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NOTA

COMPARISON OF H/AL STOICHIOMETRY OF MINERAL AND ORGANIC SOILS IN BRAZIL(1)

Daniel Vidal Perez(2), Lúcia Helena Cunha dos Anjos(3), Adierson Gilvani Ebeling(4) & Marcos Gervasio Pereira(3)

SUMMARY

Exchangeable Al has been used as a criterion for the calculation of lime requirement in several Brazilian States. However, the laboratory method with extraction by a 1 mol L^{-1} KCl solution followed by indirect alkaline titration is not accurate for some Brazilian soils, mainly in the case of soils with high organic matter content. The objective of this study was therefore to evaluate the stoichiometry of H^+/Al^{3+} in KCl soil extracts. The results suggested that organically complexed Al is the main contributor to exchangeable acidity in soils enriched with organic matter. Liming recommendations for organic soils based exclusively on exchangeable Al determined by the NaOH titration method should therefore be revised.

Index terms: acid-base titration; ICP-OES; KCl; Histosols.

RESUMO: *COMPARAÇÃO DA ESTEQUIOMETRIA H/Al EM SOLOS MINERAIS E ORGÂNICOS BRASILEIROS*

A determinação de alumínio trocável é utilizada como critério para cálculo de calagem em vários estados brasileiros. Contudo, a determinação indireta pela titulação com NaOH, após extração com solução de KCl 1 mol L^{-1}, pode não ser adequada para certos tipos de solos brasileiros, notadamente aqueles que apresentem altos teores de carbono orgânico. Dessa forma, o principal objetivo deste trabalho foi avaliar a estequiometria da relação H^+/Al^{3+} em extratos de KCl. Os resultados obtidos sugerem que o Al complexado pela matéria orgânica,

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[2] Researcher, Embrapa Solos, Jardim Botânico 1024, CEP 22460-000 Rio de Janeiro (RJ). E-mail: daniel@cnps.embrapa.br

[3] Professor, Soils Dept., Universidade Federal Rural do Rio de Janeiro – UFRRJ. Km 47 CEP 23890-000 Seropédica (RJ). E-mails: lanjos@ufrrj.br; gervasio@ufrrj.br

[4] Ph.D. Student, Soils Dept., UFRRJ. E-mail: adiersonge@gmail.com

em solos orgânicos, é o principal contribuinte para a acidez trocável obtida por titulação. Dessa forma, a recomendação de calagem em solos orgânicos baseado somente na determinação de alumínio trocável por titulação com NaOH deve ser revista.

Termos de indexação: titulação ácido-base; ICP-OES; KCl; Organossolos.

INTRODUCTION

The determination of Al is a permanent concern of soil fertility management. Soil chemists are constantly testing methods that take into account the effective soil exchange capacity, organic matter content, texture, and the pH-dependent charges of various clays minerals (Menzies, 2003).

The titrimetric determination of Al^{3+} in 1 mol L^{-1} KCl soil extract using bromothymol blue as indicator has been widely used in Brazil (Raij et al., 1994; Bernardi et al., 2002). However, in fact, this procedure determines H^+ in the KCl extract. This is recognized as the exchangeable acidity (Sposito, 1989). In this context, there is therefore no differentiation between the "exchangeable H^+" and H^+ developed by Al^{3+} hydrolysis.

From very acid mineral soils with neutral salt solutions, such as KCl, more Al^{3+} than H^+ is extracted (Veith, 1977; Bloom et al., 2005), while in the organic soil horizons, the quantity of extractable H^+ typically exceeds Al^{3+} (Bloom et al., 2005). But Sparks (2003) observed that much of the H^+ that appears to be exchangeable in organic soils may be due to Al^{3+} hydrolysis in the organic matter resulting in H^+.

An important tool for the differentiation between H^+ and Al^{3+} is based on the use of the titration/back-titration procedure (Bertsch & Bloom, 1996). This method was first described by Yuan (1959). However, Coscione et al. (1998) showed the lower sensitivity of exchangeable Al^{3+} determined by back-titration. Al determination by spectrophotometric methods, such as ICP-OES, is doubtlessly more sensitive and reliable (Bertsch & Bloom, 1996). The purpose of this study was therefore the evaluation of H and Al in 1 mol L^{-1} KCl extracts to determine whether the theoretical value of 3 of Al hydrolysis predominates in the exchangeable acidity.

MATERIALS AND METHODS

The method for exchangeable Al extraction of most Brazilian soil laboratories is based on the Al exchange from the surface of soil colloids using a non-buffered 1 mol L^{-1} KCl solution (Embrapa, 1997; Bernardi et al., 2002). A soil:solution mixture, ratio 1:10, was vigorously shaken for 5 min and left to stand overnight. Then a 25 mL aliquot of the supernatant was sampled and Al was indirectly quantified by titration with 0.025 mol L^{-1} NaOH using Bromothymol Blue as indicator. In this case, each mol of NaOH neutralizes 1 mol H^+. Thus, the number of H^+ mmoles in the 25 mL aliquot is (A x 0.025), where A is the volume (mL) of NaOH consumed in titration. Considering that the initial volume of KCl was 100 mL and the soil mass was 10 g, the result could be expressed as (A x 10) mmol kg^{-1} or A cmol kg^{-1} of H^+. For further discussions in the text, this type of mass concentration unit will be used, since it expresses the real titration, i.e., H^+ rather than Al^{3+}. However, to clarify the use of titration in Al^{3+} routine analysis, the full calculation will be shown here. To express the result in terms of Al^{3+}, it must be assumed that each Al^{3+} produces 3 H^+ after complete hydrolysis. Thus, the result would be expressed as (A x 10)/3 mmol kg^{-1} or (A/3) cmol kg^{-1} of Al^{3+}. Since the mmol Al^{3+} is equivalent to 3 $mmol_c$ Al^{3+}, the final result will be expressed as (A x 10) $mmol_c$ kg^{-1} or A $cmol_c$ kg^{-1} of Al^{3+}.

For a direct quantification of Al in the KCl extract, another aliquot of the supernatant was analyzed using an inductively coupled plasma atomic emission spectrometer (Perkin Elmer Optima 3000). The operating frequency was 50–60 MHz at a power of 1,500 W with a torch argon flow rate of 15 L min^{-1}. The selected Al atomic line was at 308.211 nm. A nitrogen gas purge flow rate of 5.0 L min^{-1} was used throughout the analysis. The sample flow rate was 2.0 L min^{-1}. In this case, the result was expressed as B mg kg^{-1} of Al^{3+}, considering that the initial volume of KCl was 100 mL and the soil mass was 10 g. Since the mmol of Al is, approximately, 27 mg, the result could be expressed as (B/27) mmol kg^{-1} or (B/270) cmol kg^{-1} of Al^{3+}. For further discussions in the text, this kind of mass concentration unit will be used, since it expresses the real mass concentration of the element. However, to clarify the use of spectrophotometric determinations in Al^{3+} routine analysis, we will show the full calculation. Since the mmol Al^{3+} is equivalent to 3 $mmol_c$ Al^{3+}, the final result will be expressed as (B/9) $mmol_c$ kg^{-1} or (B/90) $cmol_c$ kg^{-1} of Al^{3+}.

In the case of soils with high organic matter content, Al extraction by $CuCl_2$ 0.2 mol L^{-1} was performed according to Bertsch & Bloom (1996). The Al determination followed the ICP-OES procedure described above.

Thirty seven acid soil samples were selected representing different soil classes (Oxisol, Ultisol, Inceptisol, Entisol, Histosol) from different Brazilian States (RJ, AM, MS, SP, AL, PB, PE, PR, MG, and DF). Their main properties are shown in table 1.

Table 1. Soil classification and localization of 37 selected soil samples

Sample	Horizon	Depth	Soil classification(1)		County, State
			SiBCS	Soil taxonomy	
		cm			
03.0954	A2	6–20	Latossolo Vermelho-Amarelo	Oxisol	Itaperuna, RJ
03.0955	BA	20–39	Latossolo Vermelho-Amarelo	Oxisol	Itaperuna, RJ
03.0988	A1	0–17	Cambissolo Húmico	Inceptisol	Bom Jesus de Itabapoana, RJ
03.0989	A2	17–46	Cambissolo Húmico	Inceptisol	Bom Jesus de Itabapoana, RJ
03.1484	A1	0–22	Latossolo Amarelo	Oxisol	Porciuncula, RJ
03.1485	A2	22–42	Latossolo Amarelo	Oxisol	Porciuncula, RJ
04.0224	Bi2	63–98	Cambissolo Háplico	Inceptisol	Benjamin Constant, AM
04.0225	BC	109–121	Cambissolo Háplico	Inceptisol	Benjamin Constant, AM
04.0217	Bi1	24–62	Cambissolo Háplico	Inceptisol	Benjamin Constant, AM
04.1229	AB	20–42	Latossolo Vermelho	Oxisol	Ponta Porã, MS
04.1230	BA	42–63	Latossolo Vermelho	Oxisol	Ponta Porã, MS
04.1252	Cgf	83–110	Plintossolo Háplico	Entisol	Bela Vista, MS
04.1386	Bt1	36–52	Argissolo Vermelho	Ultisol	Caracol, MS
04.1387	Bt2	52–88	Argissolo Vermelho	Ultisol	Caracol, MS
04.1408	Bt2	60–80	Argissolo Amarelo plíntico	Ultisol	Bela Vista, MS
05.0577	C2	52–100	Neossolo Quartzarênico	Entisol	Santa Maria Boa Vista, PB
05.0578	C3	100–150	Neossolo Quartzarênico	Entisol	Santa Maria Boa Vista, PB
05.0579	C4	152–200	Neossolo Quartzarênico	Entisol	Santa Maria Boa Vista, PB
RJ1O1	O	--	Cambissolo Húmico	Inceptisol	Itatiaia, RJ
RJ1O2	O	--	Cambissolo Húmico	Inceptisol	Itatiaia, RJ
RJ1O3	O	--	Cambissolo Húmico	Inceptisol	Itatiaia, RJ
RJ 1O4	O	--	Cambissolo Húmico	Inceptisol	Itatiaia, RJ
RJ4 H2	H	--	Organossolo Mésico	Histosol	Nova Friburgo, RJ
RJ4 H3	H	--	Organossolo Mésico	Histosol	Nova Friburgo, RJ
RJ4 H4	H	--	Organossolo Mésico	Histosol	Nova Friburgo, RJ
PR2 H1	H	--	Organossolo Mésico	Histosol	Tijucas do Sul, PR
PR2 H2	H	--	Organossolo Mésico	Histosol	Tijucas do Sul, PR
PR2 H3	H	--	Organossolo Mésico	Histosol	Tijucas do Sul, PR
AL2 H1	H	--	Organossolo Tiomórfico	Histosol	Coruripe, AL
AL2 H2	H	--	Organossolo Tiomórfico	Histosol	Coruripe, AL
SP1 HP1	Hp	--	Organossolo Mésico	Histosol	Taubaté, SP
SP1 HP2	Hp	--	Organossolo Mésico	Histosol	Taubaté, SP
DF1 H1	H	--	Organossolo Mésico	Histosol	Guara, DF
DF1 H2	H	--	Organossolo Mésico	Histosol	Guara, DF
DF1 H3	H	--	Organossolo Mésico	Histosol	Guara, DF
MS2 2H	H	--	Organossolo Mésico	Histosol	Eldorado, MS
MG2 H2	H	--	Organossolo Mésico	Histosol	Coronel Pacheco, MG

(1) SiBCS: Brazilian Soil Classification System (Embrapa, 2006); Soil Taxonomy (Soil Survey Staff, 1999).

RESULTS AND DISCUSSION

In a first approach, it is possible to arrange the soil samples in two groups (Tables 2 and 3). The first (Table 2) consisted of 18 horizons of mineral soils where the main dominant clay mineralogy is kaolinite and/or iron/aluminum oxy-hydroxides. In this group, the mean H/Al ratio was around 3.4. In addition to the potential titration errors in a routine aluminum analyses, the presence of soluble Mn^{2+} and Fe^{3+} in KCl soil extract (Table 2) could represent a small contribution of H^{+} through the hydrolysis of these metals, which would explain a positive variation from the expected 3.0 ratio. Our results corroborate the findings of McLean (1976), Veith (1977) and Bloom et al. (2005) that most of the protons measured in the salt extract of mineral soils, i.e., the exchangeable acidity, may come from the hydrolysis of exchangeable Al^{3+}.

The second group (Table 3) was composed of organic horizons with a H/Al ratio of around 0.4. In this case, the lower H^{+} concentration suggested that the “exchangeable H^{+}” pool was not the major part of exchangeable acidity in the studied organic soils. This may be explained by the findings of Ross et al. (2008). They showed that the quantity of exchangeable H^{+} may be insignificant at a pH above 4.5. The mean pH of the studied organic soils was around 4.9 (Table 3).

Another fact that corroborates the insignificant contribution of exchangeable H^{+} to exchangeable acidity is related to the stoichiometry of the organic-

Table 2. Some chemical analyses of 18 mineral soil samples

Sample	Al-ICP[1]	H-Tit[2]	H/Al	Organic C[3]	pH	Fe[1]	Mn[1]
	mmol kg^{-1}			g kg^{-1}	water	mmol kg^{-1}	
03.0954	3.9	15.0	3.9	12.1	4.2	0.22	0.08
03.0955	3.8	14.0	3.7	7.9	4.4	0.14	0.08
03.0988	5.0	16.0	3.2	39.7	4.7	0.71	0.09
03.0989	4.3	14.0	3.2	33.3	4.6	0.60	0.08
03.1484	7.7	27.0	3.5	23.0	4.3	0.41	0.08
03.1485	7.1	24.0	3.4	18.7	4.4	0.33	0.08
04.0224	38.0	124.0	3.3	3.5	4.9	0.06	0.09
04.0225	35.6	117.0	3.3	2.6	5.2	0.05	0.09
04.0217	25.0	82.0	3.3	6.5	4.8	0.12	0.09
04.1229	7.9	26.0	3.3	8.8	4.8	0.16	0.09
04.1230	7.6	26.0	3.4	8.0	4.7	0.14	0.09
14.1252	14.4	48.0	3.3	2.3	5.4	0.04	0.10
04.1386	4.2	14.0	3.3	4.6	5.1	0.08	0.09
04.1387	8.7	28.0	3.2	2.4	5.1	0.04	0.09
04.1408	4.4	15.0	3.4	3.0	4.8	0.05	0.09
05.0577	4.6	15.0	3.3	1.5	4.5	0.03	0.08
05.0578	4.8	17.0	3.6	1.3	4.4	0.02	0.08
05.0579	5.6	20.0	3.6	1.0	4.3	0.02	0.08
Average	10.7	35,7	3.4	10.0	4.7	0.18	0.09
SD[4]	10.8	35,0	0.2	11.4	0.3	0.20	0.01
CV (%)[5]	101	98	5	114	7	114	7

[1] Extracted by 1 mol L^{-1} KCL and determined by ICP-OES. [2] Extracted by 1 mol L^{-1} KCL and determined by acid-based titration. [3] Determined by dichromate wet oxidation (Embrapa, 1997). [4] SD mean standard deviation. [5] CV mean coefficient of variation.

Table 3. Some chemical analyses of 19 organic soil samples studied

Sample	Al-ICP[1]	H-Tit[2]	H/Al	Organic C[1]	pH	Fe[1]	Mn[1]	Al-$CuCl_2$
	mmol kg^{-1}			g kg^{-1}	water	mmol kg^{-1}		
RJ1O1	10.4	5.0	0.5	63.5	5.1	0.10	2.08	255.9
RJ1O2	7.8	2.0	0.3	38.0	5.1	0.05	0.46	218.1
RJ1O3	12.2	2.0	0.2	49.9	5.0	0.20	0.13	262.2
RJ1O4	9.2	1.0	0.1	55.3	5.1	0.08	0.02	358.9
RJ4 H2	4.2	0.0	0.0	99.5	5.9	0.03	0.08	239.2
RJ4 H3	4.2	0.0	0.0	69.8	5.9	0.03	0.02	335.6
RJ4 H4	2.0	0.0	0.0	44.8	5.8	0.01	0.02	337.4
PR2 H1	18.2	7.0	0.4	144.1	4.4	0.21	0.41	411.1
PR2 H2	18.5	45.0	2.4	192.8	4.1	0.11	0.21	777.0
PR2 H3	31.1	29.0	0.9	270.0	4.5	0.16	0.13	773.0
AL2 H1	32.9	6.0	0.2	305.8	3.2	0.44	0.05	448.5
AL2 H2	18.2	13.0	0.7	508.1	3.0	0.10	0.03	118.0
SP1 HP1	31.6	4.0	0.1	207.4	5.2	0.16	0.20	729.6
SP1 HP2	25.3	3.0	0.1	144.4	5.1	0.05	0.04	590.0
DF1 H1	0.7	0.0	0.0	101.7	5.9	0.07	0.16	177.4
DF1 H2	11.6	3.0	0.3	132.4	5.4	0.25	0.07	383.0
DF1 H3	13.9	1.0	0.1	196.6	5.6	0.08	0.08	530.0
MS2 2H	15.6	22.0	1.4	189.3	4.3	0.62	0.64	197.4
Average	14.9	7.9	0.4	158.9	4.9	0.15	0.27	396.80
SD[4]	10.1	12.2	0.6	115.3	0.8	0.16	0.48	206.38
CV (%)[5]	68	154	147	73	17	102	180	52

[1] Extracted by 1 mol L^{-1} KCL and determined by ICP-OES. [2] Extracted by 1 mol L^{-1} KCL and determined by acid-based titration. [3] Determined by dichromate wet oxidation (Embrapa, 1997). [4] SD mean standard deviation. [5] CV mean coefficient of variation.

bound Al. The high values of $CuCl_2$-extracted Al compared with those obtained by KCl (Table 3) are generally related to organic-bound Al (Shuman, 1990; Soon, 1993; Barra et al., 2001). In this case, there is a relative preference for hydroxyl-Al ions over Al^{3+} (Schnitzer & Skinner, 1963; Bloom et al., 1979). Hargrove & Thomas (1982) showed that as the Al content of the organic matter increased, the effective valence of the adsorbed Al varied from 2.12 to 0.93. Nissinen et al. (1999) and Simonsson (2000) reported binding stoichiometry values ranging from 1.1 and 2.4 in literature. Therefore, the forced hydrolysis of organic-bound Al by alkaline titration should generate lower H/Al ratio values.

The results obtained in the mineral soils showed that most of the soil exchangeable acidity is primarily due to Al^{3+}. However, in the case of the studied organic soils, the contribution of hydroxyl Al bound to the organic matter is probably the main pool of exchangeable acidity. The contribution of exchangeable H^+ does not seem to be relevant for the studied soils. Considering that most authors indicate that the toxic aluminum is Al^{3+} and the monomeric Al-hydroxy species (Bloom et al., 2005), all liming recommendations for organic soils based exclusively on exchangeable Al determined by NaOH-titration should therefore be revised. These findings corroborate the studies of Pereira et al. (2005) and Ebeling et al. (2008). They pointed out the need of new analytical routine methods to properly study and monitor the management of Histosols in Brazil. Besides, the relationship between exchangeable acidity determined by acid-based titration and Al determined directly by spectrophotometry (AAS or ICP) could be a useful index to characterize organic horizons.

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