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Microwave Acid Extraction to Analyze K and Mg Reserves in the Clay Fraction of Soils

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ABSTRACT: Extraction of K and Mg with boiling 1 mol L^{-1} HNO_3 in an open system for predicting K and Mg uptake by plants is a method of low reproducibility. The aim of this study was to compare the extraction capacity of different acid methods relative to hydrofluoric acid extraction for K and Mg. A further objective was to develop a chemical extraction method using a closed system (microwave) for nonexchangeable and structural forms of these nutrients in order to replace the traditional method of extraction with boiling HNO_3 on a hot plate (open system). The EPA 3051A method can be used to estimate the total content of K in the clay fraction of soils developed from carbonate and phyllite/mica schist rocks. In the clay fraction of soils developed from basalt, recoveries of K by the EPA 3051A (pseudo-total) method were higher than for the EPA 3052 (total hydrofluoric extraction) method. The relative abundance of K and Mg for soils in carbonate rocks, phyllite/mica schist, granite/gneiss, and basalt determined by aqua regia digestion is unreliable. The method using 1 mol L^{-1} HNO_3 in an closed system (microwave) showed potential for replacing the classical method of extraction of nonexchangeable forms of K (boiling 1 mol L^{-1} HNO_3 in an open system - hot plate) and reduced the loss of Si by volatilization.

Keywords: EPA 3051A, EPA 3052, aqua regia, boiling nitric acid, microwave extraction, nonexchangeable K.

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INTRODUCTION

There is a dynamic balance among K forms in the soil. As plants take up K from the soil solution, there is buffering of dissolved K by exchangeable, nonexchangeable, and structural forms of K (Kirkman et al., 1994). Similarly, the release of structural forms of Mg to plants depends on exchange reactions and weathering of Mg minerals in the soil (Christenson and Doll, 1973). Biotite ($K(Mg_2Fe)AlSi_3O_{10}(OH)_2$), containing about 180 g kg^{-1} MgO, may be an important source of structural Mg in soils (Jackson, 1979). This nutrient is found in the soil only in the structural, exchangeable, and solution forms, differing from K, which may present a nonexchangeable form as well.

The methodological difference between nonexchangeable or fixed K and structural K is that the release of fixed K is a reversible process, while release of the structural element is irreversible, because it involves dissolution of the structure (Kirkman et al., 1994). In extraction procedures, the term “nonexchangeable K” used by several authors refers only to K reserves potentially available to plants, as the extraction method (boiling HNO_3) normally also dissolves structural forms of K.

The procedures for determining pseudo-total forms of metals listed in the manuals of the United States Environmental Protection Agency (Usepa SW-846) include methods 3050B (HNO_3 / HCl [3/1 v/v]) in an open system, and 3051A (HNO_3 / HCl [3/1 v/v]) in a microwave oven (Usepa, 1998). The pseudo-total term is used due to incomplete dissolution of the soil mineral matrix with the HNO_3 / HCl mixture. Complete dissolution of silicate minerals is only possible with the addition of concentrated hydrofluoric acid (HF). Publications typically indicate the efficiency of the combined acid extractions (pseudo-total) of soils as the percentage recovery of metals relative to the total determined by hydrofluoric acid digestion (EPA 3052 - Usepa, 1996) (Link et al., 1998; Silva et al., 2013). The extraction of pseudo-total forms of metals in soils is often accomplished by digestion with aqua regia (Öztan and Düring, 2012). This method, processed in an open system, uses the same concentrated acids of the EPA 3051A procedure, but with a reversed ratio of added volumes (HCl/HNO_3 = 3/1 v/v).

Several chemical extraction procedures have been used to estimate and distinguish the mineral reserves of K and Mg in soils around the world. Among these, extraction with boiling 1 mol L^{-1} HNO_3 (Knudsen et al., 1986) is the most widely used to estimate the contributions of nonexchangeable and structural forms of K and Mg in plant nutrition (Alves et al., 2013).

The release of K by boiling 1 mol L^{-1} HNO_3 involves a hydrolysis reaction, attacking the outer layers of soil minerals, but does not achieve complete dissolution of mineral particles (Simard et al., 1992). Despite the effectiveness of this method in estimating nonexchangeable forms of K and Mg (Alves et al., 2013), the analytical procedure uses an open system (hot plate),which is slow and has low accuracy and reliability due to cross-contamination of samples. The classic extraction procedure involves partial immersion of a thick-walled glass vessel containing soil and 1 mol L^{-1} HNO_3 in a hot vegetable oil bath (113 °C) for 25 min (Knudsen et al., 1986). The use of oil contaminates the extraction environment. With these limitations in mind, it is clearly desirable to develop new methodologies of extraction of nonexchangeable forms of K and Mg in a closed system (microwave). Chemical extraction in a closed system requires shorter digestion times and reduced consumption of acids and has a reduced risk of contamination and loss of elements by volatilization (Silva et al., 2013).

As working hypothesis, the EPA 3051A digestion method extract more pseudo-total forms of K and Mg than aqua regia and the estimative of reserve forms of this nutrients by 1 mol L^{-1} HNO_3 can be done in close system with the same precision of the open system. The objective of this study was to compare the extraction capacity of K and Mg in soil clay for different chemical acid methods in relation to total hydrofluoric acid digestion. A further aim was to develop a chemical method of extraction using a closed system (microwave oven) for nonexchangeable and structural forms of these nutrients to replace the traditional method of extraction with boiling nitric acid on a hot plate.

MATERIALS AND METHODS

Soil sampling

Soils from areas with different parent materials and from native forest were sampled to measure the recovery of K and Mg by several chemical acid methods. The soils had different levels and forms of mineral K and Mg in the clay fraction (Table 1): i) area 1 - carbonate rocks (strong rolling topography); ii) area 2 - mica schist and phyllite (strong rolling topography); iii) area 3 - granite / gneiss (rolling topography); and iv) area 4 - basalt (flat topography).

Clay separation

The soil samples were air dried, ground, and sieved (2 mm mesh) to obtain fine air-dried soil (FADS). Oxidation of organic compounds was performed by treating 20 g FADS with H_2O_2 (30 % v/v) in a water bath at 70 °C.

For separation of clay, FADS was dispersed in 0.2 mol L^{-1} NaOH. The sand fraction was retained in a 0.053 mm sieve mesh, and silt and clay fractions were separated by sedimentation, according to Stokes Law (Jackson, 1979).

X ray diffraction (XRD)

The dried clay fraction was ground (0.25 mm) and analyzed (powder sample) by X ray diffraction (XRD). The XRD patterns were obtained with a vertical goniometer with a scan speed of 0.5 °2θ min^{-1} and range from 2 to 50 °2θ. The diffractometer, equipped with a graphite monochromator and CuKα radiation, was generated at 40 kV and 20 mA.

Table 1. General characteristics and clay content of the soils

Area/ Profile	Location (state)	Geographical coordinate	Parent material	Sample identification	Horizon	Depth	Clay(5)
						m	$g\ kg^{-1}$
1/1(1)	Adrianópolis (Paraná)	24° 40’ 58” S - 48° 55’ 04” W	Carbonate	3	A1	0.00-0.15	270
1/1(1)	Adrianópolis (Paraná)	24° 40’ 57” S - 48° 55’ 07” W	Carbonate	4	A2	0.15-0.25	310
2/2(1)	Adrianópolis (Paraná)	24° 50’ 20” S - 49° 00’ 11” W	Phyllite - mica schist	15	-	0.00-0.15	270
2/3(1)	Adrianópolis (Paraná)	24° 50’ 20” S - 49° 00’ 11” W	Phyllite - mica schist	16	-	0.00-0.15	260
2/4(1)	Adrianópolis (Paraná)	24° 50’ 19” S -49° 00’ 11” W	Phyllite - mica schist	17	-	0.00-0.15	170
2/5(1)	Adrianópolis (Paraná)	24° 50’ 18″ S - 49° 00’ 12″W	Phyllite - mica schist	23	-	0.00-0.15	140
3/6(2)	São José dos Pinhais (Paraná)	25° 35’ 32” S - 49° 03’ 47” W	Granite - gneiss	IN	Bi	0.38-0.60	446
4/7(3)	Londrina (Paraná)	23° 23’ 30” S - 51° 11’ 05” W	Basalt	MO	Bt	0.19-0.42	655
4/8(4)	Londrina (Paraná)	23° 32’ 25” S - 51° 10’ 39” W	Basalt	OX	Bw1	0.15-0.95	831

(1) Entisol. (2) IN: Inceptisol. (3) MO: Molisol. (4) OX: Oxisol. The identification with non sequential numbers (3, 4, 15, 16, 17, 23) aimed to maintain consistency with other studies done in the same areas.(5) Clay: extracted by pipette method (Claessen, 1997).

Standardization of clay fraction samples and extractants

The use of the clay fraction recognizes the importance of this fraction in providing plant nutrients and minimizes the differential effect of dilution by coarser fractions on concentrations, since soil textures are diverse (Table 1).

The dried clay samples were ground and then sieved through a 0.25 mm mesh and placed in an oven at 45 °C, where they remained until chemical analysis. All extracting solutions were made with ultrapure water (18.2 MΩ cm^{-1} at 25 °C - Millipore Direct-Q System). High purity acids were used in the extractions (Merck PA®) and all extracts were filtered with a slow filter paper (Macherey Nagel®). All chemical analyses were carried out in triplicate.

Exchangeable K and Mg

About 1 g of clay was stirred for 1 h with 10 mL of 0.5 mol L^{-1} $Ca(NO_3)_2$. The suspension was filtered, and exchangeable K and Mg were determined by atomic emission spectroscopy using an inductively coupled plasma spectrometer (ICP-AES) (Varian, model 720-ES). Calibration curves were made with standard multielement SPECSOL - standard ICP solution.

Total K and Mg

The clay (0.5 g) was placed in Teflon tubes together with 9 mL of concentrated HNO_3 and 3 mL of concentrated HF (EPA 3052 - Usepa, 1996). The samples were subjected to microwave irradiation (MARSX press) for 5.5 min to reach 180 °C and a maximum pressure of 16 atm. After these ramp conditions, samples were digested for about 4.5 min at constant temperature and pressure. Potassium, Mg, Si, and Al concentrations were determined by ICP-AES.

Pseudo-total K and Mg - aqua regia (AR) (HCl/HNO_3 - 3/1)

The clay (0.5 g) was placed in a long glass and thick wall tube for digestion. After addition of 1 mL of concentrated HNO_3, the tubes were kept in a digester block for 15 min at 110 °C. The tubes were removed from the block and cooled for 10 min. After addition of 3 mL of concentrated HCl, the tubes were once more placed in the block at 110 °C. The temperature was maintained for 10 min, and after progressive increases in temperature, the tubes were kept in the block for 1 h at 130 °C (Berrow and Stein, 1983). The K and Mg concentrations were determined by ICP-AES.

Pseudo-total K and Mg - EPA 3051A (HNO_3/HCl - 3/1)

The clay (0.5 g) was placed in a Teflon tube in the presence of 9 mL of concentrated HNO_3 and 3 mL of concentrated HCl. The tube was sealed and placed in a microwave oven (MARSX press 6) for 8 min and 40 s using a temperature ramp to reach 175 °C. The temperature was maintained for an additional period of 4 min and 30 s (Usepa, 1998). Potassium and Mg concentrations were determined by ICP-AES.

Nonexchangeable and structural K and Mg - boiling nitric acid in an open system (hot plate)

The clay (1 g) was placed in a 50 mL Teflon beaker and 10 mL of 1 mol L^{-1} HNO_3 was added. The beaker was capped with a watch glass and placed in an oil bath at 113 °C, remaining under boiling for 25 min (Knudsen et al., 1986). Potassium, Mg, Si, and Al concentrations were determined by ICP-AES.

Nonexchangeable and structural K and Mg - boiling nitric acid in a closed system (microwave)

A new method to replace the classical method (hot plate) for extraction of nonexchangeable K and Mg in an open system has been developed. Approximately 0.5 g of clay was transferred to a Teflon tube in the presence of 5 mL of 1mol L^{-1} HNO_3. The tube was sealed and heated in a microwave oven (MARSX press 6) for 5 min and 30 s until the temperature reached 100 °C. This temperature was maintained for an additional period of 4 min 30 s. Potassium, Mg, Si, and Al concentrations were determined by ICP-AES.

RESULTS AND DISCUSSION

Mineral sources of K and Mg

The contrasting mineralogy of the clays (Figure 1) reflects the diversity of soil parent material from areas 1 to 4 (Table 1). Clay in soils developed from carbonate rocks (samples 3 and 4) are dominated by smectite, with small amounts of kaolinite and goethite. Fixation of K (nonexchangeable form) in smectite soils is usually due to the inclusion of layers of vermiculite and weathered mica in the smectite structure. For these minerals to fix K (nonexchangeable form), a high level of isomorphous substitution in the tetrahedral sheet (replacing Si^{4+} by Al^{3+}) is required. This makes the electrical field in the interlayer portion strong enough to overcome the hydration energy of the K (Melo et al., 2009). Some studies have shown the presence of interstratified mineral mica-smectite in silt and clay fractions with basal reflections (001) in 2.4 nm, a value obtained by the regular interstratified layers of 1.0 and 1.4 nm (Havlin et al., 1985). Biotite layers inside the smectite are sources of structural forms of Mg.

The parent materials (phyllite/mica schist) in area 2 are rich in micaceous minerals with a basal reflection at 1.0 nm (muscovite and/or biotite, which have resisted weathering in clays 15 to 23 (Figure 1).

Biotite can be the main source of Mg in soil, as it contains about 180 g kg^{-1} MgO (Jackson, 1979). Muscovite and biotite may be the main sources of Kin soils. Both minerals have a typical K_2O concentration of 100 g kg^{-1}. Clays 15 to 23 are mostly kaolinite, and minor smectite is also present, except for clay 23, where smectite is more abundant.

Clays of Inceptisol (IN) and Molisol (MO) soils also showed a predominance of kaolinite, with goethite in IN and considerable hematite in MO (Figure 1). Normally, the K concentration in kaolinite particles is very low. Analysis of individual particles of kaolinite by transmission electron microscopy/EDS for southwest Australian soils showed K_2O concentrations ranging from 1 to 2.9 g kg^{-1} (Singh and Gilkes, 1992). These authors concluded that the K in kaolinite was in interleaved layers of muscovite. According to the K_2O content, the concentration of muscovite layers was about 10 to 29 g kg^{-1}. On the other hand, a study of kaolinitic clay from several classes of Brazil soils showed interstratification of biotite layers in kaolinite (Melo et al., 2001).

The clay of the Oxisol (OX) soil contains no mica and has clay minerals with limited potential to hold reserve forms of K and Mg (smectite and kaolinite). This clay consists predominantly of oxides (hematite and gibbsite) (Figure 1), which contain little or no K and Mg.

Acid extractions of K and Mg

Clays 3, 16, and 23 showed higher levels of exchangeable K (149, 147, and 143 mg kg^{-1}, respectively) (Figure 2c). Clay 23 from area 2contains a great deal of smectite (Figure 1) and has the highest level of exchangeable Mg (929 mg kg^{-1}) (Figure 2a).

Among the clays of soils developed from basalt (MO and OX), MO clay has the highest exchangeable Mg and a low ratio between acid-extractable and exchangeable K and Mg contents (Figure 2b). The low values of this ratio indicate the low binding energy of K and Mg in the mineral colloids and a larger contribution from exchangeable forms of these nutrients. Generally, Mg showed lower binding energy compared to K because there are no nonexchangeable Mg forms in soils. The high ratio of Mg from acid extraction/exchangeable

Mg for OX can be attributed to the occurrence of residues of biotite (structural Mg) that resisted weathering inside microaggregates (Melo et al., 2002). Basal reflections of micaceous minerals (illite and interstratified illite / kaolinite) after sequential treatments

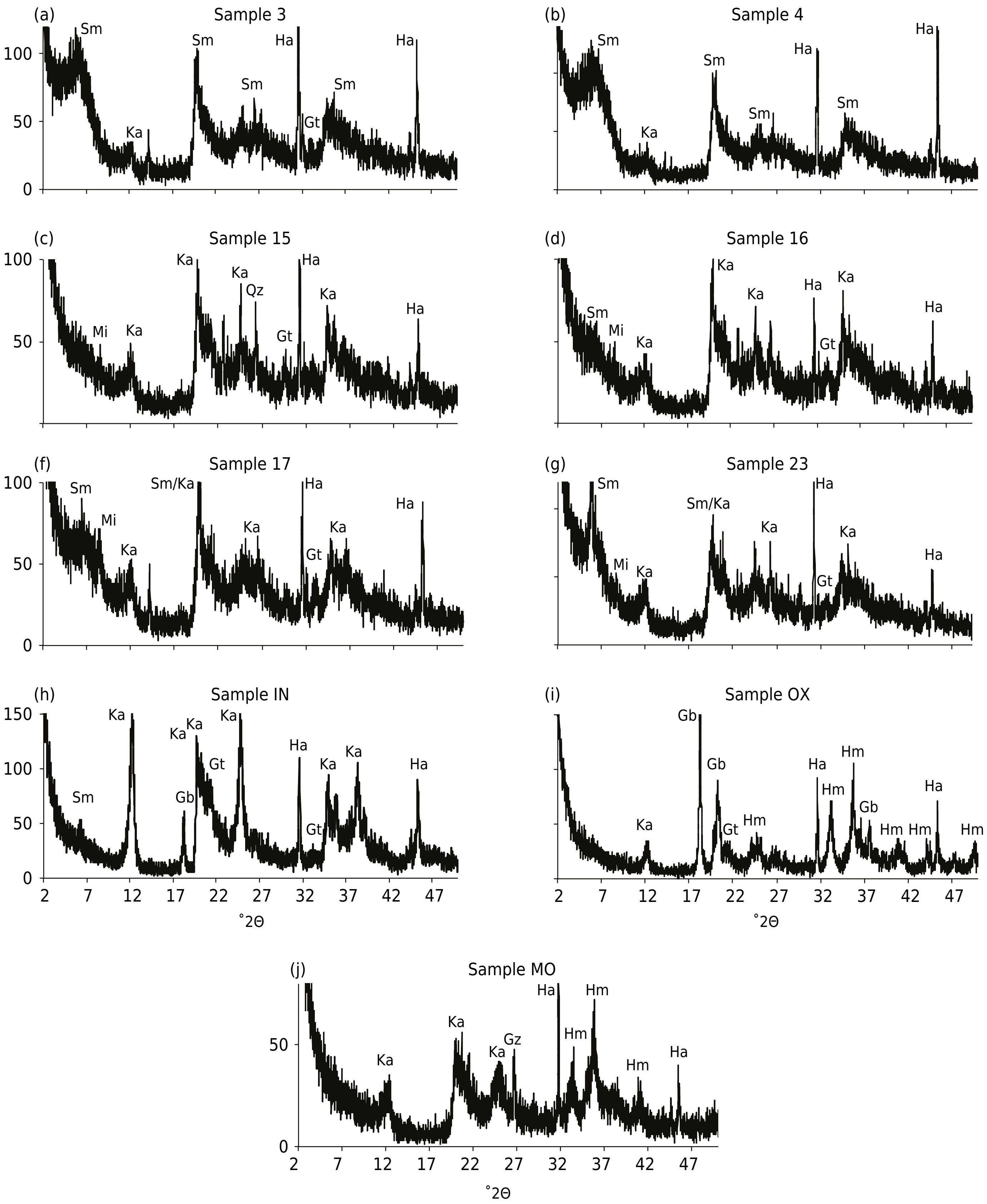

Figure 1. X ray diffraction patterns (CuKα radiation) of clay samples. Ka: kaolinite; Sm: smectite; Gb: gibbsite; Gt: goethite; Hm: hematite; Qz: quartz; Mi: mica; Ha: halite (halite does not belong to the soil clay fraction - this mineral was added to the samples as internal standard for correction of the peaks positions). IN: Inceptisol; OX: Oxisol; MO: Molisol.

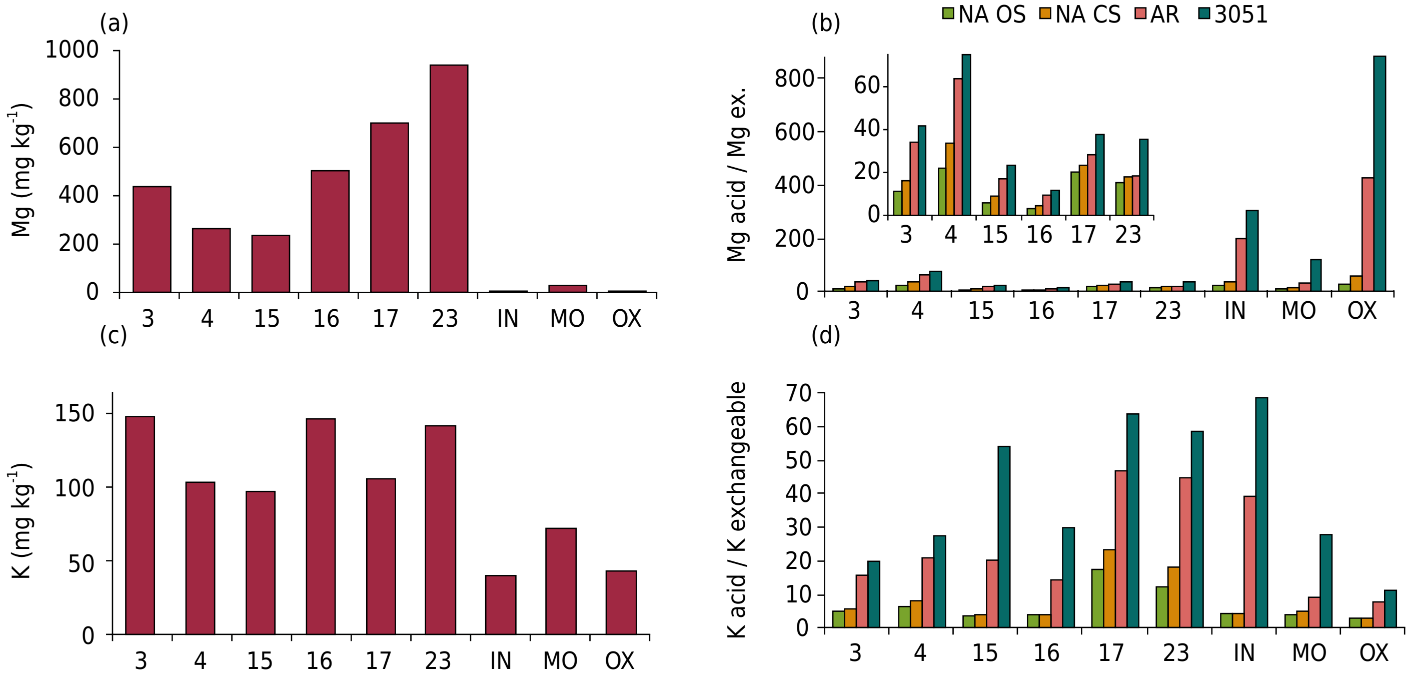

Figure 2. Exchangeable Mg and K of the clay fraction (a, c) and ratios between contents extracted by acid solutions (nitric acid in open system (NA OS), nitric acid in a closed system (NA CS), aqua regia (AR), and EPA 3051A (3051)) and exchangeable (ex.) Mg and K (b, d). IN: Inceptisol; OX: Oxisol; MO: Molisol.

for removal of Fe and Al oxides and kaolinite were observed for Oxisols from various regions of Brazil by DRX (Melo et al., 2003). In the present study, the ratio between Mg extracted by the 3051A method / exchangeable Mg was 873 for OX.

The total K and Mg concentrations (EPA 3052) (Figure 3) reflect the clay mineralogy of the soils (Figure 1). The lower concentrations are for the oxidic clay (OX) and the highest for clay 23, which contains mica and smectite. For IN clay, total K is much higher than total Mg, which may indicate dissolution of K-feldspar by hydrofluoric acid extraction. This mineral is common in young soils originating from granite / gneiss (Nwadialo and Lietzke, 1989). However, the K-feldspar content of the clay fraction of IN should be less than about 40 g kg^{-1}, considered as a minimum limit to enable the appearance of the mineral reflections in XRD patterns (Melo et al., 2009). For clay 23, the behavior was the opposite, since mica schist is rich in biotite, and this mineral contains more Mg (144 g kg^{-1}) than K (83 g kg^{-1}) (Jackson, 1979). The total content of Mg and K in clay 23 were 32,701 and 9,441 mg kg^{-1}, respectively (Figure 3).

Recoveries of K by extraction with the 3051A method compared to hydrofluoric extraction (3052) were as follows (Figure 3): i) statistically equal levels - clays 3, 4, 15, and 17; ii) higher levels with 3052 method - clays 16, 23, and IN; iii) higher levels with the 3051A method - MO and OX. Despite being set up as a pseudo-total extraction method (Öztan and Düring, 2012), the 3051A method can be used to estimate the total content of K in clay soils in the first group. In the clay of soils originating from basalt, the total concentration of K would be better estimated by extraction by 3051A than by 3052. Possibly, the high Fe content of MO and OX consumed much of the HF acid (only 3 mL), reducing the extraction efficiency of the 3052 method. Future studies should be conducted to confirm (or reject) this premise. Furthermore, the best ratio of the volume of HNO_3 and HF for total extraction from soil and clay with a ferric and perferric character (Santos et al., 2013) should be established. Mg contents for 3051A and 3052 extractions were similar (Figure 3). Clearly, aqua regia should not be used to determine the total concentration of these nutrients, as the percentages of recovery by aqua regia ranged from 33 to 81 %.

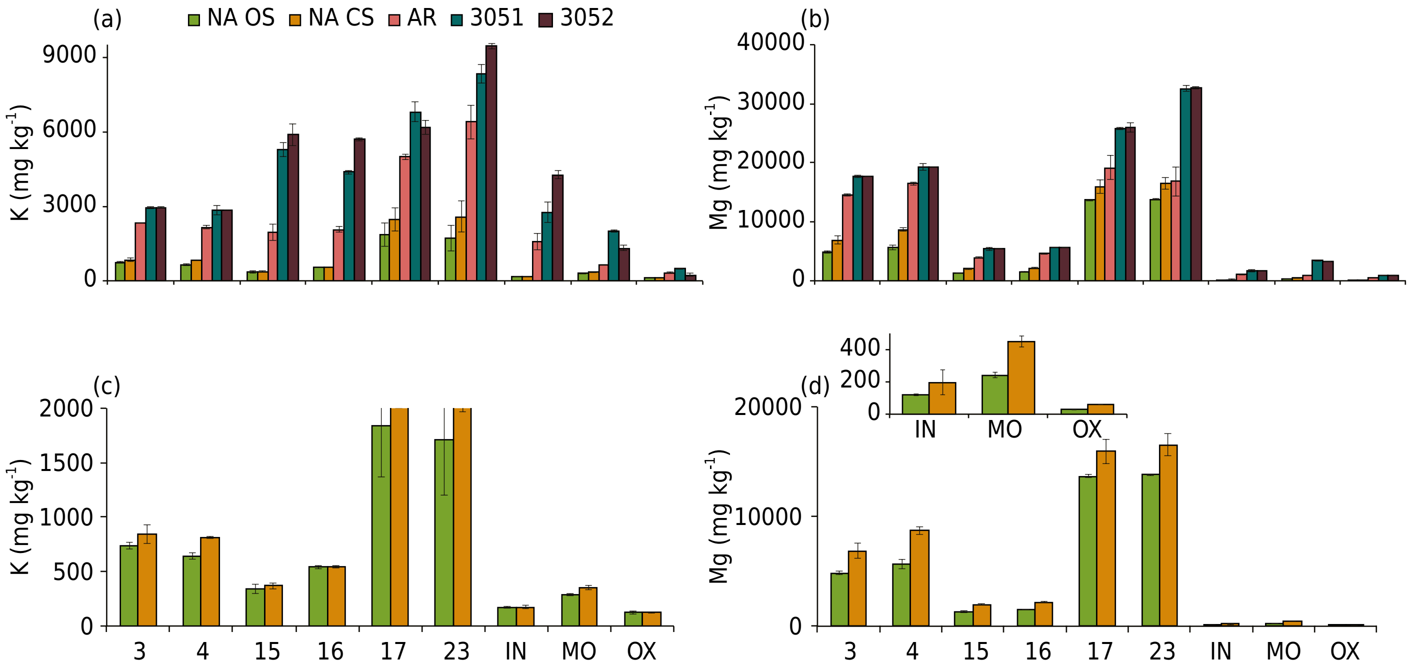

Figure 3. Contents of K and Mg clay fraction extracted by different acid extractants: nitric acid in an open system (NA OS), nitric acid in a closed system (NA CS), aqua regia (AR), EPA 3051A (3051), and EPA 3052 (3052). The last two figures show only extractions and NACS and NA OS to allow better comparison between open and closed extraction systems. IN: Inceptisol; OX: Oxisol; MO: Molisol.

The aqua regia and especially the EPA 3051A and EPA 3052 methods dissolve some or all of the mineral matrix of the soil and extract structural forms of K and Mg that are not accessible to plants and other soil organisms (Martins et al., 2004). For this reason, it is common to use milder extractions and methods to dissolve elements in amounts that correlate with plant uptake, such as boiling 1 mol L^{-1} HNO_3 in an open system (NA OS) (Alves et al., 2013). The lower extraction efficiency of the NA OS method may be desirable, as is evident from the small percentage of Al_2O_3 dissolved in relation to that extracted by the 3052 method. Only 6 to 29 % of Al_2O_3 was recovered by NA OS, indicating minor dissolution of the mineral matrix. The corresponding recovery of K and Mg was higher, reaching 53.1 %.

The boiling 1 mol L^{-1} HNO_3 method attacks the outer layers of crystals, feldspars, and micas, releasing some of the structural K and Mg (Simard et al., 1992). This method is also expected to extract all nonexchangeable K in wedge sites in micaceous minerals and between the layers of 2:1 minerals with high charge density, exchanging the K in these specific adsorption sites. With the exception of basalt clays (MO and OX), Mg recoveries by NA OS, compared to the 3052 method, were greater than recoveries of K. This behavior highlights the occurrence of the biotite in the clays of areas 1 and 2 and may indicate the greater difficulty in hydrolyzing particles of K-feldspar by HNO_3.

The new method (boiling 1 mol L^{-1} HNO_3 in a closed system [NA CS]) extracted equivalent amounts of K compared to the original method of extraction of nonexchangeable and structural forms of K (NA OS) (Figure 3). For Mg, the closed system extracted slightly higher amounts compared to the open system. Clay 23 had the highest nonexchangeable K content determined by the NA CS method (2,582 mg kg^{-1}). This similarity in the K extracted by open and closed systems enables replacement of the NA OS method by the NA CS method, with gains in safety, practicality, and reliability. Digestion in a microwave oven is easier operationally and provides more reproducible results, due in part to more precise control of temperature during the extraction process (Link et al., 1998). Another advantage of microwave-assisted extraction is reduced processing time due to more rapid heating (Öztan and Düring, 2012). The closed system also prevents volatilization of elements and cross-contamination between samples, which are common in the open system (Santos and Alleoni, 2013).

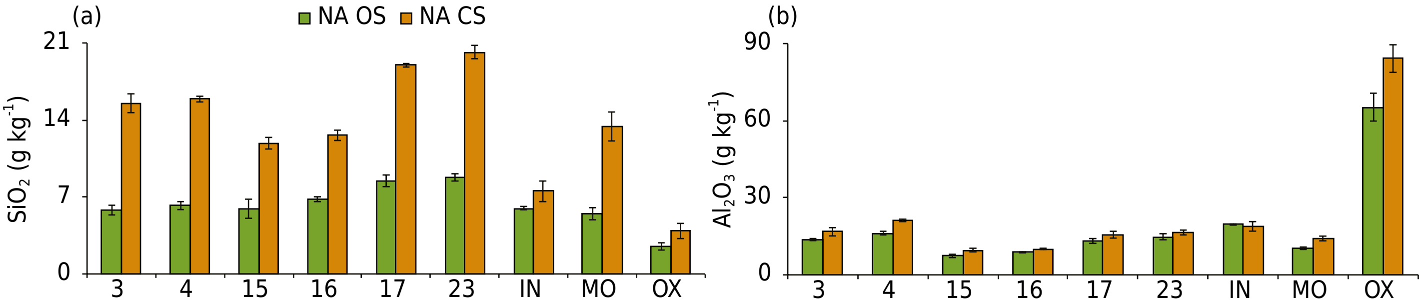

Figure 4. Contents of SiO_2 and Al_2O_3 of the clay fraction extracted by nitric acid in an open system (NA OS) and nitric acid in a closed system (NA CS). IN: Inceptisol; OX: Oxisol; MO: Molisol.

The amounts of Al extracted by the NA OS and NA CS methods were quite similar (Figure 4), which indicates that the same materials were dissolved by these two methods. The loss of Si in the form of volatile compounds in the open system (Silva et al., 2013) resulted in smaller concentrations of Si for NA OS relative to NA CS (Figure 4).

CONCLUSIONS

The element Mg has lower binding energy compared to K in mineral soil colloids. Total K and Mg reflected the clay mineralogy of soils.

The EPA 3051A method (pseudo-total content) can be used to estimate the total content of K in the clay fraction of soils developed from carbonate and phyllite / mica schist rocks. In the clay fraction of soils derived from basalt, the recovery rates of K by EPA 3051A were higher than for EPA 3052 (hydrofluoric extraction). Aqua regia cannot be used to estimate total K and Mg in any environments in terms of relative abundance of K and Mg (carbonate, phyllite / mica schist, granite / gneiss, or basalt).

Boiling 1 mol L^{-1} HNO_3 in a closed system (microwave) procedure can replace the classic method of extraction of nonexchangeable and structural forms of K (boiling 1 mol L^{-1} HNO_3 in an open system - hot plate) with increased efficiency and a reduction in loss of Si by volatilization.

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