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Acidity control in Latosols under long-term pastures in the Cerrado region, Brazil

P. R. S. Vendrame[A,F], *O. R. Brito*[B], *E. S. Martins*[C], *C. Quantin*[D], *M. F. Guimarães*[B], and *T. Becquer*[E]

[A]Department of Geosciences, State University of Londrina, 86051-970, Londrina, PR, Brazil.
[B]Department of Agronomy, State University of Londrina, 86051-970, Londrina, PR, Brazil.
[C]Empresa Brasileira de Pesquisa Agropecuária (Embrapa Cerrados), BR 020, km 18, 73310-970, Planaltina, DF, Brazil.
[D]UMR 8148 IDES, Univ. Paris Sud - CNRS, 91405 Orsay Cedex, France.
[E]IRD, UMR 210 Eco&Sols, 2 Place Viala, F-34060 Montpellier Cedex 2, France.
[F]Corresponding author. Email: vendrame@uel.br

Abstract. High acidity and aluminium saturation are among the main limiting factors for crop production in tropical soils. The aim of this work was to measure the acidity of Latosols under pastures in the Brazilian Cerrado and to assess the influence of clay mineralogy as a controlling parameter of soil acidity. Topsoils ($n = 73$, 0–0.2 m depth) of Latosols developed on different parent materials were sampled in two sub-regions of the Cerrado region. The main chemical characteristics were determined by standard procedures, and kaolinite and gibbsite contents were determined by dissolution with sulfuric acid and thermogravimetric analyses. The exchangeable concentrations of calcium (Ca), magnesium (Mg), and potassium (K) varied considerably among soil samples, with ranges of 0–13.9 $cmol_c\,kg^{-1}$ (mean ± standard deviation 1.77 ± 1.91 $cmol_c\,kg^{-1}$) for Ca; 0.2–3.2 $cmol_c\,kg^{-1}$ (1.13 ± 0.68 $cmol_c\,kg^{-1}$) for Mg; and 0–1.0 $cmol_c\,kg^{-1}$ (0.24 ± 0.24 $cmol_c\,kg^{-1}$) for K. The mean concentration of exchangeable aluminium (Al) was 0.55 ± 0.61 $cmol_c\,kg^{-1}$ (range 0–2.3 $cmol_c\,kg^{-1}$). The content of kaolinite (282 ± 96 $g\,kg^{-1}$) was higher than of gibbsite (106 ± 77 $g\,kg^{-1}$). The amount of exchangeable Al and Al saturation rate varied according to the mineralogy of the clay fraction of the soils. The content of exchangeable Al^{3+} remained low when gibbsite was the predominant mineral, whereas it increased with kaolinite content. The ratio kaolinite/(kaolinite + gibbsite) could be used as a useful indicator of the sensitivity of soils affected by acidity and Al toxicity.

Additional keywords: Brazilian Cerrado soils, gibbsite, kaolinite, protonation, soil acidification.

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Introduction

Vast areas throughout the tropics have lost their natural vegetation to make way for pastures in recent decades (McAlpine *et al*. 2009). This is particularly true of the Cerrado Region of Brazil (Brossard and Barcellos 2005). The Cerrado is the second largest Brazilian biome, with high plant and animal biodiversity, and ranks twelfth on a list of global 'hot spot' areas that contain high levels of plant endemism (Mittermeier *et al*. 1998). Indeed, the Cerrado's biodiversity is estimated at 160 000 species of plants, fungi, and animals (Ratter *et al*. 1997). It is a vast, tree-rich savannah, mainly located in the states of Goiás and Minas Gerais on the Brazilian high Plateau, and is one of the most endangered ecosystems in South America, notably due to land clearing for pasture and intensive agriculture. Latosols occupy ~45% of the area of the Cerrado region (Adamoli *et al*. 1985), and although the Cerrado soils were for a long time considered rather unproductive, the region has been the focus of intense agricultural expansion since the 1970s. Cultivated pastures cover 54 million ha of the Cerrado region, representing 80% of the total area used for agriculture in this region (Sano *et al*. 2008). Consequently, the Cerrado ecoregion is under threat.

Most of the cattle production in the region is based on extensive pasture systems (Boddey *et al*. 2004; Brossard and Barcellos 2005), due to low beef prices and the high cost of lime and fertilisers, and also for sociological reasons such as securing land tenure and preventing land speculation. In the Cerrado region, the pastures were established after clearing the native vegetation, application of lime and fertilisers, and 1 or 2 years of grain cropping, usually upland rice. Thereafter, it is rare for landowners to apply any fertilisation with nitrogen (N), phosphorus (P), and/or potassium (K) in pastures (Pereira *et al*. 2009).

The high biomass productivity of the introduced grass species, combined with low fertiliser inputs, has resulted in major declines in soil chemical, physical, and biological quality. Thus, estimates show that 80% of the pastures are on soils with various levels of degradation, exhibiting low productivity (Lilienfein *et al*. 2003; Brossard and Barcellos 2005).

High acidity and aluminium (Al) saturation are among the main limiting factors for crop production in tropical soils (Sanchez *et al*. 1982; Abreu *et al*. 2003). Soil acidification is a naturally occurring phenomenon (Van Breemen *et al*. 1983), resulting in the loss of large amounts of 'basic' alkali and alkali-earth cations by leaching, to be replaced by acidic ions such as Al^{3+} and H^{+} (Krishnaswamy and Richter 2002). Noble *et al*. (2008) assumed that acidification at depths below 20 cm is increased by the highly productive grass species due to their uptake of excess cations, resulting in a net excretion of protons to maintain plant electro-neutrality. Although the export of basic cations by pastures is low (equivalent to 40–90 kg $CaCO_3$ ha^{-1} year^{-1}) compared with cereal–legume rotations (135–169 kg $CaCO_3$ ha^{-1} year^{-1}) (Slattery *et al.*1991), the poor adoption of liming in these grazing systems has led to a decrease in basic cation content and a consequent increase in soil acidity. Surface addition of lime can cause problems in pastures. It leads mostly to the stratification of the profile, with a 1–2 cm topsoil generally less acidic than the soil below (Scott *et al.*2000), and hence a decrease in phosphorus (P) and micronutrient availability, due to higher retention in soils with variables charges (Van Ranst *et al*. 1998).

Pasture soil degradation through acidification is a widespread problem at the continental scale (Scott *et al*. 2000). However, we lack a clear understanding of its extent in the Cerrado region and of the soil types most sensitive to acidification, which is needed to improve future management strategies. In highly weathered Latosols, the potential capacity to take up protons, i.e. the potential acid-neutralising capacity, is mainly due to cation desorption and to primary and secondary mineral weathering (Watanabe *et al*. 2008). Whereas primary minerals release Al to the soil solution through irreversible chemical weathering, which is kinetically limited, secondary solid phases, i.e. kaolinite and gibbsite in Latosols, may control dissolved Al in the short term through dissolution–precipitation equilibrium (Gustafsson *et al*. 2001). In order to improve understing of the factors controlling acidity in the Cerrado Latosols, the aims of this work were: (*i*) to assess the acidity levels of Latosols under pasture in the Brazilian Cerrado; (*ii*) to determine the influence of clay mineralogy as a controlling parameter of soil acidity.

Materials and methods

Study sites

The dominant climate in the Cerrado region is megathermic or humid tropical (Aw) according to the Köppen classification (Köppen 1931), and is characterised by temperatures in the coolest month >22°C and precipitation in the driest month of <60 mm. Mean annual rainfall ranges from 1500 to 2000 mm, with the highest rainfall in December–March and the lowest in May–September.

The geomorphology of the Cerrado Region on the Central Plateau of Brazil has been presented by Braun (1971) and reviewed by Motta *et al*. (2002). The region corresponds to two main geomorphic surfaces, the South American surface (SAS) and the Velhas surface (VS). The SAS corresponds to a vast peneplain produced at the end of the Cretaceous. During the Tertiary, tectonic uplift and sea regression initiated erosion and carved new valleys, exposing older underlying rocks and sediments to weathering and resulting in new erosion surfaces (VS).

We selected two subregions dominated by cultivated pasture and sharing the common geomorphic features described above, but differing in the underlying geology and therefore in soil parent materials. The areas investigated are in the Tocantins Province, a Neoproterozoic orogenic area, corresponding to the metasedimentary fold belts known as the Brasília and Paraguay fold belts (Pimentel *et al*. 1996; D'el-Rey Silva and Barros Neto 2002). Subregion A, namely the area between the towns of Goiânia, Goiás State, and Barra do Garças, Mato Grosso State, is near the Paraguay belt deposited on the southern margin of the Amazon craton. Subregion B, namely the north-east Minas Gerais region comprising the cities of Unaí and Paracatu, is on the eastern edge of the Brasilia fold belt over the Vazante and Paracatu formations (Dardenne 1979), on the western edge of the São Francisco craton. In summary, two main lithological associations are recognised in the 'metamorphic basement' in subregion A (Pimentel *et al*. 1996): (*i*) Archean and Neoproterozoic calcic to calco-alkaline, plutonic orthogneisses, varying in composition from tonalitic to granitic; and (*ii*) Neoproterozoic metavolcanic–metasedimentary sequences made of metavolcanic rocks ranging in composition from low-K metatholeiites to metarhyolites. A group of high-K granite intrusions was emplaced into the orthogneisses and metavolcanic–metasedimentary sequences. These Precambrian terrains are partially covered by the Phanerozoic sedimentary rocks of the Paraná Basin. Subregion B is included in the external zone of the Brasilia belt, corresponding mainly to the Meso-Neoproterozoic formations of the Canastra group, which is mainly composed of quartzites and schists, and to the Vazante group, which is mainly composed of dolomites and metasiltites.

The main soil classes present in the studied subregions (Radambrasil 1983) are Latosols and Argisols in the Brazilian Soil Taxonomy (Santos *et al*. 2006), which correspond roughly to Oxisols and Ultisols, respectively, in Soil Taxonomy (Soil Survey Staff 1998). In the Cerrado Region, the main factor differentiating these two soil classes is the relief. Latosols are commonly on flat or slightly undulating land, whereas Argisols are usually found on steeper terrain.

Soil sampling and analysis

The sampling sites were selected with the purpose of sampling only Latosols under pasture (Fig. 1). The soil samples were collected from flat or fairly even landscapes. We chose sites that had received as little human disturbance as possible and were >100 m away from roads. Topsoils (n = 73, 0–0.2 m depth) were sampled with an Edelman auger. Two augerings were carried out at each sampling site, and the samples were mixed to create a single composite sample. Deeper horizons (0.6–0.8 m) were also sampled in order to verify that all of the soils were Latosols (data not shown). These soils were ascribed to Latosols based on field observations, namely the presence of

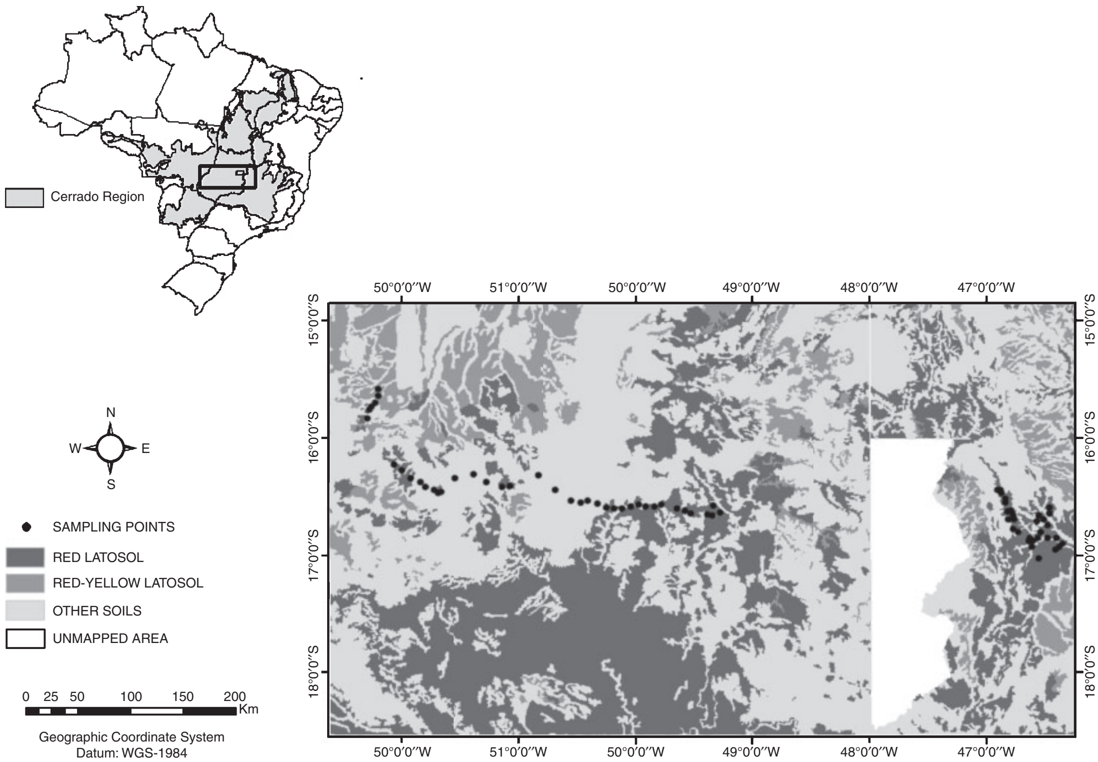

Fig. 1. Cerrado region in central Brazil and detail showing the study areas and the sampling points (ANEEL 1999).

a *latosolic horizon* (similar to the Ferralic horizon; IUSS Working Group WRB 2006), namely a subsurface horizon resulting from a long and intense weathering in which the clay fraction is dominated by low-activity clays such as kaolinite and iron (Fe) and Al (hydr)oxides), and on some analytical determinations made on the B_w horizons (particle size distribution and SiO_2/Al_2O_3 molecular ratio, Ki and $SiO_2/Al_2O_3 + Fe_2O_3$ molecular ratio, Kr) (data not shown). Full details of the site locations and soil classification were described by Vendrame (2005).

Physical and chemical analyses of soils were performed on air-dried material <2 mm. Particle size distribution was determined using the pipette method after dispersing with 1 N NaOH. The pH was measured in 0, 01 M $CaCl_2$ and in 1 M KCl suspensions using 1 : 2.5 (w : v) soil : solution ratio. Total carbon (C) was analysed by dry combustion in a 2400 CHN Analyzer (PerkinElmer Inc., Waltham, MA). Exchangeable Ca^{2+}, Mg^{2+} and Al^{3+} were extracted with 1 M KCl. Determination of Ca^{2+} and Mg^{2+} was by titration with EDTA solution (0.0125 N) and Al^{3+} by titration with 0025 N NaOH. Available K^+ was extracted with Mehlich-1 solution (0.0125 mol L^{-1} of H_2SO_4 + 0.050 mol L^{-1} of HCl) and determined by flame spectrophotometry; H^+ and Al^{3+} were extracted with a pH 7.0 oxalate/oxalic acid buffer and determined by titration with 0.060 N NaOH.

Standard cation exchange capacity (CEC_{pH_7}) was determined as the sum of Ca^{2+}, Mg^{2+}, K^+, H^+, and Al^{3+}; exchangeable bases (EB) as the sum of Ca^{2+}, Mg^{2+}, and K^+; effective cation exchange capacity (ECEC) as the sum of Ca^{2+}, Mg^{2+}, K^+, and Al^{3+}; base saturation (V) as $EB/CEC_{pH_7} \times 100$; and aluminium saturation (m) as $Al^{3+}/ECEC \times 100$.

The mineralogical constituents were evaluated using sulfuric acid extraction (SAE) and thermogravimetric analysis (TGA). Total contents of Fe_2O_3, Al_2O_3, and SiO_2 were measured by inductively coupled plasma-atomic emission spectroscopy after extraction with sulfuric acid (1 : 1 distilled water/concentrated H_2SO_4 volume ratio), corresponding to a 9.38 M concentration. This acid dissolves the clays, Fe oxyhydroxides, and Al hydroxides. Contents of kaolinite, gibbsite, and iron oxides (goethite and hematite) were then calculated according to Reatto *et al.* (2009). Kaolinite and gibbsite contents were also determined by TGA with a TGA-50 Analyzer (Shimadzu Corp., Kyoto) using 10 mg of finely crushed soil. Analyses were conducted from 25 to 625°C under a nitrogen atmosphere, and gibbsite (using the theoretical water loss of 31.2%) and kaolinite (theoretical water loss of 14.0%) as well as the ratio kaolinite/(kaolinite + gibbsite) (R_{KGb}) were deduced (Melo *et al.* 2001).

The data were submitted to descriptive statistical analyses (SigmaPlot, v. 7.0; SPSS Inc., Chicago, IL) to obtain the mean, standard deviation (s.d.), amplitude of the variations (minimum and maximum), first and third quartile, median, and skewness and kurtosis values, and to perform the Shapiro–Wilk test. The correlation pattern was analysed by principal component analysis (PCA) in order to relate chemical variables associated with soil acidity and the overall dependent chemical and mineralogical variables, using ADE-4 software (Thioulouse *et al.* 1997). This analysis makes it possible to take into account simultaneously co-variations between all studied soil variables and, according to Gomes *et al.* (2004), is an appropriate tool for comparison and understanding of differences and similarities in different soil environments. After this, we tested multiple regressions to linked exchangeable Al with pH and mineralogy. The data were transformed to their logarithm plus 0.5 ($\log x + 0.5$) to improve homoscedasticity or homogeneity of variance. Although this transformation did not normalise the distributions of all datasets, they were substantially improved in nearly every case.

Results

Physico-chemical properties

The main physico-chemical properties of the soils are shown in Table 1. The clay content of the soils ranged from 150 to 770 g kg^{-1}, so the texture varied from sandy to heavy clay. Soils were generally acidic, with the pH_{CaCl_2} ranging from 3.4 to 5.7 and pH_{KCl} from 3.5 to 6.7, with means of 4.4 ± 0.5 and 4.7 ± 0.7, respectively. The value of the third quartile was 4.7 for pH_{CaCl_2}, indicating that most of the soils sampled have a level of acidity considered moderate for most tropical crops, and 25% (first quartile) have values considered too low (pH_{CaCl_2} <4.0).

The C content varied from 3.3 to 33.5 g kg^{-1} with a mean of 14.4 ± 6.1 g kg^{-1}. The positive correlation between C content and CEC_{pH_7} ($r = 0.64$, $P < 0.001$) emphasises the important contribution of soil organic matter (SOM) to the exchange properties of these soils. Sá *et al.* (2009) reported that SOM contributed 70–90% of the total CEC in other Brazilian Latosols.

The exchangeable contents of Ca^{2+} and Mg^{2+} and available K^+ varied considerably among samples, with ranges of 0–13.9 $cmol_c$ kg^{-1} for Ca, 0.2–3.2 $cmol_c$ kg^{-1} for Mg, and 0–1.0 $cmol_c$ kg^{-1} for K^+. The means for Ca^{2+}, Mg^{2+}, and K^+ were 1.77 ± 1.91, 1.13 ± 0.68, and 0.24 ± 0.24 $cmol_c$ kg^{-1}, respectively. Although 25% of the samples had values of Ca^{2+} above 2.39 (third quartile value), most had very low values of exchangeable Ca^{2+}. The wide variation in exchangeable Ca^{2+} and Mg^{2+} contents may be related to the fact that samplings were conducted on soils under pasture of various landowners, which may or may not have been subjected to lime application. The wide ranges of EB (0.2–7.3 $cmol_c$ kg^{-1}), ECEC (0.2–8.9 $cmol_c$ kg^{-1}), CEC_{pH_7} (1.2–13.8 $cmol_c$ kg^{-1}), and V (4.9–89.7%) values also emphasised the probable effects of liming, with cases of excessive liming in some instances.

Mean exchangeable Al^{3+} was 0.55 ± 0.61 $cmol_c$ kg^{-1}, with a range of 0–2.3 $cmol_c$ kg^{-1}. The potential acidity (exchangeable $H^+ + Al^{3+}$) ranged from 0.6 to 6.5 $cmol_c$ kg^{-1} with a mean of 2.8 ± 1.4 $cmol_c$ kg^{-1}. The Al^{3+} saturation ranged from 0 to 76% with a mean of 27 ± 25%. Under natural soils, Lopes and Cox (1977) reported that the mean Al saturation was 59% for the Cerrado region. This parameter also shows the effectiveness of liming in the soils under pastures. The pH_{CaCl_2} and exchangeable Al^{3+} content were significantly negatively correlated ($r = -0.73$, $P = 0.0001$), as were pH_{CaCl_2} and m (exchangeable Al saturation) ($r = -0.65$, $P = 0.0001$), whereas pH_{CaCl_2} and V (base saturation) were significantly positively correlated ($r = 0.70$, $P = 0.0001$). The increase in soil pH led to a decrease in exchangeable Al^{3+} (Fig. 2) according to equation: $Al^{3+} = 379.95*10^{(-0.67*pH\ CaCl_2)}$.

Mineralogy

The total values of SiO_2, Al_2O_3, and Fe_2O_3 varied considerably among samples, with ranges of 46–200 g kg^{-1} for SiO_2, 39–239 g kg^{-1} for Al_2O_3, and 14–325 g.kg^{-1} for Fe_2O_3 (Table 2). The corresponding means and standard deviations were 108 ± 42, 155 ± 47 and 75 ± 43 g kg^{-1}, respectively. The mean contents of kaolinite, gibbsite, goethite, and hematite, calculated according to Reatto *et al.* (2009), were 233, 98, 70, and 14 g kg^{-1}, respectively. The mean contents of kaolinite and gibbsite determined by TGA were 282 and 106 g kg^{-1}, respectively. Paired *t*-tests suggested non-significant differences for both kaolinite and gibbsite estimates between the two estimation modes, with correlations of 0.77 ($P = 0.0001$) for kaolinite and 0.80 ($P = 0.0001$) for gibbsite.

In contrast to Fe_2O_3 content, the Fe-oxide (i.e. goethite and hematite) content varied little, with range 47–85 g kg^{-1} for goethite and 12–16 g kg^{-1} for hematite in 50% of the samples. Only three soil samples showed values >25% of goethite + hematite. The kaolinite and gibbsite concentrations varied greatly, with a kaolinite/(kaolinite + gibbsite) ratio, i.e. R_{KGb} (Melo *et al.* 2001), calculated from the TGA, ranging from 0.45 to 0.94 (Table 2). The R_{KGb} values calculated by the two methodologies were also highly correlated ($r = 0.81$, $P = 0.0001$). Almost half of the soil samples (32) are considered gibbsitic according to the IUSS Working Group WRB (2006)

Table 1. Clay content and chemical characteristics of the upper horizons (0–0.2 m) of Latosols under pasture in the Brazilian Cerrado region
EB, Exchangeable bases ($Ca^{2+} + Mg^{2+} + K^+$); CEC_{pH_7}, cation exchange capacity ($EB + H^+ + Al^{3+}$); ECEC, effective CEC ($EB + Al^{3+}$); V, bases saturation (EB/CEC_{pH_7}) × 100; m, aluminium saturation (Al/ECEC) × 100; s.d., standard deviation; Swilk, Shapiro–Wilk test

Variables	Clay	C	pH_{CaCl_2}	pH_{KCl}	Ca^{2+}	Mg^{2+}	K^+	Al^{3+}	$H^+ + Al^{3+}$	EB	ECEC	CEC	V	m
	(g kg^{-1})							($cmol_c$ kg^{-1})					(%)	
Min.	150	3	3.40	3.52	0.00	0.17	0.03	0.00	0.55	0.18	0.24	1.21	4.93	0.00
Max.	770	34	5.70	6.71	13.91	3.18	0.96	2.33	6.50	7.31	8.92	13.81	89.65	75.80
Mean	442	14	4.35	4.73	1.77	1.13	0.24	0.55	2.79	1.91	2.47	4.70	37.07	26.70
s.d.	162	6	0.52	0.68	1.91	0.68	0.24	0.61	1.36	1.71	1.70	2.28	19.70	24.52
Median	430	15	4.20	4.47	1.40	0.94	0.13	0.34	2.67	1.19	2.45	4.41	30.30	18.05
1st Qu	310	9	4.00	4.28	0.64	0.65	0.08	0.07	1.67	0.73	1.05	2.91	22.71	38.68
3rd Qu	563	18	4.70	5.05	2.39	1.41	0.34	0.82	3.71	2.65	3.37	6.32	49.89	48.59
Skewness	0	0	0.58	1.04	3.86	1.27	1.37	1.33	0.60	1.46	1.30	0.88	0.81	0.43
Kurtosis	–1	0	–0.29	0.32	22.66	1.25	0.75	1.01	0.17	1.56	2.14	1.68	0.04	–1.313
SWilk W	1	1	0.96	0.89	0.68	0.88	0.78	0.82	0.96	0.81	0.89	0.93	0.94	0.87
SWilk Prob	0.024	0.163	0.011	<0.001	<0.001	<0.001	<0.001	<0.001	0.023	<0.001	<0.001	<0.001	<0.001	<0.001

criterion, i.e. containing ≥25% gibbsite in the fine earth fraction. These results emphasise the importance of gibbsite in the mineral constituents of the Cerrado soils. Nevertheless, according to the Brazilian Soil Taxonomy (Santos *et al.* 2006), only nine soil samples were classified as gibbsitic (*gibbsiticos oxidicos*), i.e. with Ki ≤0.75 and Kr ≤0.75

Discussion

Control of soil acidity by the mineralogy

A close relationship between pH and exchangeable Al^{3+} content of soils has been demonstrated (Thomas and Hargrove 1984; Nachtigall and Vahl 1989; Pereira *et al.* 1998; Abreu *et al.* 2003). In the case of the Cerrado Latosols, this relationship presents a significant but low coefficient of determination, accounting for 54% of the variation in the exchangeable Al^{3+} contents (Fig. 2). This value is similar to reports by Nachtigall and Vahl (1989) and Pereira *et al.* (1998), which showed, in various classes of Brazilian soils, that 47–65% of the variation in the contents of exchangeable Al^{3+} was a function of the pH. A highly significant relationship between pH_{CaCl_2} and base saturation (V) has also been observed.

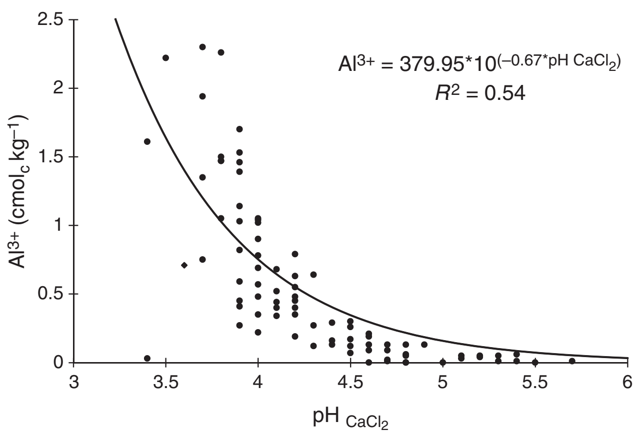

Fig. 2. Relationship between soil pH_{CaCl_2} and exchangeable aluminium concentration for the 0–20 cm depth horizon of the Latosols under pasture in the Brazilian Cerrado region.

Multivariate analysis was applied to the relationships between the chemical and mineralogical variables and parameters related to soil acidity (Thioulouse *et al.* 1997). The PCA revealed that the two primary axes explained 60.8% of the total variance of the data, i.e. 36.3% and 24.5% by the first and second axes, respectively (Fig. 3). Axis 1 was influenced especially by exchangeable Ca, Mg, EB, and C with negative autovectors.

Axis 2 was influenced by gibbsite and pH_{CaCl_2} with a positive autovector and R_{KGb}, $H^+ + Al^{3+}$, and Al^{3+} with negative autovectors. The same direction between the autovectors of R_{KGb} and exchangeable Al^{3+} means that the contents of exchangeable Al are lower in the soils with higher percentages of gibbsite.

To evaluate the extent of the correlation between exchangeable Al^{3+} and mineralogy, an empirical model was used (Fig. 4). When gibbsite was the predominant mineral (R_{KGb} <0.6), the exchangeable Al^{3+}content was low. This confirms results obtained by PCA (Fig. 3), where the autovector of exchangeable Al^{3+} was opposite to that of the gibbsite percentage.

Multiple regression analysis was performed to correlate the measured exchangeable Al to pH and mineralogical components. The assumptions of normality and independence of residuals were verified. The multiple regression model to predict exchangeable Al is given as: $Al = 10^{(8.270-3.397pH+0.335pH^2+0.00035Kt)} - 0.5$, with $R^2 = 0.883$ and $R^2_{adjusted} = 0.878$. This model, including the quantity of kaolinite (Kt), substantially increased the determination coefficient compared the model with only pH. So, we have to consider that the amount of exchangeable Al^{3+} is controlled by the pH, as already demonstrated in the literature, but the mineralogy, too, has an important contribution in explaining the amount of exchangeable Al^{3+}.

These results highlight the different responses of the soils to acidification. It has been proposed that the two main consequences of H^+ input in soil are: (*i*) an increase in positive surface charge through protonation; and (*ii*) the dissolution of minerals, particularly Al-bearing hydroxides and clays (Zhu *et al.* 2005). The first process occurs mainly in variable-charge soils, rich in organic matter, and Fe and Al

Table 2. Mineralogical characteristics of the upper horizons (0–0.2 m) of Latosols under pasture in the Brazilian Cerrado region
Kt, Kaolinite; Gb, gibbsite; Hm, hematite; Go, goethite; Ki, 1.7 (SiO_2/Al_2O_3); Kr, [1.7 × ($SiO_2/(Al_2O_3 + 0.6375 \times Fe_2O_3)$)]; K^{tga}, Gb^{tga}, kaolinite and gibbsite from thermogravimetric analysis; R_{KGb}, kaolinite/(kaolinite+gibbsite) from thermogravimetric analysis; s.d. standard deviation; Swilk, Shapiro–Wilk test

Variables	SiO_2	Al_2O_3	Fe_2O_3	Kt	Gb	Hm	Go	Ki	Kr	K^{tga}	Gb^{tga}	$R_{KGb}{}^{tga}$
				($g\ kg^{-1}$)						($g\ kg^{-1}$)		
Min.	46.0	39.0	14.0	98.8	0.0	5.2	8.8	0.4	0.3	107.0	10.0	0.5
Max.	200.0	239.0	325.0	429.6	277.3	36.1	321.5	2.2	1.8	553.0	330.0	0.9
Mean	108.2	155.3	74.8	232.7	97.6	14.1	69.6	1.2	1.0	282.0	105.5	0.8
s.d.	41.7	46.8	42.9	88.7	65.1	4.3	42.9	0.4	0.3	95.8	76.6	0.1
Median	101.5	166.5	73.5	219.1	95.2	14.1	69.0	1.3	1.0	269.0	89.0	0.8
1st Qu	72.0	125.0	55.5	154.7	44.1	11.7	46.5	0.9	0.7	207.8	40.0	0.7
3rd Qu	136.2	189.5	91.3	293.7	140.3	15.9	85.0	1.6	1.2	351.5	141.8	0.9
Skewness	0.4	–0.7	2.9	0.4	0.5	2.0	2.9	0.0	0.1	0.5	0.9	–0.5
Kurtosis	–0.7	–0.3	15.2	–0.7	–0.1	9.3	15.5	–0.7	–0.6	–0.1	0.5	–0.6
SWilk W	1.0	0.9	0.8	1.0	1.0	0.8	0.8	1.0	1.0	1.0	0.9	1.0
SWilk Prob	0.01	0.00	<0.001	0.02	0.06	<0.001	<0.001	0.38	0.53	0.16	<0.001	0.01

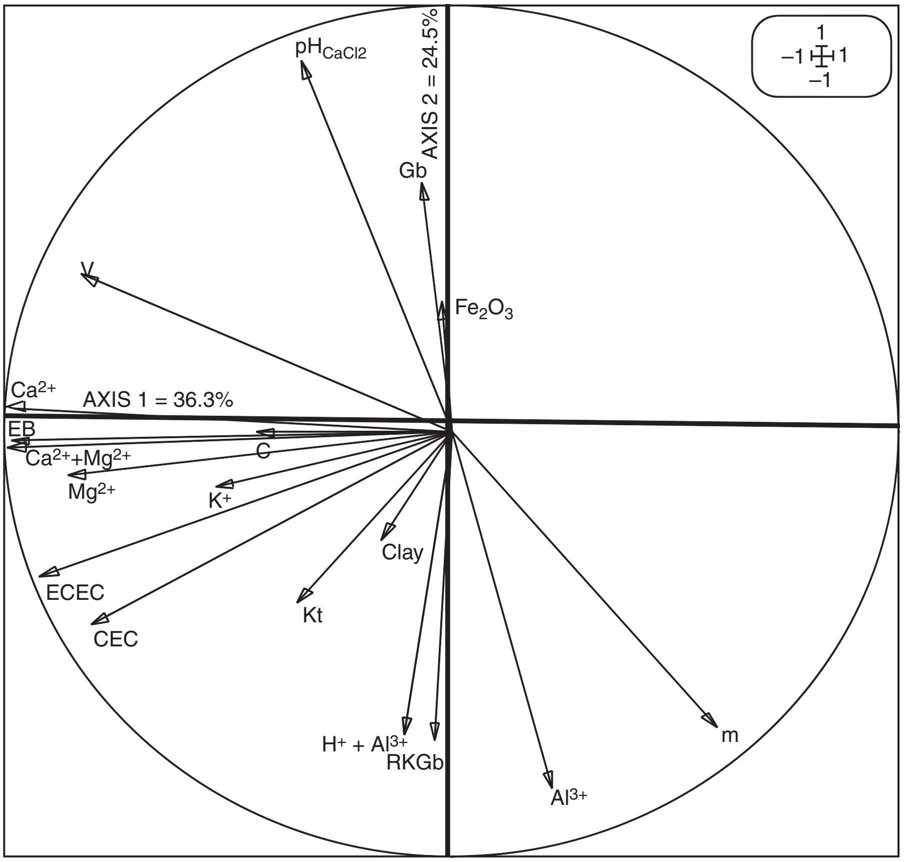

Fig. 3. Principal component analysis between chemical and mineralogical soils characteristics of the Latosols under pasture in the Brazilian Cerrado region.

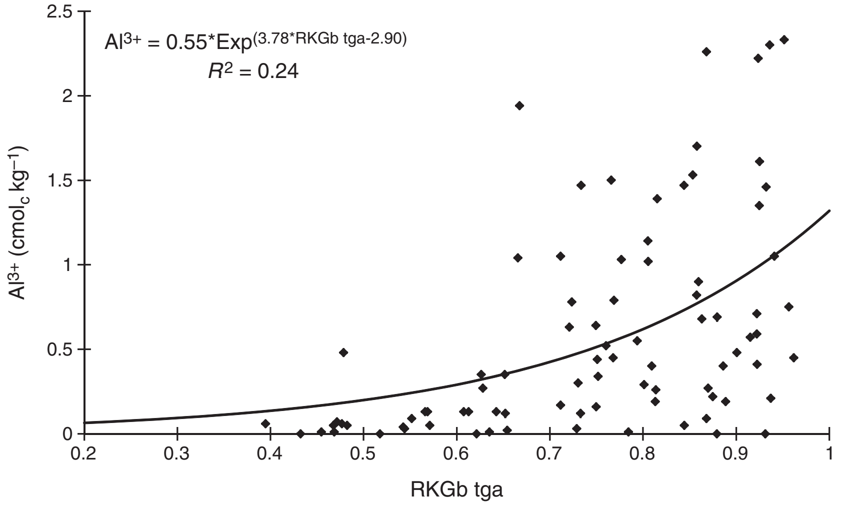

Fig. 4. Relationship between exchangeable aluminum and the ratio kaolinite/(kaolinite + gibbsite) (R_{KGb}) of the Latosols under pastures in the Brazilian Cerrado region.

oxides. In kaolinite-rich soils, this process is only of minor importance, although protonation of the edges of the clay particles cannot be excluded (Zhu *et al.* 2005). Proton consumption through mineral weathering is due mainly to the dissolution of Al-containing minerals, i.e. kaolinite and gibbsite in our soils, and results in the release of Al. The equilibrium constant of the reaction for the main Al-containing minerals in our soils showed that amorphous $Al(OH)_3$ is the most soluble over the present pH_{CaCl_2} ranges (3.4–5.7), followed by gibbsite, with kaolinite being the least soluble (Percival 1995; Stumm and Morgan 1996). However, the higher stability of *in-situ* natural kaolinite over gibbsite is debatable, as shown by Watanabe *et al*. (2006). Various studies have shown that kaolinite formed in the upper horizons of Latosols is submicron-sized and poorly crystalline, and usually includes some Fe within its structure, which decreases its stability compared with standard kaolinite (Muggler *et al*. 2007). Hence, in gibbsite-rich (or Al and Fe oxide rich) Latosols, the consumption of H^+ ions is thought to be mainly related to the protonation of variable-charge minerals, whereas in kaolinite-rich Latosols, the dissolution of kaolinite with the release of Al is thought to be the most important process.

Aluminium excess v. *base deficiencies: agronomic implications*

The first studies on chemical fertility of the soils of the Cerrado region highlighted the high acidity and exchangeable Al content as the main deleterious features towards farming and cattle development (Lopes and Cox 1977; Goedert 1983; Adamoli *et al*. 1985). To reduce the effect of acidity, liming was the main method proposed. Exchangeable Al has been used as a basis for the calculation of lime requirement in the Cerrado region (Souza and Lobato 2004). However, Ritchey *et al*. (1982) considered the deficiency of base cations, mostly Ca^{2+}, as the main limitation to plant growth in this region.

The results of our study indicate that the adverse effect of Al can vary according to the mineralogy of the soil clay fraction. Soils with a predominance of kaolinite tend to contain higher quantities of exchangeable Al (Figs 3 and 4). In these conditions, the use of lime can be recommended, as it will promote pH increase, Al precipitation, and potential alleviation of Al toxicity, and decrease Ca and Mg deficiency (Alleoni *et al*. 2005). In soils where gibbsite is the main mineral in the clay fraction, the lime requirement calculated in this way will be low. As the major problem is then Ca and Mg deficiency alone, it would be useful to take into account the levels of exchangeable Ca and Mg to calculate lime requirement.

The origin of the variation in kaolinite and gibbsite contents was recently re-examined by Reatto *et al*. (2008). They proposed a model to explain the variation of the kaolinite and gibbsite contents in the Latosols developed on the Brazilian Central Plateau that combines: (*i*) a regional variation mainly associated with the age of the two main geomorphic surfaces, the gibbsite content being higher in the older SAS than in the VS; and (*ii*) a local variation mainly associated with the hydraulic conditions along the toposequence, the gibbsite content being higher at the top of the slope, where SiO_2 removal has been higher. Thus, the gibbsitic Latosols occur mainly in the centre of the 'chapadas' (tablelands) on the SAS, where a better internal drainage favours the formation of gibbsite as a result of the silica leaching necessary for the formation of the kaolinite. For the soils of the second geomorphic surface and the areas of most recent dissection, the contribution of the rocky substrate has a greater influence and favours the formation of kaolinite, due to greater $Si(OH)_4$ availability. In this geomorphic surface, richer in kaolinite, higher exchangeable Al content can be expected using R_{KGb} as a mineralogical soil attribute for mapping the potential levels of exchangeable Al. As shown in a companion study (Vendrame *et al*. 2012), the R_{KGb} ratio is extremely well predicted by near-infrared reflectance spectroscopy in these soils, and could be used as a fast and non-expensive method to evaluate exchangeable Al content.

Conclusion

Soil acidity and Al toxicity are among the most important soil-related constraints for agriculture development in the tropics. Our study has shed light on the influence of clay mineralogy on soil acidity parameters. Both the amount of exchangeable Al^{3+} and Al saturation depend on clay-sized soil constituents. When gibbsite was the predominant mineral, exchangeable Al remains low. The ratio kaolinite/(kaolinite + gibbsite) (R_{KGb}) may be a useful indicator for the sensitivity of soils to acidification and Al toxicity. Management strategies for liming the gibbsitic and kaolinitic Latosols need to be re-examined in the light of these results.

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