.37	1.11	18.16
						Regosols						
9	Ah1	0–15	1.31a	1.97a	5.17b	0.66	3.86	3.20	1.50	3.95	2.62	178.92
	Ah2	15–30	2.15a	2.80a	11.81b	0.65	9.66	9.01	1.30	5.49	4.22	169.35
10	Ah	0–20	3.09a	4.11a	11.14b	1.02	8.05	7.03	1.33	3.61	2.71	163.82
	C1	20–40	1.95a	3.31b	8.03c	1.36	6.08	4.72	1.70	4.12	2.43	68.49
11	Ah	0–20	0.86a	2.69b	3.50b	1.83	2.64	0.81	3.13	4.07	1.30	192.86
	A/C	20–45	0.67a	2.29b	3.14b	1.62	2.47	0.85	3.42	4.69	1.37	47.77

Table 4: Correlation coefficient matrix (r) between the amounts of Al extracted by different extractants, and values of cation exchange capacity (CEC), and content of clay, total organic C (SOC), aluminium and iron by acidified ammonium oxalate (Alo and Feo) and by sodium pyrophosphate (Alp and Fep) in studied soils. Symbol: *, **, *** significant at the 0.001, 0.01, and 0.05 probability (P) levels, respectively.

Extractants	r, P Soil constituents						
	CEC	clay	SOC	Alo	Alp	Feo	Fep
			All horizons				
1 M KCl	0.80***	ns	0.70***	0.62***	0.71***	0.74***	0.79***
0.33 M $LaCl_3$	ns	0.46*	ns	ns	ns	ns	0.48*
0.5 M $CuCl_2$	0.85***	ns	0.69***	0.84***	0.89***	0.72***	0.78***
			Surface horizons				
1 M KCl	0.80**	0.66*	0.83***	0.74**	0.85***	0.77**	0.83**
0.33 M $LaCl_3$	0.66*	0.63*	0.72**	0.60**	0.73**	0.66*	0.81**
0.5 M $CuCl_2$	0.68*	0.61*	0.79**	0.85***	0.88***	0.71**	0.75**
			Subsurface horizons				
1 M KCl	0.83**	ns	0.68*	0.54*	0.65*	0.76**	0.78**
0.33 M $LaCl_3$	ns	ns	ns	ns	ns	ns	ns
0.5 M $CuCl_2$	0.96***	ns	0.83***	0.84**	0.92***	0.86**	0.90***

KCl, 0.33 M $LaCl_3$, and 0.5 M $CuCl_2$ were only positively correlated with clay content in the surface horizon ($r = 0.66$, 0.63, and 0.61, $P < 0.05$, resp.).

A strong positive correlation of SOC content with those of Al determined by studied extractants was also observed. For instance, positive correlations (r) of SOC content with those of Al extracted by the KCl, $LaCl_3$, and $CuCl_2$ were observed in the surface horizons (0.83, $P < 0.001$; 0.72 and 0.79, $P < 0.01$, resp.), while in the subsurface horizons, the correlation was only observed for the content of Al extracted by the KCl and $CuCl_2$ ($r = 0.68$, $P < 0.05$ and 0.83, $P < 0.001$, resp.). The significant positive correlation between the content of Al extracted by $CuCl_2$ and that of SOC is in agreement with results reported by Barra et al. [54], for a wide range of Brazilian soils from the Rio de Janeiro State.

Strong positive correlations between the values of the difference between the Al extracted by $CuCl_2$ and $LaCl_3$ and between Al extracted by $CuCl_2$ and KCl with the SOC content were observed ($r = 0.70$ and 0.69, $P < 0.001$, resp.), while that between values of the difference between the Al extracted by $LaCl_3$ and KCl and SOC was not significant, suggesting stronger association of Al bound to organic matter as extracted by 0.5 M $CuCl_2$ rather than by the 0.33 M $LaCl_3$ in the studied soils. In fact, the surface and subsurface horizons of Luvisols (pedons 7 and 8) and pedon 11 (Regosol) with low SOC content (3–27 $\mathrm{g\,kg^{-1}}$) showed the lowest content of Al extracted by 1 M KCl, 0.33 M $LaCl_3$, and 0.5 M $CuCl_2$ (0.7–1.7, 1.3–3.8, and 1.8–4.1 $\mathrm{cmol_c\,kg^{-1}}$, resp.). Other studied soils containing high amount of SOC (36–80 $\mathrm{g\,kg^{-1}}$) also showed high content of Al by 1 M KCl, 0.33 M $LaCl_3$, and 0.5 M $CuCl_2$ (1.3–3.3, 2.0–4.4, and 3.5–13.5 $\mathrm{cmol_c\,kg^{-1}}$).

In Luvisols, the Al content may mostly be associated with high clay content, while, in other soils (mostly Umbrisols and Cambisols), Al content may be associated with organic matter content. In the latter, subsurface horizons with less SOC and similar clay contents showed higher contents of Al extracted by the 0.5 M $CuCl_2$ than the surface ones. This may be associated with a greater saturation of organic matter by Al in the subsurface horizons of Umbrisols and Cambisols, given their low SOC/Alp and $CuCl_2$-$LaCl_3$/$CuCl_2$ molar ratios (see Tables 2 and 3). The greater accumulation of fulvic acids reported for subsurface horizons [61] may support such hypothesis. Therefore, extracted Al by the 0.5 M $CuCl_2$ may be dependent on the organic matter type and its degree of saturation by Al.

In the surface horizons, the content of Al extracted by 1 M KCl was strongly correlated with Alo and Alp contents ($r = 0.74$ and 0.85, $P < 0.01$–0.001, resp.), while the correlation in the subsurface horizons was only observed with Alp ($r = 0.65$, $P < 0.05$). Similar trend was obtained between the content of Al extracted by $CuCl_2$, and Alo and Alp in the surface ($r = 0.85$ and 0.88, $P < 0.01$–0.001, resp.) and subsurface ($r = 0.84$ and 0.92, $P < 0.01$–0.001, resp.) horizons. Positive correlations of the content of Al extracted by 1 M KCl with Feo and Fep contents were also observed in both surface ($r = 0.77$ and 0.83, $P < 0.05$, resp.) and subsurface ($r = 0.76$ and 0.78, $P < 0.05$, resp.) horizons. There was also a positive correlation of the content of Al extracted by $CuCl_2$ with those of Feo and Fep in the surface ($r = 0.71$ and 0.75, $P < 0.05$, resp.) and subsurface ($r = 0.86$ and 0.90, $P < 0.001$, resp.) horizons.

Positive correlations of Al extracted by KCl and $CuCl_2$ with the aforementioned soil constituents suggest that different proportions of Al dissolved by each extractant may be associated with short-range ordered noncrystalline or amorphous Al oxides and Al layer silicates, and organically complexed forms of Al in studied soils [62]. In fact, the values of the Alo/Alp ratio in Luvisols and in some Umbrisols were less than 1, suggesting that high proportion of Al removed by studied extractants was associated with organic matter. However, this ratio was lesser compared to other studied soils (1.0–1.6).

Positive relationships of Alo, Alp, Feo, and Fep with the Al determined by used extractants suggest the essential role of Al and Fe constituents in the stabilization of SOC content in study soils [63, 64]. This process involved ligand exchange between mineral surface hydroxyl groups and negatively charged organic functional groups [65, 66]. The content of Al extracted by $CuCl_2$ in Luvisols accounted 36–69% of the Alp, while, in other soils rich in SOC, they were only 10–23%, suggesting that Al extracted by the $CuCl_2$ in the latter only represents a low proportion of that extracted by the pyrophosphate, which represents the forms of Al complexed with organic matter. Such low proportion may be associated with a high $CuCl_2$-$LaCl_3$/$CuCl_2$ molar ratio which was within the range reported by García-Rodeja et al. [33], for organic horizons of European volcanic soils areas.

3.4. Total Concentration of Ions in Unlimed Soil and Lime Effects. The differences in the total concentrations of basic and metallic ions in studied soil solutions as affected by the application of different rates of lime are shown in Tables 5 and 6. The total concentrations of Ca^{+2}, Mg^{+2}, K^+, and Na^+ ions in unlimed soils ranged 25–157, 2–24, 625–4020, and 67–195 μM L^{-1}, respectively, and increased significantly to 67–962, 31–150, 172–24605, and 108–310 μM L^{-1}, respectively, after the addition of 6 t lime ha^{-1} ($CaCO_3$). The total K^+ ion concentration was significantly higher than the others, which may be associated with the clay and soil organic C contents, corroborating trends to those reported by Hamdan et al. [67], for deeply weathered soils over granite from Peninsular Malaysia. The highest total concentrations of Ca^{+2} and K^+ ions were observed in the Ah horizon of pedon 7 (Luvisol) (962 and 24605 μM L^{-1}, resp.), while the highest total concentrations of Mg^{+2} and Na^+ ions were shown in the Ah horizon of pedon 11 (Regosol), with the application of 6 t lime ha^{-1}. The increase of Ca^{+2} ions in the soil solution may be partly attributed to the addition of Ca^{+2} from the liming agent, whereas the increase in Na^+ and K^+ and Mg^{+2} ions may be associated with the strong ability of Ca^{+2} to replace Mg^{+2} Na^+ and K^+ ions in the exchange complex. As a general trend, lime application increased the availability of basic cations which may be beneficial for crop use. However, in areas where soils are subjected to high precipitation conditions (i.e., in Umbrisols and Cambisols), these cations may be lost apparently due to leaching. The presence of these bases may not persist for long time as high rainfall conditions may easily subject them to eventually leach from these soils. Such conditions are evident on these soils showing low values of base cations (0.2–0.8 cmol$_c$ kg^{-1}) and base saturation degree (0.5–4%) associated with rainy conditions (mean annual precipitation of 1600–2400 mm) [3].

In unlimed soils, the total concentrations of Fe^{+3} (5–162 μM L^{-1}) and Al^{+3} (10-1116 μM L^{-1}) were higher than those of Mn^{+2}, Zn^{+2}, and Cu^{+2} (3–54, 1–110 and 0.1–1.3 μM L^{-1}, resp.), while total concentration of $SO_4{}^{-2}$ and $PO_4{}^{-3}$ ions ranged 398–6425 and 0.4–10 μM L^{-1}, respectively. In contrast to the basic cations, these ions in soil solution strongly decreased with increasing rates of lime application. Total Fe^{+3} concentration significantly reduced (1–9 μM L^{-1}, while those of Al^{+3}, Mn^{+2}, Zn^{+2}, Cu^{+2}, $SO_4{}^{-2}$, and $PO_4{}^{-3}$ ions were near and/or less than detection limits as determined by inductively coupled plasma atomic emission spectrometry (ICPAES). In the case of Al^{+3}, Cu^{+2}, and $SO_4{}^{-2}$ ions, they were not detected after the application of 2 t lime ha^{-1}. Such decrease of these ions may be associated with the increase in soil solution pH due to lime application. The decrease in the total concentration of Zn^{+2} and Cu^{+2} agrees with results reported by Nascimento [68], for limed Brazilian soils. Shuman [69] also reported a decrease in the total concentrations of Zn^{+2}, Mn^{+2}, and Fe^{+3} ions with increasing rates of calcium containing lime. Raising the pH to >5 markedly reduces the total concentrations of Mn^{+2} and Fe^{+3}, corroborating trends reported by Shamshuddin and Auxtero [70], for acid sulfate soils of Malaysia. The decrease in the $SO_4{}^{-2}$ and $PO_4{}^{-3}$ ligands in all studied soil solutions may be associated with the precipitation of these ligands with Ca^{+2} from the liming material ($CaCO_3$) applied.

3.5. Lime Effects on Soil Solution pH and Activities of Ions. The solutions of unlimed soils showed strongly acidic conditions (pH 4.5–5.0). Application of 2 t lime ha^{-1} ($CaCO_3$) has resulted in an increase in pH of the studied solutions. The lowest soil solution pH (4.5) observed in the Ah horizon of pedon 10 (Regosol) was raised to pH 6.9. In other studied soil solutions (pH 4.6–5.0), the pH was raised between 6.0 and 6.8.

The activities of ions in soil solutions, as speciated using the GEOCHEM program, are shown in Table 7. The activities of Ca^{+2}, Mg^{+2}, K^+, and Na^+ ions in unlimed soil solution ranged 32–133, 27–214, 30–187, and 108–313 μM L^{-1}, respectively. With the addition of 6 t lime ha^{-1}, the activities of Ca^{+2}, Mg^{+2}, K^+, and Na^+ ions significantly increased and ranged 74–588, 65–343, 1654–21750, and 200–2554 μM L^{-1}, respectively, suggesting increased availability of these cations. The high increase in the activities for Mg^{+2} and K^+ ions (588 and 21750 μM L^{-1}, resp.) was noted in the Ah horizons of pedon 7 (Luvisol) and in pedons 5 (Ah horizon) and 3 (Bt horizon), for Mg^{+2} and Na^+ ions (343 and 2554 μM L^{-1}, resp.), which conforms with the high sum of bases measured in these soils (Table 2). The increase in the activities of Ca^{+2} and Mg^{+2} ions may be attributed to the addition $CaCO_3$ as liming agents, while the increase in the activities of Na^+ and K^+ ions may have been enhanced by the replacement of these ions with Ca^{+2} on the exchange complex. Such results associated with lime application may be related to improve availability of basic cations, making them more available for crop use. However, in soils like Umbrisols and Cambisols, with high prevailing annual precipitation conditions (1800–2400 mm), these cations may be easily lost by leaching [3].

Unlimed soils showed that the activities of Al^{+3}, Mn^{+2}, and Zn^{+2} (15–418, 2–46, and 0.9–104 μM L^{-1}, resp.) were high compared to those of Fe^{+3}, Cu^{+2}, $SO_4{}^{-2}$, and $PO_4{}^{-3}$ ions which were less than detection limit by ICPEAS. The activities of free and soluble complexes of Al varied among

Table 5: Total concentration of calcium (Ca^{+2}), magnesium (Mg^{+2}), potassium (K^{+}), and sodium (Na^{+}) ions in unlimed (control) and limed studied soil solutions as determined by inductively coupled plasma atomic emission spectrometry. Means in the same horizon followed by different letters in column are significant at $P < 0.05$ by the Tukey test.

Pedon	Horizon	$CaCO_3$ added ($t\,ha^{-1}$)	Ca^{+2}	Mg^{+2}	K^{+}	Na^{+}
				($\mu M\,L^{-1}$)		
			Umbrisols			
1	Ah1	0	95.8a	8.2a	2450.3a	87.4a
		2	137.7b	17.3b	3522.4b	90.0b
		4	148.7b	27.9b	3803.1b	107.4b
		6	154.2b	48.6c	3943.5b	200.9c
3	Ah1	0	60.9a	8.2a	1556.9a	105.7a
		2	61.9a	9.1b	1582.5a	118.8a
		4	81.8b	9.9b	2093.0b	134.8b
		6	99.8c	130.0c	2552.4b	303.6c
4	Ah1	0	24.5a	1.6a	625.3a	31.3a
		2	32.9b	3.3b	842.3a	60.9b
		4	59.9c	6.6c	1531.5b	86.6c
		6	67.4d	59.3d	1722.9b	108.3d
			Cambisols			
5	Ah	0	30.9a	6.6a	791.3a	50.9a
		2	61.4b	14.8b	1569.8b	127.0b
		4	225.1c	15.6c	5755.8c	136.1b
		6	366.3d	83.9d	9367.5d	166.2c
6	Ah1	0	32.9a	4.9a	842.3a	58.3a
		2	75.3b	9.1b	1927.1b	91.8b
		4	93.3c	11.5b	2386.5c	133.9b
		6	154.7d	60.9c	3956.3d	141.4c
			Luvisols			
7	Ah	0	157.2a	23.9a	4020.1a	148.8a
		2	895.2b	25.5a	22895.4b	150.1a
		4	897.2b	35.5b	22946.4b	156.2a
		6	962.1c	94.7c	24605.0b	190.1b
8	Bt	0	69.4a	15.6a	1773.9a	89.2a
		2	82.8a	24.7b	2118.5b	118.3b
		4	197.6b	27.9b	5053.8c	142.2c
		6	546.4c	31.2c	13974.6d	280.9d
			Regosols			
10	Ah	0	38.4a	10.7a	982.7a	67.9a
		2	123.8b	15.6a	3165.0b	116.1b
		4	174.4c	24.7b	4901.6c	136.6c
		6	232.0d	110.3c	5934.4d	151.8d
11	Ah	0	82.8a	10.7a	2118.5a	194.9a
		2	86.8a	11.5a	2220.6a	203.6b
		4	163.2b	13.2a	4173.2b	207.5b
		6	434.1c	149.8b	11103.1c	309.7c

studied soils (Table 8). The dominant form of Al species in unlimed soils existed principally as Al^{+3} and as complexes of hydroxides, sulfate, and phosphate ions. The highest activity of free Al^{+3} ($418\,\mu M\,L^{-1}$) in unlimed soils was observed in the surface horizon of pedon 10 (Regosol), while that of $Al(OH)_2{}^{+}$ species ($171\,\mu M\,L^{-1}$) was noted in the Ah horizon of pedon 4 (Umbrisol). In contrast, the Ah horizon of pedon 8 (Luvisol) showed the lowest activities of Al^{+3}, $Al(OH)^{+2}$, and $Al(OH)_2{}^{+}$ species (15, 15, and $12\,\mu M\,L^{-1}$, resp.). The activities of monomeric forms of Al in unlimed Umbrisols, Cambisols, and Regosols (320–581, 201–298, and 383–588 $\mu M\,L^{-1}$, resp.) were higher than those measured for Luvisols (44–167 $\mu M\,L^{-1}$). Such activities (especially for free Al^{+3} species) may be potentially toxic to plants [14, 71]. In

Table 6: Total concentration of iron (Fe^{+3}), aluminium (Al^{+3}), manganese (Mn^{+2}), zinc (Zn^{+2}), sulfate (SO_4^{-2}), and phosphate (PO_4^{-3}) ions ($\mu M\,L^{-1}$) in unlimed (control) and limed studied soil solutions, as determined by inductively coupled plasma atomic emission spectrometry Symbol: DL: detection limit ($Al^{+3} = 0.25$, $Mn^{+2} = 0.03$, $Zn^{+2} = 0.06$, $SO_4^{-2} = 0.002$, and $PO_4^{-3} = 0.006\,\mu M\,L^{-1}$, resp.). Means in the same horizon followed by different letters in column are significant at $P < 0.05$ by the Tukey test.

Pedon	Horizon	$CaCO_3$ added ($t\,ha^{-1}$)	Fe^{+3}	Al^{+3}	Mn^{+4}	Zn^{+2} ($\mu M\,L^{-1}$)	Cu^{+2}	SO_4^{-2}	PO_4^{-3}
				Umbrisols					
1	Ah1	0	22a	1046	30a	3a	0.3	404	1a
		2	6b	<DL	2b	0.9b	<DL	<DL	0.8b
		4	5b	<DL	1b	0.6b	<DL	<DL	0.7b
		6	3b	<DL	0.4b	0.5b	<DL	<DL	0.3b
3	Ah1	0	202a	444	13a	2a	0.2	510	2
		2	2b	<DL	1b	2a	<DL	<DL	<DL
		4	2b	<DL	0.4b	0.9b	<DL	<DL	<DL
		6	1b	<DL	<DL	<DL	<DL	<DL	<DL
4	Ah1	0	30a	785	3a	2a	0.7	883	10a
		2	2b	<DL	0.4b	0.6b	<DL	<DL	1.0b
		4	1b	<DL	<DL	0.6b	<DL	<DL	0.7b
		6	1b	<DL	<DL	<DL	<DL	<DL	<DL
				Cambisols					
5	Ah	0	5a	134	54a	2a	0.2	6425	3a
		2	2b	<DL	1b	0.6b	<DL	<DL	0.5b
		4	2b	<DL	1b	0.5b	<DL	<DL	0.3b
		6	1b	<DL	0.4b	<DL	<DL	<DL	<DL
6	Ah1	0	9a	280	32a	4	0.2	4466	2a
		2	3b	<DL	1b	1	<DL	<DL	0.1b
		4	2b	<DL	<DL	<DL	<DL	<DL	0.1b
		6	2b	<DL	<DL	<DL	<DL	<DL	<DL
				Luvisols					
7	Ah	0	23a	178	23a	2a	0.3	794	3
		2	13b	<DL	0.4b	0.6b	<DL	<DL	0.4
		4	12b	<DL	<DL	<DL	<DL	<DL	<DL
		6	9b	<DL	<DL	<DL	<DL	<DL	<DL
8	Bt	0	11a	10	15a	2a	0.1	398	7a
		2	4b	<DL	3b	1a	<DL	<DL	1b
		4	3b	<DL	2b	0.6	<DL	<DL	0.9b
		6	2b	<DL	<DL	<DL	<DL	<DL	0.7b
				Regosols					
10	Ah	0	162a	1116	50a	110a	1.3	5992	0.4a
		2	4b	<DL	6b	8b	<DL	<DL	0.3a
		4	3b	<DL	0.7b	0.6c	<DL	<DL	0.1a
		6	2b	<DL	0.4b	0.6c	<DL	<DL	<DL
11	Ah	0	23a	501	38a	1a	0.2	489	1a
		2	18b	<DL	2b	0.6b	<DL	<DL	0.4b
		4	11b	<DL	1b	<DL	<DL	<DL	0.4b
		6	5b	<DL	0.4b	<DL	<DL	<DL	0.2b

fact, a study of Cameron et al. [72] showed a decreased in root growth of barley seedlings with $>10\,\mu M\,L^{-1}$ activity of Al.

With the application of increasing rates of lime, the activities of free and soluble complexes of Al in all studied solutions were markedly altered. In acid soils, the beneficial effects of liming are often largely associated with the inactivation of the Al present in the soil [73]. Our results showed that addition of 2 t lime ha^{-1} showed no measurable activities of Al^{+3} and Al soluble complexes. This is in agreement with the results of Pavan et al. [74], who reported alteration of the distribution of Al species in Ultisols and Oxisols by

Table 7: Values of soil solution pH, and activities of calcium {Ca^{+2}}, magnesium {Mg^{+2}}, potassium {K^{+}}, sodium {Na^{+}}, iron {Fe^{+3}}, manganese {Mn^{+2}}, zinc {Zn^{+2}}, and sulfate {SO_4^{-2}} ions (μM L^{-1}) in unlimed (control) and limed studied soil solutions, as speciated by the GEOCHEM program. Symbol: DL: detection limit. Values followed by the same letter in column are not significantly different at $P < 0.05$ level.

Pedon	Horizon	$CaCO_3$ added ($t\,ha^{-1}$)	pH	{Ca^{+2}}	{Mg^{+2}}	{K^{+}}	{Na^{+}}	{Fe^{+3}}	{Mn^{+2}}	{Zn^{+2}}	{SO_4^{-2}}
				(μM L^{-1})							
Umbrisols											
1	Ah1	0	4.6	118.9a	213.8a	187.3a	200.4a	$7.07E-05$	34.9a	2.2a	5.58
		2	5.0	124.0b	250.0b	3320.0b	273.4b	<DL	1.2b	0.5b	<DL
		4	5.8	193.9c	255.7b	3570.0c	288.9b	<DL	0.9c	0.4b	<DL
		6	6.0	280.2d	268.2c	3694.0d	366.2c	<DL	0.2d	0.2b	<DL
3	Ah1	0	4.9	88.4a	62.7a	59.2a	313.2a	$7.99E-05$	9.7a	1.4a	0.11
		2	5.0	135.1b	116.1b	1513.0b	400.3b	<DL	0.6b	1.3a	<DL
		4	6.4	149.4c	123.2c	1993.0b	414.1b	<DL	0.3c	0.7b	<DL
		6	6.6	161.6d	145.6d	2421.0c	477.6b	<DL	<DL	<DL	<DL
4	Ah1	0	4.8	58.1a	52.1a	67.5a	108.4a	$1.60E-05$	2.3a	2.2a	17.40
		2	6.6	64.1b	55.6a	815.9b	155.8b	<DL	0.3b	0.5b	<DL
		4	6.8	68.4b	65.6b	1473.0c	179.5b	<DL	<DL	0.5b	<DL
		6	6.9	74.2c	75.8c	1654.0c	200.0c	<DL	<DL	<DL	<DL
Cambisols											
5	Ah	0	4.7	37.8a	99.6a	69.6a	138.9a	$3.49E-06$	45.9a	1.6a	9.61
		2	6.2	51.7b	180.9b	1504.0b	217.5b	<DL	0.9b	0.5b	<DL
		4	6.4	170.4c	239.1c	5370.0c	220.3b	<DL	0.8b	0.4b	<DL
		6	6.5	259.8d	343.3d	8597.0d	244.3b	<DL	0.2c	0.4b	<DL
6	Ah1	0	4.6	65.7a	53.2	34.6a	142.8a	$6.57E-05$	24.5a	3.9a	9.62
		2	6.4	69.7a	58.4	1849.0b	184.0b	<DL	0.6b	0.9b	<DL
		4	6.6	77.8b	59.6	2281.0c	223.6c	<DL	<DL	<DL	<DL
		6	6.8	123.6c	64.7	3741.0d	228.2c	<DL	<DL	<DL	<DL
Luvisols											
7	Ah	0	5.2	133.1a	80.4a	107.3a	186.2a	$1.08E-06$	17.8a	1.2a	0.47
		2	6.2	557.6b	78.2a	2034.0b	222.2b	<DL	0.2b	0.4b	<DL
		4	6.6	558.0b	140.0b	20370.0c	227.4b	<DL	<DL	<DL	<DL
		6	6.8	587.8b	180.0c	21750.0c	256.5b	<DL	<DL	<DL	<DL
8	Bt	0	5.3	72.1a	27.4a	29.9a	277.30	$3.91E-06$	11.5a	1.0a	0.48
		2	5.5	75.8a	46.4b	1702.0b	305.50	<DL	2.2b	0.5b	<DL
		4	6.0	154.0b	52.9c	4749.0c	321.60	<DL	1.4c	0.5b	<DL
		6	6.2	373.1	213.6d	12700.0d	2554.00	<DL	<DL	<DL	<DL
Regosols											
10	Ah	0	4.5	31.8a	95.89a	89.8a	151.4a	$1.41E-04$	37.9a	103.7a	4.54
		2	5.1	100.6b	96.06a	3006.0b	160.3a	<DL	4.7b	6.7b	<DL
		4	5.6	147.1c	120.83b	1823.0c	190.9a	<DL	0.6c	0.5c	<DL
		6	6.1	177.8d	184.51c	5552.0d	242.0b	<DL	0.2c	0.5c	<DL
11	Ah	0	5.1	71.7a	130.7a	137.3a	308.1a	$2.03E-06$	29.2a	0.9a	<DL
		2	6.4	73.4a	174.9b	2118.0b	194.1b	<DL	1.2b	0.5b	<DL
		4	6.5	130.6b	244.9c	3947.0c	196.2b	<DL	0.8b	<DL	<DL
		6	6.6	302.9c	294.0c	10150.0d	283.7c	<DL	0.3b	<DL	<DL

decreasing the concentration of Al^{+3} and Al bound with OH^{-} groups. There was also a reduced activities of $Al(OH)_3^{0}$ and $Al(OH)_4^{-}$, which is also in agreement with the findings of Liu et al. [35], for acid natural waters and Vieira et al. [37], for acidic soils. Calculated activities of soluble complexes of Al bound to inorganic ligands ($AlSO_4^{-}$ and $AlPO_4^{-}$ species) were also not detected after the addition of 2 t lime ha^{-1}, which may not pose toxic effects in soils [15, 75]. The low activity of $AlPO_4^{-}$ species may be ascribed to its precipitated or poorly reversible form. This fact corroborates

TABLE 8: Activities of soluble complexes of Al (μM L^{-1}) in unlimed (control) studied soil solutions, as speciated by the GEOCHEM program.

Pedon	Horizon	Free Al^{+3}	$Al(OH)^{+2}$	$Al(OH)_2{}^+$	$Al(OH)_3{}^0$	$Al(OH)_4$	$AlSO_4{}^+$	$AlPO_4{}^-$	Al_{mono}
				Umbrisols					
1	Ah1	375.7	150.0	46.8	0.4	0.01	7.4	0.6	580.8
3	Ah1	137.0	108.0	68.5	1.1	0.11	3.3	2.0	320.0
4	Ah1	269.0	171.0	84.2	1.1	0.09	5.6	8.6	539.5
				Cambisols					
5	Ah	173.2	86.1	34.5	0.4	0.02	3.3	0.4	297.9
6	Ah1	128.6	51.7	16.2	0.1	0.01	2.7	1.7	201.1
				Luvisols					
7	Ah	32.9	61.1	67.8	2.1	0.44	0.1	2.5	166.9
8	Ah	14.8	14.9	11.7	0.2	0.03	0.3	2.4	44.3
				Regosols					
10	Ah	418.4	133.0	33.1	0.2	0.01	2.5	0.3	587.5
11	Ah	107.5	137.0	134.0	3.4	0.55	0.1	1.0	383.4

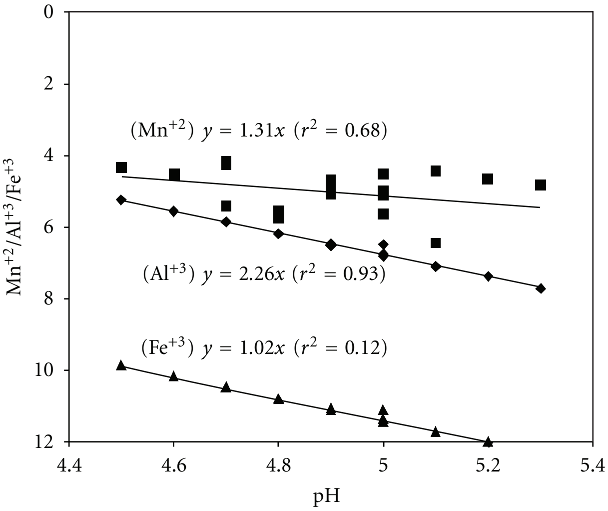

FIGURE 1: Concentration of Mn^{+2}, Fe^{+3}, and Al^{+3}(−log) in soil solution in relation to pH in unlimed soils.

with the trends reported by Hairiah et al. [76] for acid soils. The capacity of $CaCO_3$ to increase pH of soil solution as reported by Kleber et al. [65] and therefore eliminating the detrimental effects Al^{+3} and Al soluble complexes is in agreement with the studies of Haynes [20] and Mokolobate and Haynes [21], who reported that application of lime reduces the activities of metallic ions and may eliminate the yield-limiting effects of Al for most agronomic field crops.

The activities of other ions (Fe^{+3}, Mn^{+2}, Zn^{+2}, Cu^{+2}, $SO_4{}^{-2}$, and $PO_4{}^{-3}$) also decreased with increasing rates of lime application. Such decrease in the activities may be associated with increased soil solution pH. In fact, the activities of Mn^{+2} and Zn^{+2} ions showed significant negative correlations with soil solution pH ($r = -0.75$ and -0.35, $P > 0.05$, resp.). Positive correlation ($r = 0.93$, $P > 0.05$) of soil solution pH was stronger with the activities of Al^{+3} ions than with those of Fe^{+3} and Mn^{+2} ions (Figure 1). Application of 2 t lime ha^{-1} raised the pH above 5, and, at these conditions, no activities of Al^{+3}, Fe^{+3}, Cu^{+2}, $SO_4{}^{-2}$, and $PO_4{}^{-3}$ ions were measurable. The reduced activity of Fe^{+3} ion may be due to precipitation as $Fe(OH)_3$ in soil solution [77]. There were also negligible activities of Mn^{+2} and Zn^{+2} ions when soil solution pH was raised above 6 after 2 t lime ha^{-1} application. The decrease in the activities of $SO_4{}^{-2}$ and $PO_4{}^{-3}$ ions below detection limit by ICPAES suggests that these anions may be less available for crop use in limed soils.

4. Conclusions

The distribution of Al determined by various extractants was in the order: 0.5 M $CuCl_2$ > 0.33 M $LaCl_3$ > 1 M KCl, ranged from 1.8–13.5, 1.3–4.4, and 0.7–3.0 cmol$_c$ kg^{-1}, respectively. These contents were positively correlated with the values of cation exchange capacity and contents of total organic C, clay, forms of amorphous and organically bound aluminium and iron in the surface horizons. Application of lime (6 t $CaCO_3$ ha^{-1}) significantly increased the total concentrations and activities of Ca^{+2}, Mg^{+2}, K^+, and Na^+ ions and significantly reduced those of free Fe^{+3}, Cu^{+2}, Mn^{+2}, Zn^{+2}, and Al^{+3} ions, and soluble complexes of Al in the soil solution. The activities of monomeric Al species were lower in Luvisols associated with low contents of soil organic C than other soils. Such activities exceed the levels corresponding to the toxicity threshold for Al but were reduced to negligible levels with the application of 2 t $CaCO_3$ ha^{-1} application. Future study may focus on the yield limiting effects of Al and the beneficial effects of lime in reducing the concentrations and activities of metallic ions of free Al and soluble complexes of Al in soil solution in some agronomic test crops grown on these soils.

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