

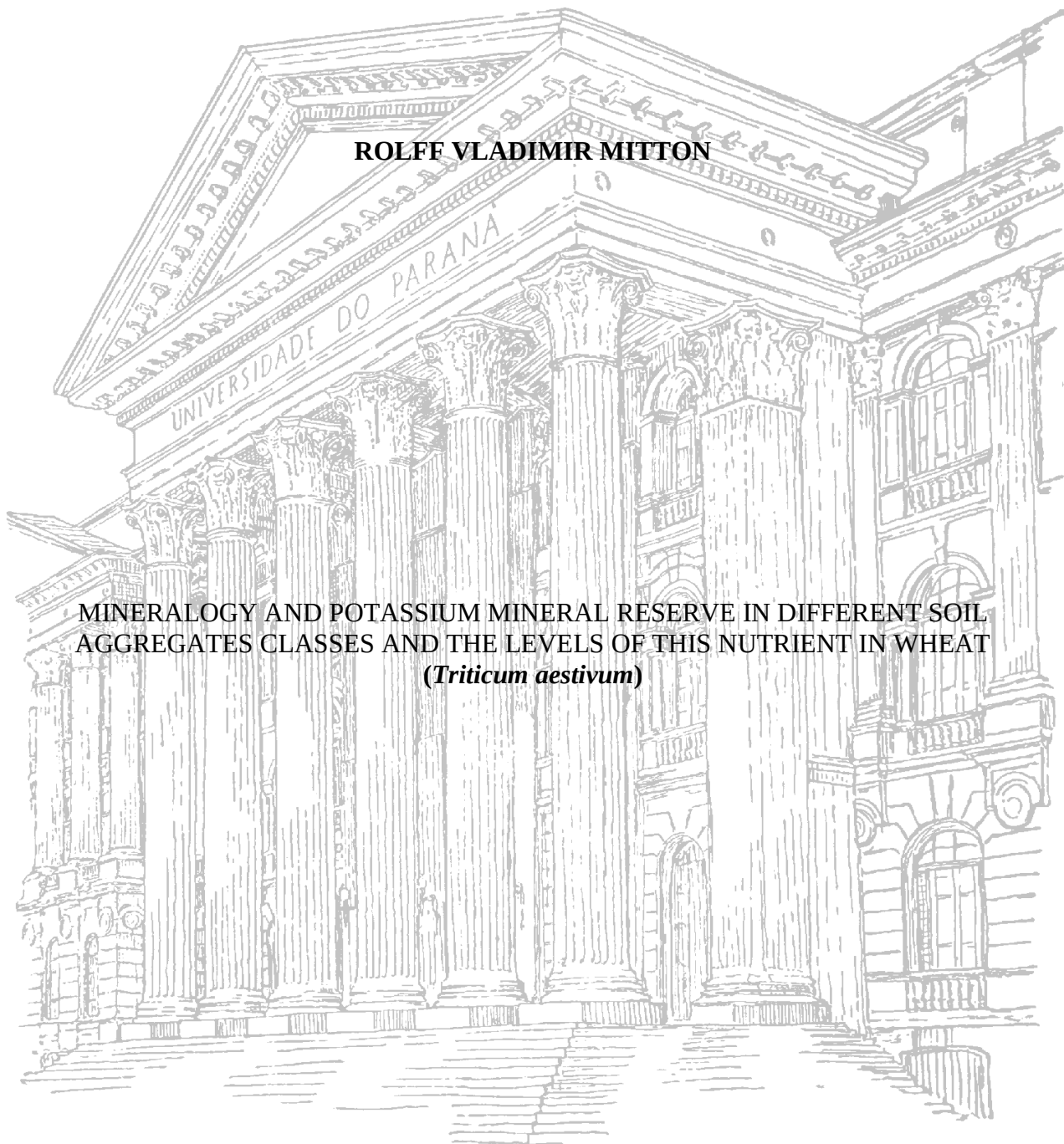
UNIVERSIDADE FEDERAL DO PARANÁ
SETOR DE CIÊNCIAS AGRÁRIAS
PROGRAMA DE PÓS-GRADUAÇÃO EM CIÊNCIA DO SOLO

ROLFF VLADIMIR MITTON

**MINERALOGY AND POTASSIUM MINERAL RESERVE IN DIFFERENT SOIL
AGGREGATES CLASSES AND THE LEVELS OF THIS NUTRIENT IN WHEAT
(*Triticum aestivum*)**

CURITIBA

2017



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Dissertation submitted to the Graduate Program
in Soil Science, Concentration Area: Soil and
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Advisor: Prof. Dr. Vander De Freitas Melo

Co-Advisor: Prof. Dr. Volnei Pauletti

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This Dissertation is dedicated to my Parents: Frantz and Rose Cecile Mitton for their unconditional support, to my younger brother Keven Mitton, to Frieda Caplan for Always believing in me and last but not the least to my advisor Vander De Freitas Melo.

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MINERALOGIA E RESERVA MINERAL DE POTÁSSIO EM DIFERENTES CLASSES DE AGREGADOS DE SOLO E TEORES DESTE NUTRIENTE EM TRIGO (*Triticum aestivum*)

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RESUMO GERAL

A biodisponibilidade do K em suas diferentes formas minerais é muito variável e depende de vários fatores (concentração na solução do solo, capacidade de troca catiônica (CTC), grau de intemperismo do solo, etc.) que influenciam o equilíbrio químico do nutriente dentro do solo. O objetivo do presente trabalho foi estudar a dinâmica das diversas formas minerais do Potássio (K) em diferentes classes de agregados de solos jovens (Cambissolo) e altamente intemperizados (Latossolo), desenvolvidos a partir de granito/gnaiss e basalto respectivamente na mineralogia do solo e avaliar a importância da reserva do K na nutrição das plantas de trigo. Para este estudo, foram consideradas duas classes de solo da taxonomia brasileira do solo, um CAMBISSOLO HAPLICO Tb distrófico e um LATOSSOLO VERMELHO Distroférrico típico. Ambos os solos foram separados em tamanho de agregados; o Latossolo em 5 (> 4 mm, 2 - 4 mm, 0,5 - 2 mm, 0,21 - 0,5 mm e < 0,21 mm) e o Cambissolo em 4 (> 4 mm, 2-4 mm, 0,5-2 mm e < 0,5 mm). Diferentes formas de K foram determinadas em cada tamanho de agregado em ambos os solos e essas formas no solo foram correlacionadas com a absorção de K por plantas de trigo. Em cada classe de agregado também foi estudada a mineralogia das frações areia, silte e argila. Foi cultivado o trigo separadamente nas diferentes classes de agregados e após a colheita das plantas, os teores de K foram determinados na parte aérea e nas raízes. A fração argila do Cambissolo apresentou a predominância da caulinita altamente cristalizada, enquanto no Latossolo, os minerais predominantes foram a gibbsita e a hematita com grau de cristalinidade moderado a alto. Houve pequena variação entre os agregados de cada solo quanto a mineralogia da fração argila. O K trocável pela extração de Mehlich-1, foi identificado como a forma mineral de K mais preditiva da disponibilidade deste nutriente no trigo. As formas não-trocáveis de K, tanto pelo HNO₃ como pelo HF, refletiram a natureza do material de origem do Cambissolo

(granito/gnaiss) e do Latossolo (basalto). O K não-trocável também contribuiu para a nutrição do trigo, variável em função do tamanho do agregado. Para o Cambissolo esta contribuição ocorreu apenas nos maiores tamanho de agregados (> 4 mm e $4 - 2$ mm), enquanto para o Latossolo a contribuição foi observada em todos os tamanhos de agregados.

Termos de indexação: nutrição de plantas, formas de K, mineralogia

MINERALOGY AND POTASSIUM MINERAL RESERVE IN DIFFERENT SOIL AGGREGATES CLASSES AND THE LEVELS OF THIS NUTRIENT IN WHEAT (*Triticum aestivum*)

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GENERAL ABSTRACT

The bioavailability of K in its different mineral forms is very variable and depends on several factors (concentration in the soil solution, cation exchange capacity (CEC), degree of soil weathering, etc.) that influence the chemical balance of the nutrient within the soil. The objective of the present study was to study the dynamics of the different mineral forms of K in various aggregates size in young (Inceptisol) and highly weathered (Oxisol) soils in the State of Paraná, Brazil, developed respectively from granite / gneiss and basalt in soil mineralogy, and to evaluate the importance of the K reserve in the nutrition of wheat plants. For this study, two soil classes were considered: an Inceptisol and an Oxisol. Both soils were separated into aggregate size; the Oxisol in 5 classes (> 4 mm, 2 – 4 mm, 0.5 – 2 mm, 0.21 – 0.5 mm, and < 0.21 mm) and the Inceptisol in 4 classes (> 4 mm, 2 – 4 mm, 0.5 – 2 mm, and < 0.5 mm). Different K forms were determined in each aggregate size in both soils and these soils were correlated with K uptake by the wheat plants. In each class of aggregate was also studied the mineralogy of the sand, silt and clay fractions. The wheat was grown separately in the different classes of aggregates, and after the plants were harvested, the K contents were determined in the aerial part and in the roots. The clay fraction of the Inceptisol showed the predominance of highly crystallized kaolinite, while in the Oxisol, the predominant minerals were gibbsite and hematite with a moderate to high degree of crystallinity. There were small variations between the aggregates of each soil in relation to the mineralogy of the clay fraction. The exchangeable-K extraction by the Mehlich-1, was found to be the most predictive form of K for the availability of this nutrient in wheat. The non-exchangeable (HNO_3 1 mol L^{-1}) and total (HF concentrated) K forms, reflected the nature of the parental material for the Inceptisol (granite/gneiss) and the Oxisol (basalt). The non-exchangeable K also contributed to the wheat nutrition, which varied according to the size of the aggregate.

For the Inceptisol, this contribution occurred only in the greater aggregates sizes (> 4 mm and $4 - 2$ mm), while for the Oxisol, the contribution was observed in all the aggregate sizes

Key-Words: Plant nutrition, K forms, mineralogy

GENERAL INTRODUCTION

The soil is formed by a solid phase (minerals and organic material) and a porous phase. The proportion of these phases varies from one soil type to another and even within the same soil, this variation can be seen from horizon to horizon. The aggregation of the particles allows the existence of voids within the soil, called pores filled with water and air. The solid phase of the soil is of great importance. Therefore, it is essential to have a very detailed knowledge of how it influences the liquid phase, from which the soil solution derives

The potassium (K) is an essential macronutrient for plant development and has a very important role in human and animal nutrition. The adequate supply of this nutrient is essential for the physiological processes of plants. There is a K deficiency in soils worldwide and it has been affecting directly and consistently the established agricultural productive systems (Cong et al., 2016). One alternative is the use of fertilizers to supply the growing demands. Unfortunately, the sources of these fertilizers are being depleted all around the world and worst, they are not renewable (He et al., 2015).

Potassium is present in the soils in several forms: in the soil solution as free ion, in the sites of exchange of the organic matter and clay minerals, in the non-exchangeable form adsorbed specifically onto the vermiculite and onto the wedges of micas and within inner primary mineral in structural form (Blanchet et al., 2017). The prediction of the availability of this nutrient, depending on the plants demands and needs, gives a wider view on how to effectively manage the crops systems (Simonsson et al., 2009).

Although soil solution and exchangeable forms of K are considered readily available to plants, they only represent a very small percentage (up to 2%) of total K in soil. (Zorb et al., 2014). The K in structural form is the most representative in the soil. It is usually found in biotite (trioctahedral mica) in muscovite (dioctahedral mica) and feldspars.

When the plant roots absorb K from the soil solution, a chemical imbalance is created and to compensate, the roots send various signals through the exudation of organic compounds and others that generate a concentration gradient (Zorb et al, 2014). Through this concentration gradient, the K is brought closer to the roots from the diffusion exchange points until its absorption by the roots occurs. When the concentration of K in both the soil solution and the point of exchange is reduced, the non-exchangeable K can become part of the solution to maintain the chemical balance (Rosolem et al, 2012). The wheat (*Triticum aestivum*) can absorb the non-exchangeable K as well as the nutrient structural forms. The acidic wheat root

exudates force primary K based minerals to be converted into secondary minerals 2:1 increasing therefore, the release of the nutrient to soil solution.

The dissolution of most primary rock-forming minerals is limited by slow kinetics at the mineral–water interfaces. Mineral dissolution rates depend on extrinsic factors such as Temperature, pH, Eh, and exudates from microbes and plant roots, as well as on intrinsic factors such as mineral-surface properties and the presence of weathering products (Zhang et al., 2014; Jackson, 2015). Acidity and the availability of ligands promote dissolution reactions for primary minerals and govern their transformations into secondary minerals (Mavris et al., 2015).

The mineral reserve of K is strongly dependent on the nature of the parental material and the degree of soil development. In this context, to have a great variation in this reserve, in the present study, a young soil (Inceptisol) originated from rocks rich in mineral sources of K (granite-gneiss) and a highly-weathered soil (Oxisol) originated from rocks naturally poor in primary minerals sources of K (basalt) were selected.

In addition to the factors mentioned above, it was hypothesized that within the same soil matrix the mineral reserve of K differs as a function of the aggregate class. It is expected that the pedogenic factors, especially the pedo-bioturbation, are not enough to homogenize the soil matrix and the roots of the plants growing side by side along the same horizon of the soil. The roots will, therefore find different levels of K and mineralogy of the distinct clay fraction as a function of the different sizes of explored aggregates.

The standard method to estimate the mineral reserve K that effectively buffers the available forms and contributes to plant nutrition is the cultivation of agricultural and forestry species (Nachtigal and Vahl, 1991; Benipal and Pasricha., 2002; Alves et al., 2013). After harvesting the plants, it is possible to generate an output/input ledger of K of the soil-plant system to estimate the percentage contribution of the several mineral forms (Martins et al., 2004b). Simultaneously, several chemical extraction methods have been used to estimate and distinguish the level of mineral reserve of K in soil in many parts of the world. The chemical methods used to estimate the K reserves in soils and its fractions are: boiling HNO_3 1 mol L^{-1} , repeated washings with HCl 0.01 mol L^{-1} , low molecular weight organic acids (citric acid and oxalic), tetraphenyl sodium borate (NaTPB) and cation exchange resins (Simard et al., 1992; Melo et al., 1995; Martins et al., 2004a; Sharma and Sharma, 2011). Other chemical extraction methods also have the potential to estimate the mineral reserve of K. The use of NaHSO_4 (Sodium bi - sulphate) in the form of crystals, allows the complete solubilization of

secondary phyllosilicate minerals 1: 1 (kaolinite) and vermiculite and smectite and primary 2: 1 (mica). (Jackson et al., 1986; Melo et al., 2003).

There are no reports available on the study of the forms and mineral reserve of K in different classes of soil aggregate sizes. Due to the smaller diameter of the micropores it can be expected that the mineral reserve of aggregates less than 0.105 mm (lower class) would be more significant in term of the nutrient concentration, because it represents a more confined environment where less leaching of silica and bases occurs (Melo et al., 2008). Thus, in practical terms, the wheat roots growing in a soil with different aggregations of classes (undisturbed soil block of 20 cm side) will find various micro-environments in terms of fertility and K reserve.

The objective of the present study was to study the dynamics of the different mineral forms of K in various aggregates size in young (Inceptisol) and highly weathered (Oxisol) soils in the State of Paraná, Brazil, developed respectively from granite / gneiss and basalt in soil mineralogy, and to evaluate the importance of the K reserve in the nutrition of wheat plants.

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CHAPTER 1. MINERALOGY OF THE SAND, SILT AND CLAY FRACTIONS OF DIFFERENT CLASSES OF AGGREGATES OF TWO SOILS OF PARANÁ, BRAZIL

ABSTRACT

The mineralogy of the soil fractions is quite variable as a function of soil factors and processes of formation. Even within a soil, variations can occur at short vertical and horizontal distances. The objective of the present work was to evaluate the mineralogical and chemical characteristics of the sand, silt and clay fractions of different classes of aggregates from young (Inceptisol) and highly weathered (Oxisol) soils, arising respectively from granite/gneiss and basalt from the State of Paraná, Brazil. For this study, two soil classes were taken under account, a dystro-ferric Oxisol and a haplic Inceptisol. Both soils were separated into aggregate size; the Oxisol in 5 classes (> 4 mm, 2 – 4 mm, 0.5 – 2 mm, 0.21 – 0.5 mm, and < 0.21 mm) and the Inceptisol in 4 classes (> 4 mm, 2 – 4 mm, 0.5 – 2 mm, and < 0.5 mm). The mineralogy of the soil fractions was studied by X-Ray diffraction and chemical analysis. The mineralogy of the sand, silt, and clay fractions of both soils reflected the composition of the parental material. The sand and silt fractions of both the Inceptisol and the Oxisol are predominantly constituted by quartz with traces of minerals with lower intensity such as diaspore, gibbsite and Hematite. The clay fraction of Inceptisol presented the predominance of Kaolinite highly crystallized, while in the Oxisol the predominant minerals were the gibbsite and hematite with moderate to high degree of crystallinity. The ratio $[Gt/(Gt + Hem)]$ was absolute in the Inceptisol for all aggregate sizes, indicating the predominance of the goethite as iron oxide, while in the Oxisol this ratio revealed to be low, hence, making the Hematite the predominant iron oxide mineral. There was little variation among the aggregates of each soil regarding the mineralogy of clay fraction.

Key-words: kaolinite, hematite, goethite, gibbsite, degree of crystallinity

1.1. INTRODUCTION

The soil structure is considered as one of the most important properties from the agricultural view. It is related to other fundamental properties in soil-plant relationships. The study of soil structure in the morphological sense is purely descriptive, while from the physical point of view is functional (Marcos, 1968). Although the aggregates be separated, their stability extensively assessed, and their formation process widely studied, there is a lack of knowledge of any kind of law or principle commanding the soil aggregates formation, size and composition especially when looking at the biological component. (Batista et al., 2013).

The intrinsic characteristics of the parental material, climatic conditions, biological activity and profile position in the landscape, can determine the greater or lesser transformation of the soil minerals (Mavris et al., 2015). The soils' physical characteristics determined by the type, size and degree of development of the aggregates depend heavily on the proportions and crystallography of the minerals of the clay fraction, where the shape of the mineral will strongly influence the morphology of the aggregates (Araujo et al., 2012; Souza et al., 2012; Almeida et al., 2014). The hematite (Hm), gibbsite (Gb) and Goethite (Gt) interfere in the face-to-face adjustment of phyllosilicates minerals (disorganizing effect), such as kaolinite (Kt), which favors the formation of smaller structures with a spherical shape (Resende 1985, Resende et al., 1992, 1997; Ferreira et al., 1999).

The Kt under humid tropical climate conditions often has a low degree of crystallinity (Hughes and Brown, 1979; Singh and Gilkes, 1992), which depends on chemical and morphological characteristics and pedobioclimatic factors. For example, the presence of Fe^{3+} in the Kt structure is one of the factors that reduces crystallinity and increase the surface area of the mineral (Mestdagh et al., 1980; Brindley et al., 1986). In the presence of interstratification with minerals type 2: 1 (DeLuca and Slaughter, 1985), of empty octahedral positions and irregular filling of Al in the octahedral layer (Plançon et al., 1989), the reduction of Kt crystallinity becomes apparent. Several studies have identified interstice of smectite and Kt (Schultz et al., 1971; Wiewiora, 1971; Yerima et al., 1985).

Although Kt is the main mineral of soils and sediments, iron oxides are often present (Hanke, 2012; Araujo et al., 2014). The Hm and Gt have different mineralogical characteristics, such as isomorphic substitution level of Fe by Al within the mineral structure, degree of crystallinity, size and form of the mineral, depending on the parental material, stage of weathering and biopedoclimatic conditions (Filho et al., 2015).

Previous studies developed by Deshpande et al. (1968) revealed that the iron oxides played a role of secondary importance in the aggregation of tropical climate soils. In turn, Pinheiro-Dick and Schwertmann (1996) and Lima and Anderson (1997) demonstrated the participation of Fe oxides in the Oxisols aggregation. Muggler (1998) has shown that the formation processes and the mineralogy of the compounds of Fe determine their possible effect on the aggregation. As for Al oxides, the predominance of gibbsite in the clay fraction of Oxisols favors a higher aggregation, a direct consequence of the microgranular structure manutention in these soils and therefore resulting in high values of permeability (Silva, 2016).

A hierarchical theory of aggregation proposes that the microaggregates ($<250\ \mu\text{m}$) come together to forming macroaggregates ($> 250\ \mu\text{m}$) (Edwards and Bremner, 1967), and the links within the microaggregates are stronger than the bonds between them. Biological activity can also be important for the formation of structures and homogenization of the solid constituents of soils. The activity of mesofauna affects the soil structure through selective ingestion of organic and mineral particles and elimination of these such as coprolites or fecal pellets, therefore mixing soil particles and forming stable organominerals aggregates (Schaefer, 2001). It is expected that this be even more pronounced on more weathered soils, such as the Oxisols.

And so, the objective of the present work was to evaluate the chemical and mineralogical characteristics of the sand, silt and clay fractions of different classes of aggregates from young (Inceptisol) and highly weathered (Oxisol) soils, arising respectively from granite / gneiss and basalt from the state of Paraná, Brazil.

1.2. MATERIALS AND METHODS

1.2.1 SAMPLING AREA

To study the chemical and mineralogical characteristics of the different class of aggregates, two soils with different degree of development and derived from different parental material and therefore, with different release potential of the various forms of K were selected. The first one was an Oxisol from basaltic rocks in the permanent preservation area of Cascavel, PR and the second one, an Inceptisol from granite and gneiss of the “Serra do Mar”, Paraná. A trench in each soil class was opened, the surface horizon was removed thoroughly and the soil samples were collected from the subsurfaced horizon, more specifically the B horizon (Diagnostic horizon per the Brazilian soil taxonomy). As the main objective of this study was to evaluate the mineralogy and the mineral forms of K it was decided to discard the “A” horizon to minimize the influence of the organic matter in the analyzes

1.2.2. SEPARATION OF AGGREGATES

Undisturbed soil samples from the subsurfaced horizon identified as Bw and Bi horizons respectively for the Oxisol and the Inceptisol were manually crushed in the field, by applying a light pressure to cause minimal change in its original structure, and, then, wrapped in newspaper for transport. After air drying, the samples were then separated into clusters of size for each soil class, using a sieves system coupled to an orbital shaker (RETSCH K G/ 5657 Haan) with agitation for 10 min (dry aggregate stability - EMBRAPA, 1997). The machine's working speed was at range 10, when it provided options in the range from 0 to 10. The amount of sample (clods) used in the separation of aggregate classes was proportional to the receiving capacity of the upper sieve (which was of the same volume as each one of the rest). A sufficient quantity of clods was then sieved to harvest enough aggregate class for chemical and mineralogical analysis. And so, 4 classes ($> 4\text{mm}$; $4 - 2\text{ mm}$; $0.5 - 2\text{ mm}$; and $< 0.5\text{ mm}$) of aggregates were harvested for the Inceptisol and 5 classes ($> 4\text{mm}$; $4 - 2\text{ mm}$; $0.5 - 2\text{ mm}$; $0.21-0.5\text{ mm}$; and $<0.21\text{ mm}$) of aggregates for the Oxisol. For this study, the aggregates were grouped into greater size ($> 4\text{ mm} - 2\text{ mm}$) and lesser size ($0.5\text{ mm} - < 0.21\text{ mm}$). The soils presented different proportion in each aggregate class (from greater to lesser): Inceptisol - 27 %, 26 %, 24 %, 13 % and 9 %; Oxisol - 14 %, 16 %, 31 %, 25 % and 14 %.

1.2.3. MINERALOGICAL ANALYSIS OF THE SAND, SILT AND CLAY FRACTIONS OF THE DIFFERENT AGGREGATES CLASSES

1.2.3.1 Sand, silt and clay fractions separation

For the removal of the organic matter, 50 g of each sample aggregates were used. To remove the organic matter, a hydrogen peroxide solution at a concentration of 30% (v / v) was then added to each sample and kept in contact for up to two weeks (Gee and Bauder, 1986). The content was passed on to a 0.05 mm mesh sieve, holding up the sand fraction. The separation of clay and silt fractions was done by sedimentation of the particles per Stokes law (Jackson, 1979).

1.2.3.2. X-Ray Diffraction (XRD) of the Sand, Silt and Clay fraction without any treatment (natural)

To identify the minerals by XRD, samples of sand, silt and clay within each aggregate were mounted onto a Koch plate (not oriented samples). The diffraction patterns were obtained in vertical goniometer Panalytical X'Pert3 Powder, with a speed of $0.42^\circ 2\theta \text{ s}^{-1}$ and range $5 - 70^\circ 2\theta$. The diffractometer, equipped with a Ni filter and using a $\text{CuK}\alpha$ radiation operated at 40 kV and 40 mA.

The standard Hanawalt indexing method was used to properly identify the mineral species from the X-Ray diffraction pattern. With this method, after the X-Ray diffraction pattern was obtained and the three strongest reflection peaks converted from 2θ angles to d-spacing values, a search was then begun to match the d-spacing values of the unknown pattern to those in an index book (table of key lines in X-Ray powder diffraction patterns of mineral in clays and associated rocks).

1.2.3.3. Extraction of low crystallinity iron oxides in the clay fraction of different aggregate classes

The low crystallinity Fe oxides of clay fraction were extracted with ammonium oxalate $[(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}]$ 0.2 mol L^{-1} at pH 3.0 in the dark (Schwertmann, 1964). 0.4 g of TFSA and 40 mL of ammonium oxalate solution were added in a plastic tube of 50 ml volume and covered with aluminum foil. The suspensions were shaken for 2 hours on a horizontal stirrer and finally, centrifuged at 2000 rpm for 10 minutes. The Fe content was determined in the extract by the orthophenanthroline colorimetric method.

1.2.3.4. Extraction of pedogenetic Fe oxides in the clay fraction of different aggregate classes

To concentrate the kaolinite and gibbsite and to study the composition of crystallized Fe oxides, the clay samples of aggregate classes were submitted to dithionite-citrate-bicarbonate extraction (DCB) (Mehra and Jackson, 1960). The residue was washed with two types of solution applied in a specific order to remove the excess of salts (with a wash solution of $(\text{NH}_4)_2\text{CO}_3$ 1 mol L⁻¹ and deionized water). The Fe content was determined in the extract by the orthophenanthroline colorimetric method. The residue was analyzed by XRD to study the crystallographic characteristics of kaolinite and gibbsite.

1.2.3.5. Extraction of gibbsite and kaolinite in the clay fraction of different aggregates classes

To study the iron oxides by XRD, clay samples of aggregate classes were submitted to the extraction of kaolinite and gibbsite. The removal of kaolinite and gibbsite was achieved by boiling the samples with NaOH 5 mol L⁻¹, for 1h:30 min in a sand-bath at 250°C, followed by extractions with HCl 0.5 mol L⁻¹ (Norrish and Taylor, 1961; Kämpf and Schwertmann, 1982; Singh and Gilkes, 1991). After washing to remove the excess of salts and drying the residue was analyzed.

1.2.3.6. Study of the Kaolinite and Gibbsite from the DCB residue

1.2.3.6.1. Quantitative analysis of kaolinite and gibbsite in the clay fraction by thermogravimetric analysis

A sample of 15 mg of iron free clay (treated with DCB) was placed on the platinum crucible of the differential thermogravimetric analyzer and was gradually heated, from room temperature to 950 °C, using nitrogen atmosphere at a heating rate of 10 °C / min and a flow gas of 50 ml / min. The kaolinite and gibbsite content was determined by considering the mass loss per the heating of each sample.

1.2.3.6.2. Crystallographic Characteristic of the Kaolinite and the Gibbsite by XRD

The crystallite size of the kaolinite and the gibbsite was calculated from the width at half height of the intensity and of the position of the reflections of the minerals (001) and (002) respectively using NaCl as the internal standard (Melo et al., 2001a). The mixture (around 65 mg g⁻¹) of NaCl with the sample was made and homogenized into a mortar. To obtain the width at half height corrected, the equation adjusted by Melo et al. (2001b) from the data presented by Klug and Alexander (1954) was considered.

The crystallinity index (Hughes and Brown Crystallinity Index) for the kaolinite was calculated only in the Inceptisol. Due to the high levels of gibbsite in the clay samples of

Oxisol, the crystallinity of kaolinite was not estimated by XRD in DCB-treated samples. The reflection (110) of the gibbsite at $20.3^\circ 2\theta$ (CuK α radiation) makes it impossible to measure the parameter h_1 of the formula proposed by Hughes and Brown (1979). The calculation of the HBCI index for kaolinite is made by using the reflection height ratio (020) (value h_1) and the difference between the suspended baseline formed by the triplets in the region of 35 to $40^\circ 2\theta$ and the base of the diffractogram (h_2) (Figure 1).

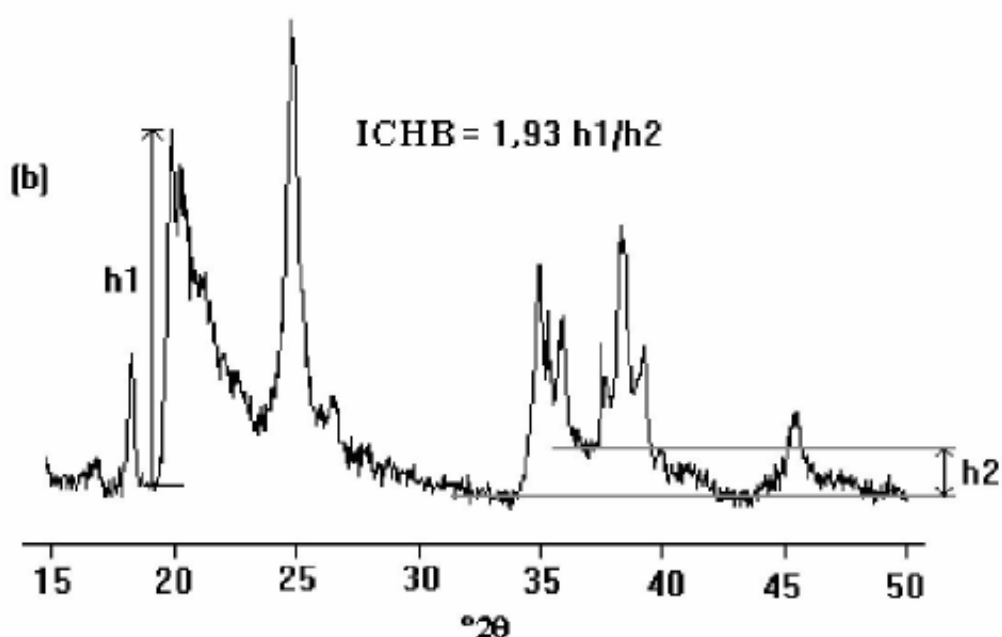


Figure 1. Hughes and Brown Crystallinity Index for Kaolinite by XRD

1.2.3.7. Study of the Fe oxides by XRD in the extraction residue with NaOH 5 mol L⁻¹

1.2.3.7.1. Ratio of goethite to hematite [Gt / (Gt + Hm)]

The ratio was calculated using the equation proposed by Camêlo (2013): $[Gt / (Gt + Hm)] = 1 - [4 \times A(Hm_{012}) / 4 \times A(Hm_{012}) + A(Gt_{110})]$. $A(Hm_{012})$ = area of the 012 reflection of the hematite; $A(Gt_{110})$ = area of the 110 reflection of goethite.

1.2.3.7.2. Al-substitution (isomorphous substitution) within the mineral structure of the hematite and the goethite

The isomorphous substitution of the Fe by the Al in the structure of iron oxide minerals was estimated by the reflection of the peak position in the XRD patterns in the clay

fraction. For the Hematite, the Al-substitution was calculated with the equation proposed in Schulze (1984) and for the Goethite, with the equation proposed in Schwertmann et al. (1979)

1.2.4. STATISTICAL ANALYSIS

All the analyzes were performed in triplicate. The data were submitted to the analysis of variance and comparison of means by Duncan test (5%) through the following programs: Statistica 10.0, Sigma Plot 12,0 and Microsoft office Excel 2016.

1.3. RESULTS AND DISCUSSION

1.3.1. MINERALOGY OF SAND, SILT AND CLAY FRACTIONS BY XRD OF DIFFERENT CLASS OF AGGREGATES

1.3.1.1. Mineralogy of sand fraction

For the Inceptisol, both greater aggregates (>4 mm) and lesser aggregates (<0.5 mm) contain mainly quartz (Figure 2a). Quartz is the predominant mineral in the sand fraction and presents a high degree of crystallinity (Muggler et al., 2006).

The XRD patterns for the Oxisol samples reveals a fair range of minerals. For both greater and lesser aggregates, the following mineral were found: quartz, Al hydroxide (gibbsite) and Fe oxide (hematite) (Figure 2a).

The sand fraction of both soils presented similar mineralogical characteristic in both the greater and the lesser aggregates. No variation was detected in minerals species when compare the XRD of the greater aggregates to that of the lesser aggregate. However, the intensity of the reflection was higher in the lesser aggregates, and that for both soil type. In the Oxisol both greater and lesser aggregate sizes revealed the presence of the mineral hematite. This may have been a result of the presence of petroplintite in the samples and hence, interacting with the copper based material of the X-Ray diffractometer and consequently causing inflorescence in the diffractogram for this soil class.

1.3.1.2. Mineralogy of silt fraction

The silt fraction of both soil contains a large amount of quartz with traces of kaolinite and feldspar in both greater and lesser aggregates for the Inceptisol (Figure 2b). The Oxisol although predominantly quartz, contains hematite more specifically in the position (104) and (110). The silt fraction contains very few of the primary minerals considered to be the source of nutrients. Therefore, presenting a low value when it comes to plant nutrition. In both soils, the lesser aggregates show specific variation regarding the greater aggregates. The intensity of the reflections revealed to be higher in the lesser aggregates. This could be an indication of high crystallinity of the minerals (Cezar et al., 2012).

1.3.1.3. Mineralogy of the clay fraction

The clay fraction of both soil present mainly kaolinite and oxides (gibbsite and hematite (Figure 2c). The Inceptisol contains a very large proportion of kaolinite along with some other minerals such as gibbsite and some primary minerals (micas and illite). The Oxisol is less heterogenous when it comes to mineral diversification. Although containing

lesser kaolinite, its clay fraction contains mainly gibbsite and hematite. The high levels of gibbsite in Oxisols are consistent with their high degree of weathering (Melo et al., 2003). The lesser aggregates for Oxisol present higher peak intensity than the greater aggregates, especially for the highly-weathered mineral such as gibbsite and hematite.

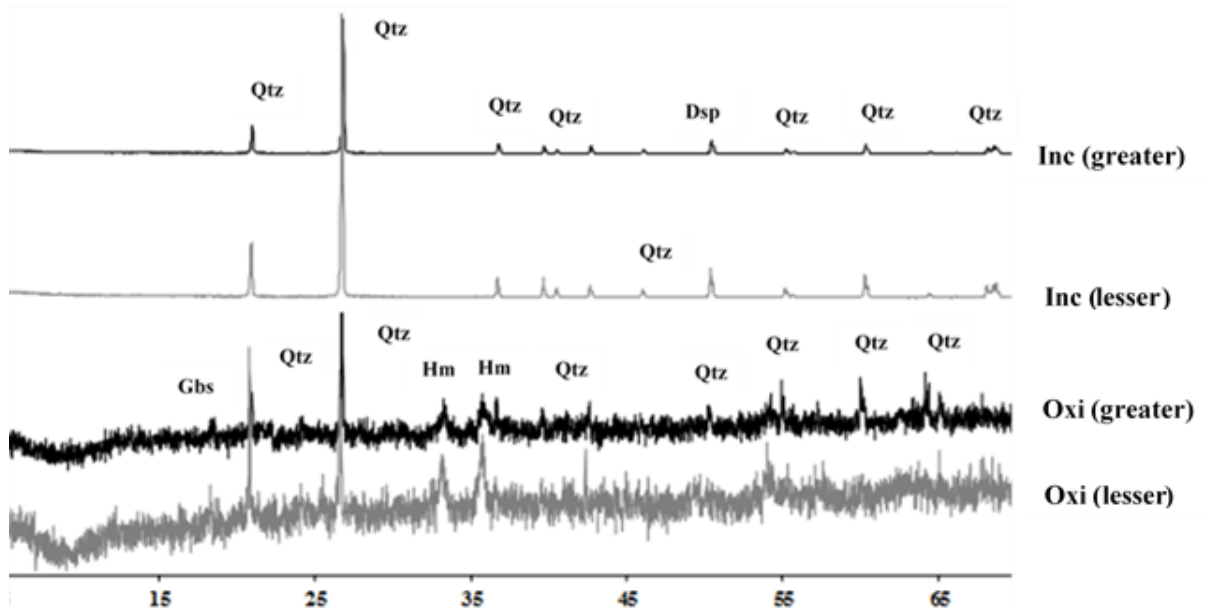


Figure 2a. Conventional XRD patterns (XRD) of the sand fraction for an Inceptisol (Inc) and an Oxisol (Oxi). Greater = > 4 mm – 2 mm, lesser = 0.5 mm - < 0.21 mm. Qtz = Quartz; Dsp = Diaspore; Gbs = Gibbsite; Hm = Hematite

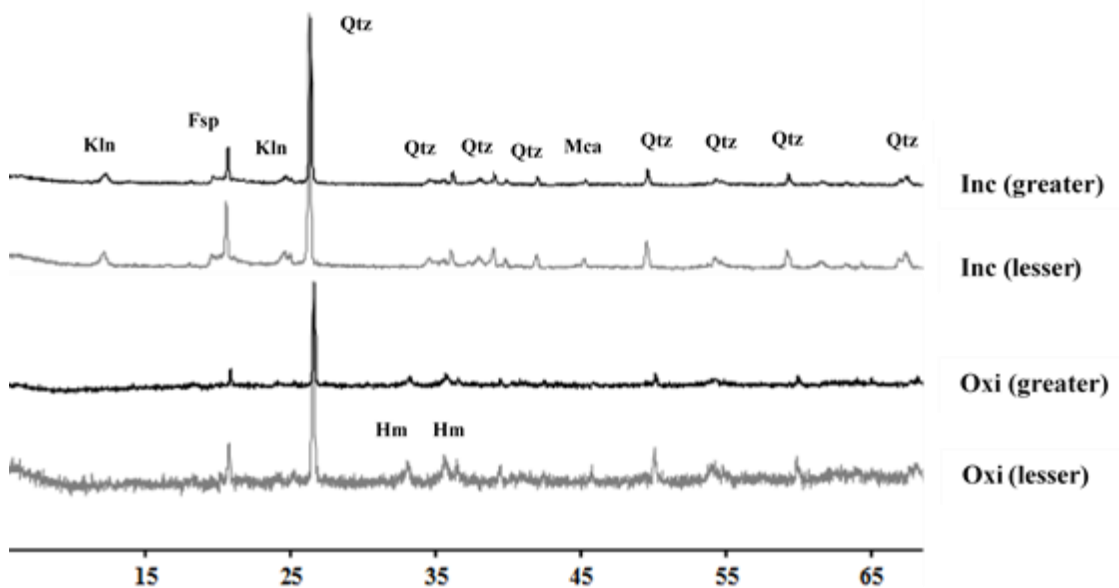


Figure 2b. Conventional XRD patterns (XRD) of the silt fraction for an Inceptisol (Inc) and an Oxisol (Oxi). Greater = > 4 mm – 2 mm, lesser = 0.5 mm - < 0.21 mm. Qtz = Quartz; Hm = Hematite; Mca = Micas; Fsp = Feldspar; Kln = Kaolinite

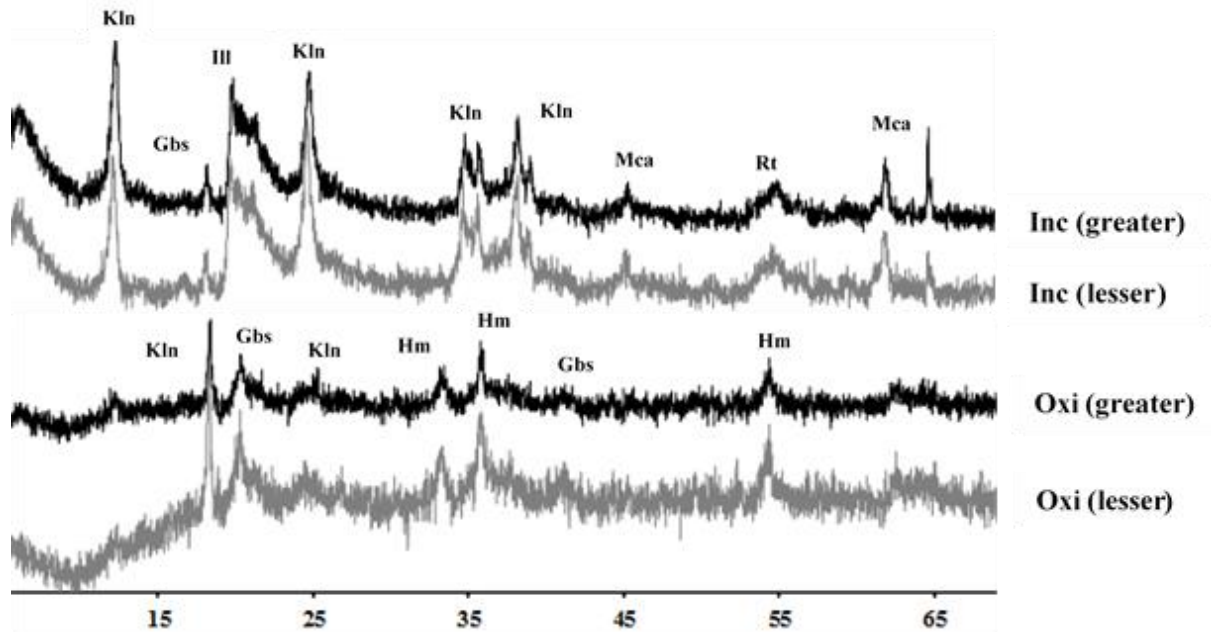


Figure 2c. Conventional XRD patterns (XRD) of the clay fraction for an Inceptisol (Inc) and an Oxisol (Oxi). Greater = > 4 mm – 2 mm, lesser = 0.5 mm - < 0.21 mm. Gbs = Gibbsite; Hm = Hematite; Mca = Micas; Fsp = Feldspar; Kln = Kaolinite; Ill = Illite; Rt = Rutile

1.3.2. MINERALOGY OF IRON OXIDES IN THE CLAY FRACTION OF DIFFERENT CLASS OF AGGREGATES

1.3.2.1 Extraction methods: Ammonium Oxalate (amorphous Fe oxides) and Dithionite-Citrate-Bicarbonate (DCB) (amorphous + crystalline Fe oxides)

The distribution of Fe oxides throughout the aggregates showed a certain heterogeneity within each soil type. While the Fe_2O_3 - DCB gives a spatial representation of the total amount of this mineral in each soil (both crystalline and amorphous), the Fe_2O_3 -OA itself presents only the concentration of the amorphous forms. Therefore, an equation where the concentration of the OA is deducted from the DCB will estimates the concentration of crystalline iron oxides.

The concentration of amorphous Fe_2O_3 for the Inceptisol varied from 5.1 to 5.6 g kg^{-1} and from 2.9 to 3.0 g kg^{-1} for the Oxisol according to the aggregate class (Figure 3a). Although there was little variation within the aggregates (both greater and lesser) for the Inceptisol, the concentration of the aggregate size 2 – 4 mm (part of the greater aggregates) was inferior to the others. The amorphous forms of Fe are not favored by the lower soil moisture, which may have resulted in lower Fe-OA levels in the larger Inceptisol aggregates. Smaller aggregates can retain more water through smaller micropore diameters. As a practical

result, for example, the smaller aggregates present higher P fixing capacity, since the amorphous Fe oxides present a high specific surface area (refer to this area ratio in amorphous). For the Oxisol, such tendency was not found and all aggregates showed similar concentration of $\text{Fe}_2\text{O}_3\text{-OA}$.

As for the concentration of the $\text{Fe}_2\text{O}_3\text{-DCB}$, no significant differences were found within the aggregates for both the Inceptisol and the Oxisol. However, in the Oxisol, the aggregate size 0.21 – 0.5 mm showed a tendency of having a lower concentration on crystalline iron oxide (Figure 3b).

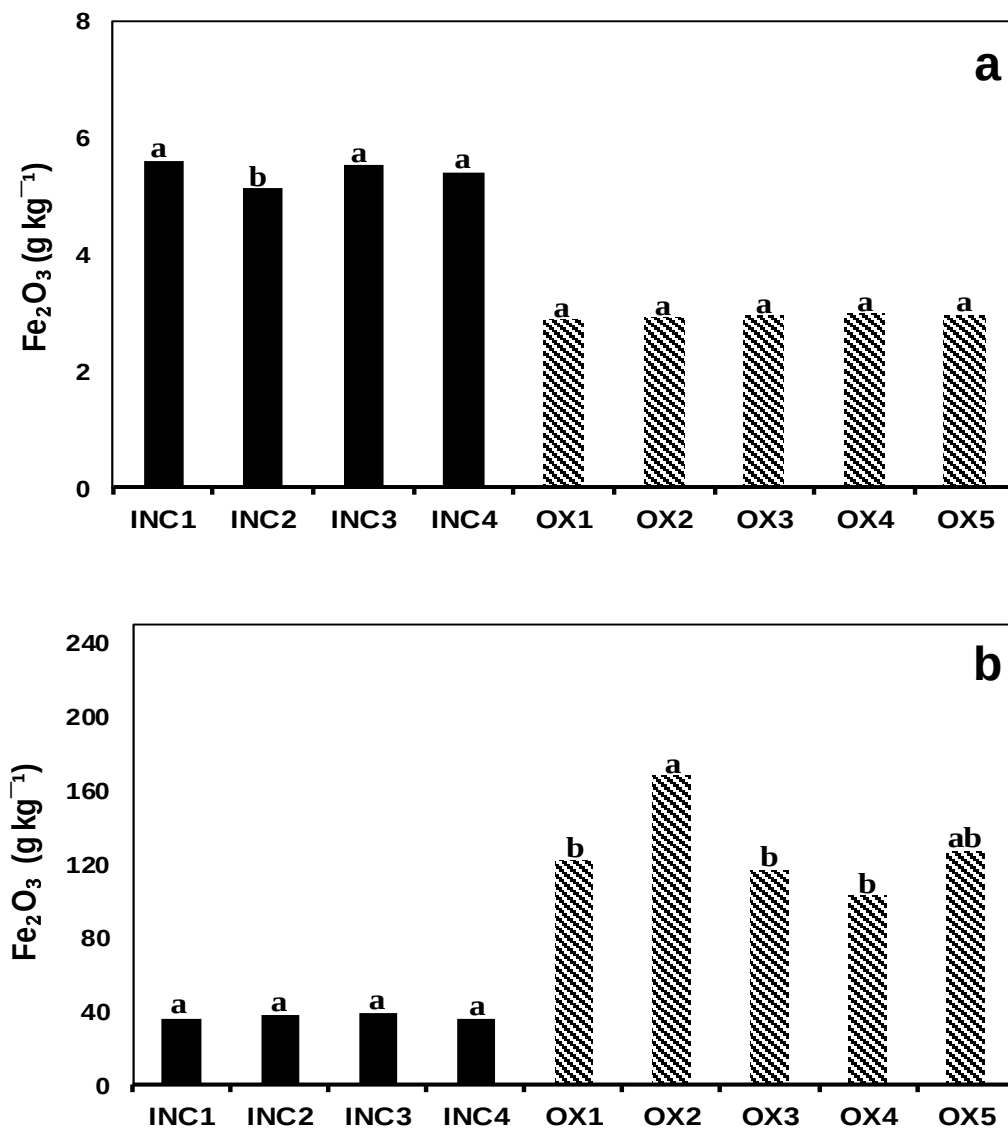


Figure. 3. (a) Ammonium Oxalate (amorphous) Fe_2O_3 (b) Dithionite Citrate-Bicarbonate (amorphous + crystalline) Fe_2O_3 . INC1 = > 4 mm; INC2 = 2 – 4 mm; INC3 = 0.5 – 2 mm; INC4 = < 0.5 mm; OX1 = > 4 mm; OX2 = 2 – 4 mm; OX3 = 0.5 – 2 mm; OX4 = 0.21 – 0.5 mm; OX5 = < 0.21 mm

1.3.2.2. Study of iron oxides by XRD within the residue of kaolinite and gibbsite extraction with NaOH 5 mol L⁻¹

Hematite and Goethite were the only iron oxide minerals in the clay fraction treated with NaOH 5 mol L⁻¹ by the XRD patterns (Figure 4). The occurrence of these iron oxide minerals can be explained through the diagenesis of primary minerals that contains Fe within their internal structure. The main factors that favor the formation of Gt in detriment to Hm in the soil and therefore compete to increase the Gt / (Gt + Hm) ratio, are lower iron content in the parental material, lower temperatures, higher humidity and Content of organic matter and lower pH values (Schwertmann and Kämpf, 1985). Hematite peaks were not observed in the clay fraction for the Inceptisol (Figure 4a) and the ratio Gt / (Gt+Hm) was 1,0 in all the aggregate classes for this soil (Table 1).

The Oxisol presented reflection of both the Hematite and the Goethite. The peak position for the Hematite were found in the following positions at degree 2 Θ : (012), (104) and (110). As for the Goethite, only one position was found: (110) (Figure 4b). The ratio Gt / (Gt+Hm) in all the aggregate classes for the Oxisol was lower than 0.3 (table 1), therefore proving the predominance of hematite.

The Gt / (Gt + Hm) ratio was similar between the classes of aggregates for both soils (Table 1), indicating that the pedogenetic conditions for hematite and goethite formation were the same for the whole matrix of each soil.

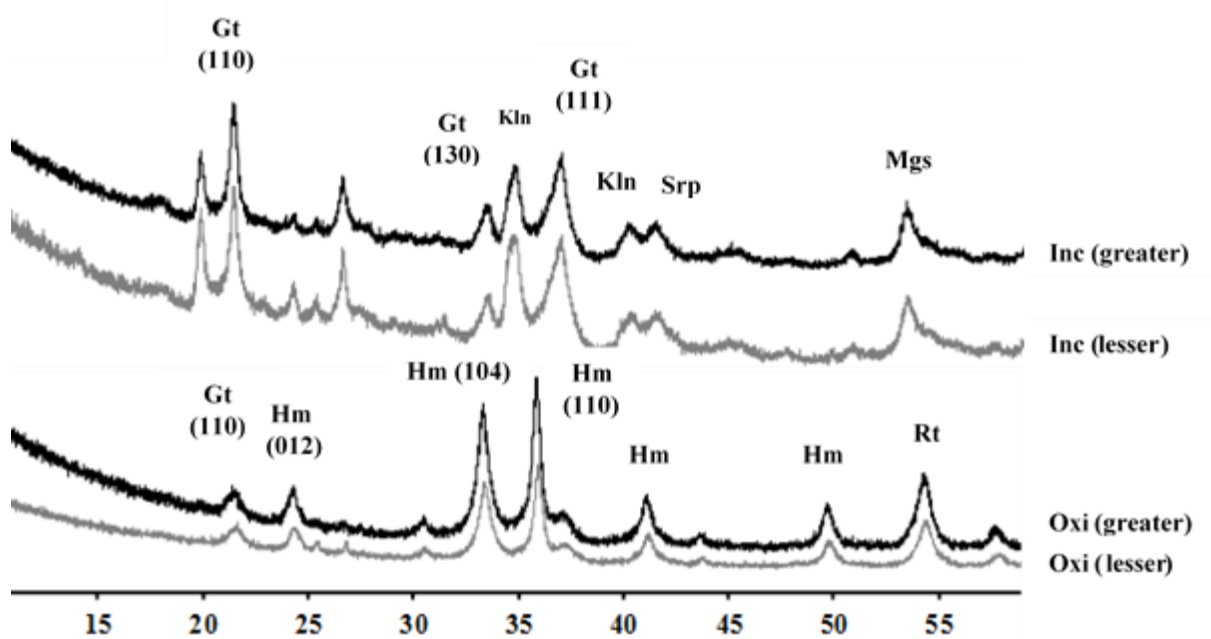


Figure 4. XRD Patterns of iron oxides (Hematite and Goethite) for an Inceptisol (Inc) and an Oxisol (Oxi). (a) Inceptisol (b) Oxisol. Greater = > 4 mm – 2 mm, lesser = 0.5 mm - < 0.21 mm. Gt = Goethite; Hm = Hematite; Kln = Kaolinite; Rt = Rutile; Srp = Serpentine; Mgs = Magnesite.

The reflection at peak position (110) for the goethite shows a negative correlation between the crystallite size of the mineral and its width at half Intensity (Table 1, figure 4). There were no significant variations in this parameter between the classes of aggregates for the two soils (Table 1)

The crystallite size of the goethite in the (110) direction was greater in the Inceptisol than in the Oxisol (Table 1). This indicates that the Goethite in the Inceptisol is much more crystalline than that in the Oxisol. The goethite and hematite crystallite size were different among the different classes of aggregates, indicating that the growth of Fe oxides in the clay fraction was differentiated within the same soil matrix. The smaller the crystal size, the greater its specific surface area and the greater its reactivity in the soil (Barbieri et al., 2013). This is equivalent to say that the aggregates of Inceptisol and Oxisol present different chemical environments when considering crystalline Fe oxides.

However, the relationship between the size of the crystallites in the various directions of Fe oxides was similar among the different classes of aggregates, especially for hematite (Table 1). Relations closer to 1.0 indicate more isodimensional crystals, with lower surface area exposure. On the other hand, very distant values of 1.0 are consistent with a more acicular form of goethite (Ristic et al., 2013). Therefore, goethite in the 2-4 mm aggregate size is expected to exhibit the highest reactivity for the Inceptisol: ratio between crystallite

size farthest from 1.0 (ratio $A = 3.0$) and lower mean crystal sizes in the directions (110) and (111). It was not expected values as far as 1.0 for the relationships between goethite crystallites size, since this mineral in the soil presents a more irregular shape, different from the acicular format of synthetic goethites (Costa and Bigham, 2009).

The isomorphic substitution (IS) in the Inceptisol was determined only in the goethite, since there was no detection of the hematite in any of the aggregates of this soil. As for the Oxisol the substitution was evaluated only in the hematite since the goethite reflection for the peak (111) presented a low intensity. In the Inceptisol the Al-substitution in the mineral goethite varied from 231.4 to 273.8 mmol mol⁻¹ among the aggregates with a tendency of being higher within the 2 – 4 mm aggregate class (Table 1). For the Oxisol the Al-substitution in the hematite was higher for the 0.5 - 2 mm aggregate size. The isomorphic substitution of Fe by Al (IS) in the structure of Gt and Hm is quite common, and as a result causes changes in unit cell size and particle crystallinity. The higher SI degree in iron oxides is usually associated with more weathered soils with higher Al activity. Due to the smaller ionic radius of Al in relation to Fe, the unit cell size, mainly in the direction of the Z axis, and the degree of crystallinity of the mineral are reduced with the IS. (Pires, 2004; Junior et al., 2010)

Table 1. Crystallite size, Crystallite size ratio, Isomorphous substitution (Al-substitution) in Goethite and Hematite and the ratio [(Gt / (Gt+Hem)] in the clay fraction of an Inceptisol and an Oxisol

Soil type	Horizon	Aggregate size [mm]	Crystallite size [nm]							Crystallite size ratio			(IS) (mmol mol ⁻¹)		WHI (°2θ)
			Gt/ (Gt+Hem)	Gt (110)	Gt (130)	Gt (111)	Hem (104)	Hem (012)	Hem (110)	A	B	C	Gt	Hem	Gt (110)
Inceptisol	B	> 4	1.0	18.1	12.5	7.6	-	-	-	2.4	1.5	-	231.4	-	0.5
Inceptisol	B	2 - 4	1.0	17.3	13.4	5.7	-	-	-	3.0	1.3	-	273.8	-	0.5
Inceptisol	B	0.5 - 2	1.0	18.5	11.8	7.8	-	-	-	2.4	1.6	-	248.3	-	0.4
Inceptisol	B	< 0.5	1.0	17.5	11.1	7.3	-	-	-	2.4	1.6	-	258.3	-	0.5
Oxisol	B	> 4	0.2	9.0	-	-	10.6	17.1	19.1	-	-	0.6	-	192.4	0.9
Oxisol	B	2 - 4	0.3	7.9	-	-	10.7	16.2	16.5	-	-	0.7	-	202.4	1.0
Oxisol	B	0.5 - 2	0.2	8.9	-	-	11.5	13.4	18.4	-	-	0.6	-	281.4	0.9
Oxisol	B	0.2 - 0.5	0.2	8.8	-	-	11.8	15.6	16.9	-	-	0.7	-	248.2	0.9
Oxisol	B	< 0.2	0.2	9.5	-	-	11.9	14.0	17.2	-	-	0.7	-	267.3	0.9

Crystallite size (CS) ratio: A= CS Gt (110) / CS Gt (111), B= CS Gt (110) / CS Gt (130), C= CS Hem (104) / CS Hem (110); (-) not determined due to the absence or the low intensity of the mineral in the reflection by XRD. IS: Isomorphous substitution. WHI: Width at Half Intensity

1.3.3. MINERALOGY OF KAOLINITE AND GIBBSITE IN THE CLAY FRACTION OF DIFFERENT CLASS OF AGGREGATES TREATED WITH DCB FOR Fe OXIDES REMOVAL

1.3.3.1. Concentration of Gibbsite and Kaolinite

The Differential Thermogravimetric Analysis of the residue of the DCB samples showed that there was a homogeneity within the greater aggregate sizes on the content of gibbsite for the Oxisol. This homogeneity was observed for all aggregate sizes for the Inceptisol.

There was a considerably lower concentration of gibbsite in the Inceptisol when compared to the Oxisol and the opposite was observed regarding the kaolinite where the higher concentration occurred in the Inceptisol (Figure 5). In the Inceptisol both greater and lesser aggregates showed an average concentration of 83.0 g kg^{-1} and 698.1 g kg^{-1} respectively for the Gibbsite and the Kaolinite. In the Oxisol the concentration of Gibbsite was in average three times (249.0 g kg^{-1}) (figure 5a) higher than that of the Inceptisol and more than two-time lower (313.1 g kg^{-1}) in Kaolinite concentration (figure 5b).

There was not a significant difference amongst the aggregate sizes of the Inceptisol for Gibbsite content (figure 5a). However, this behavior was not noticed for the aggregate sizes of the Oxisol. The lesser aggregate size (OX5) was lower in Gibbsite content when compared to the other aggregate sizes (figure 5a). It is possible that the smaller sizes of this aggregate which in turn provide a larger specific surface area, allows the retention of water in a micro type environment. Therefore, promoting the stabilization of 2:1 type minerals and retention of Silica. Herrmann (2007) found similar behavior when analyzing gibbsite formation in soils from northern Thailand and concluded that the formation of Gibbsite is not only dependent on the parental material but also on the water storage capacity. The greater the capacity, the less probable the gibbsite formation will occur.

As for the Kaolinite, the Oxisol's aggregate sizes presented no significant difference for Kaolinite content. However, in the Inceptisol, the lesser aggregate size, presented lower kaolinite content. The silica content within the aggregate size can provide resistance in the mineral complete formation and content. It has been argued throughout this study that lesser sizes aggregates have larger specific surface area and therefore have more water retention capacity, which prevent the desilication process (Ker, 1997).

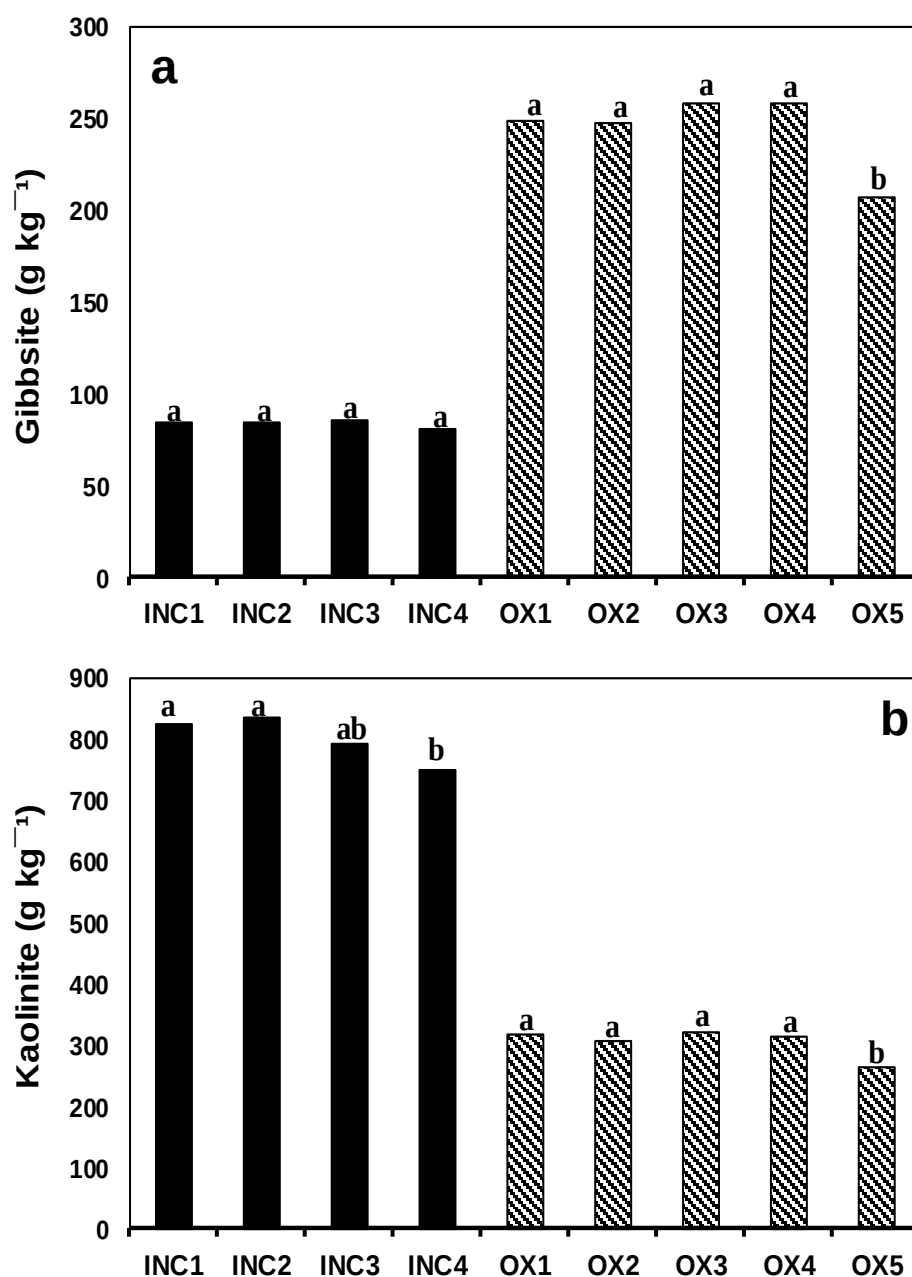


Figure 5. Concentration of Gibbsite (a) and Kaolinite (b) in the desferrous clay (treated with DCB) of different classes of aggregates of Inceptisol and Oxisol. INC1 = > 4 mm; INC2 = 2 – 4 mm; INC3 = 0.5 – 2 mm; INC4 = < 0.5 mm; OX1 = > 4 mm; OX2 = 2 – 4 mm; OX3 = 0.5 – 2 mm; OX4 = 0.21 – 0.5 mm; OX5 = < 0.21 mm

1.3.3.2. Crystallography of the Gibbsite and Kaolinite

Taking under consideration the fact that the Inceptisol only presented small quantities of the Gibbsite, it was not considered relevant to calculate the crystallography of this mineral for this specific soil type. The abundance of Kaolinite somehow did not allow the Gibbsite peak to be fully expressive. Regarding the kaolinite, both soil types were taken under consideration for the calculation of the crystallite size. And beside the crystallite size a

crystallinity index was determined (The Hughes and Brown Crystallinity Index) to further ascertain the crystallinity of the kaolinite for the Inceptisol since this mineral concentration was higher within the aggregates of this soil type.

The values encountered for crystallite size of the Gibbsite varied from 87 nm to 249 nm (figure 6a). Camargo et al. (2008) studying several types of Oxisols in Brazil found an average value of 90 nm, deducing that the degree of crystallinity was very high for the Gibbsite of this soil. Melo et al. (2001) also found similar results for Oxisols in the State of Parana in Brazil. All aggregate sizes, but OX3 presented similar values when it comes to crystallite size. However, the lesser aggregate size OX5 presented significant variations, allowing it to be similar to all other aggregate size including OX3. This behavior of the crystallite size for the Gibbsite although marked by a strong variation among the aggregate sizes of the Oxisol, shows a quasi-even distribution of gibbsite contents (all aggregate sizes with similar content except for the middle size aggregate INC3). The mineral growth was therefore differentiated according to the aggregate size INC3. (Figure 6)

The mean diameter of the kaolinite crystal differs in both soil and within aggregates (Figure 6). The crystallite size of the Kaolinite in the Inceptisol is in average almost the double (19 nm) of that of the Oxisol (figure 6b). There was no significant difference in the crystallite size between the aggregates of the Oxisol. As for the Inceptisol, all aggregates except those between 0.5 mm and 2 mm (INC3) were statistically equal. The kaolinite in this aggregate size was significantly higher than the kaolinite in the greater aggregate size (> 4 mm) for the Inceptisol. These two sizes of aggregates present the same kaolinite contents, but in the greater size, it should be expected that the kaolinite be more active in the soil. Melo et al (2002a) sampling soils from the State of Espirito Santo in Brazil found average value of 18,2 nm for the crystallite size of the kaolinite and concluded that the analyzed samples showed a high crystallinity of Kaolinite possibly due to the purity of the parental material which in turn allowed the symmetrical growth of the mineral along with its crystallinity process.

The Hughes and Brown Crystallinity Index (HBCI) is used to estimate the crystallinity of the kaolinite (Aparicio and Galan, 1999; Melo and Wypych, 2009). Unfortunately, due to some limitations that this index presents, it cannot be determined when in the sample there is high concentration of gibbsite (Melo and Wypych, 2009; Fernandes, 2017). The Inceptisol presented a HBCI from 12.4 to 15.4 with an average of 13.0. All the aggregate sizes, but INC2, presented similar crystallinity. The aggregate size INC2 presented lower crystallinity

when compared to the lesser aggregate sizes (INC3 and INC4) (figure 6c). This behavior contradicts the results found by Chittleborough and Walker (1988) in which the crystallinity of the kaolinite was verified to be higher in the greater particle of clay. According to Camargo et al., (2008) the higher crystallinity is a result of greater crystallite size and lesser width at half intensity. The evidence that the aggregate size INC2 presents a lesser crystallite size when compared with the aggregate size INC3 (figure 6a) could very well explain the reasons as to, why this aggregate size has a lower HBCI. Melo et al (2002b) found average HBCI of 10.9 for the soil of Espiritu Santo in Brazil, Melo et al (2001) found average of 12.6 for various States in Brazil, results much higher when compared to highly weathered environment

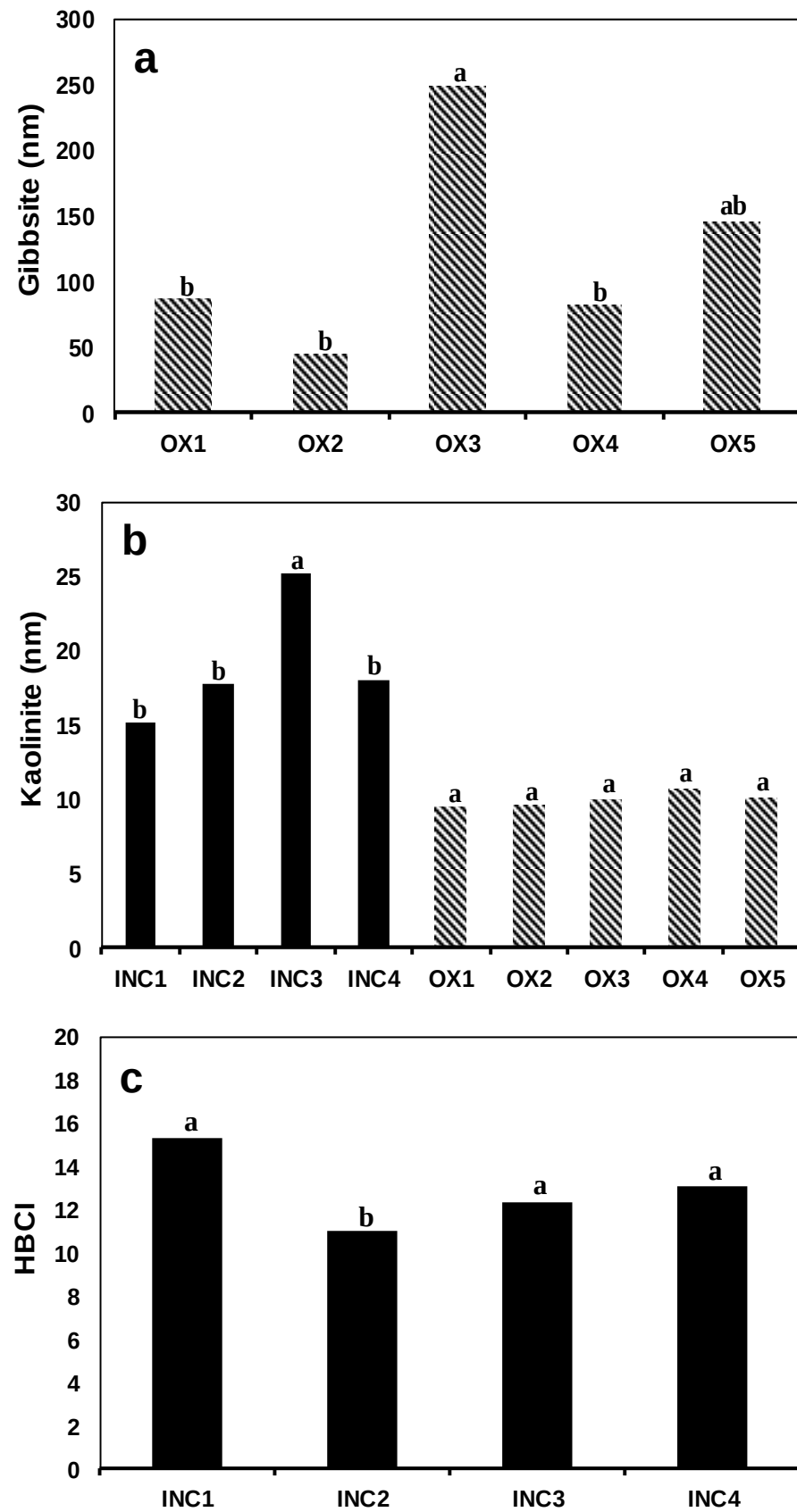


Figure 6. (a) Gibbsite crystallite size (b) Kaolinite crystallite size (c) HBCI of Kaolinite. INC1 = > 4 mm; INC2 = 2 – 4 mm; INC3 = 0.5 – 2 mm; INC4 = < 0.5 mm; OX1 = > 4 mm; OX2 = 2 – 4 mm; OX3 = 0.5 – 2 mm; OX4 = 0.21 – 0.5 mm; OX5 = < 0.21 mm

1.4. CONCLUSIONS

The sand and silt fractions of both the Inceptisol and Oxisol throughout the respective aggregate classes is predominantly constituted by the mineral quartz with traces of minerals with lower intensity such as diasporite for the Inceptisol; gibbsite and Hematite for the Oxisol. These low intensity minerals reflect the parental material of each soil type, indicator of both nutrient availability and pedogenetic formation.

The clay fraction of Inceptisol presented the predominance of the mineral kaolinite (Kt) highly crystallized within the different aggregate classes. For the aggregate classes of the Oxisol, the predominant minerals were the gibbsite and hematite with moderate to high degree of crystallinity. Throughout all the aggregate sizes, no Hematite were found in the Inceptisol and the Oxisol only contained traces of the mineral goethite. The Inceptisol for its clay mineralogy within the aggregate size ($> 4 - < 0.5$ mm) revealed to be Kaolinitic, while the Oxisol ($> 4 - < 0.21$ mm) is more oxidic.

The ratio $[Gt / (Gt + Hem)]$ was absolute in the Inceptisol for all aggregate size, indicating the predominance of the Goethite as iron oxide, while in the Oxisol this ratio revealed to be low, hence making the Hematite the predominant iron oxide mineral for both greater and lesser aggregates. The Abundance of aluminum oxide and iron oxide in the Oxisol within its aggregate classes is an indicator of the advanced weathering process when compared to that of the Inceptisol.

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CHAPTER 2. POTASSIUM NUTRITION OF WHEAT (*Triticum Aestivum*) AND MINERAL NUTRIENT RESERVE IN DIFFERENT AGGREGATE CLASSES OF TWO SOIL TYPES FROM PARANA, BRAZIL.

ABSTRACT

Approximately 98 % of K in the soils are found in feldspars and phyllosilicates in crystalline forms and therefore not available to plants. However, the bioavailability of this nutrient in its different mineral forms is very variable and depends on several factors (concentration in the soil solution, cation exchange capacity (CEC), degree of soil weathering, etc.) that influence the chemical balance of the nutrient within the soil. The objective of the present work was to study the different forms of K (mineral reserve) in different classes of young (Inceptisol) and highly weathered (Oxisol) soils aggregates developed from granite/gneiss and basalt, and to evaluate the nutrient availability for wheat plants. For this study, two soil classes from the were taken under account: a distro-ferric Oxisol and a haplic Inceptisol. Both soils were separated into aggregate size; the Oxisol in 5 classes (> 4 mm, 2 – 4 mm, 0.5 – 2 mm, 0.21 – 0.5 mm, and < 0.21 mm) and the Inceptisol in 4 classes (> 4 mm, 2 – 4 mm, 0.5 – 2 mm, and < 0.5 mm). Each aggregate size in both soils were evaluated for K uptake in its several mineral forms in wheat. The results revealed a strong linear relationship of unit slope between the Mehlich-1 extraction method for exchangeable-K and cumulative K uptake by wheat, indicating that this method is a major form of K available to plants. Thus, non-exchangeable-K contribution was dependent on the soil class and aggregate size. For the Inceptisol this contribution although little occurred only in the greater aggregate sizes (> 4 mm and 2 – 4 mm) while for the Oxisol this contribution was seen in all the aggregate sizes. The NH₄Oac extraction method for exchangeable-K was found to be uncorrelated to K uptake in wheat.

Key-words: K-balance, non-exchangeable K, total K

2.1. INTRODUCTION

Potassium deficiency is a world-wide problem (Dobermann et al., 1998). In Europe, 25% of soils routinely test low in available K (Johnston, 2003) and most soils in sub-Saharan Africa test low in available K (Smaling, 1998). At the same time, the K status of agricultural soils is also decreasing across the globe, from Europe (Fagerberg et al., 1996; Bengtsson et al., 2003), to Africa (Harris, 1998; Wortmann and Kaizzi, 1998), to Asia (Hedlund et al., 2003; Wijnhoud et al., 2003), and North America (Malo et al., 2005).

The bioavailability of K is very variable and depends on several factors such as: concentration in the soil solution, cation exchange capacity (CEC), degree of soil weathering, etc. The K in the soil solution is in the form of ion and is readily available to plants and microorganisms. The fact that it is in the form of free ions causes its degree of leaching to be very high. The exchangeable K is found in different exchange points (CEC). It is retained in soil CEC through electrostatic bonds on the surface of minerals and humic substances. Although these two forms of K are considered readily available to plants, they only represent a very small percentage (up to 2%) of K in soil (Zorb et al., 2014)

Other mineral forms of potassium in soil are non-exchangeable and structural (Andrist-Rangel et al., 2010). These two forms account for about 98 % of the total, and unfortunately are either slowly available or unavailable to plants. The K in structural form is the most representative in the soil. It is usually found in biotite (trioctahedral mica) in muscovite (mica dioctahedral) and feldspars. The weathering of these primary minerals makes the K contained within the structure to be released to the soil solution (Zorb et al., 2014). 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 the dissolution of the structure (Kirkman et al., 1994).

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; Blake et al., 1999). The retention of K in the soil and the accumulation of residues as reserves are dependent on the physical composition of the soil and the environmental factor that influence the adsorption and release of potassium as well as its leaching throughout the soil profile. The absorption of K by the roots of plants plays an important role in the control, charge balance and availability of the nutrient, due to the decrease in the concentration it generates in the rhizosphere (Sanes et al., 2013).

Due to the smaller diameter of the micropores it can be expected that the mineral reserve of aggregates less than 0.105 mm (lower class) would be more significant in term of the nutrient concentration, because it represents a more confined environment where less leaching of silica and bases occurs. Thus, in practical terms, the wheat roots growing in a soil with different aggregations of classes (undisturbed soil block of 20 cm side) will find various micro-environments in terms of fertility and K reserve (Melo et al., 2008).

The objective of this work was to study the different forms of K (mineral reserve) in different classes of young (Inceptisol) and highly weathered (Oxisol) soil aggregates developed from granite / gneiss and basalt and to evaluate the nutrient availability for wheat plants (*Triticum aestivum*).

2.2. MATERIAL AND METHODS

2.2.1 SAMPLING AREA

To study the chemical and mineralogical characteristics of the aggregates, two classes of soils were selected. Both soils derived from different parental material and therefore with different release potential of the various forms of potassium (K): The first one was a distro-ferric red Oxisol from basaltic rocks in the permanent preservation area of Cascavel, PR and the second one, a Haplic Inceptisol from granite and gneiss of the “serra do Mar”, Paraná. A trench in each soil class was opened, the surface horizon was removed thoroughly and the soil samples were collected from the subsurfaced horizon, more specifically the B horizon (Diagnostic horizon per the Brazilian soil taxonomy).

2.2.2. SEPARATION OF AGGREGATES

Undisturbed soil samples from the subsurfaced horizon identified as Bw and Bi horizons respectively for the “Oxisol” and the “Inceptisol” were manually crushed in the field, by applying a light pressure to cause minimal change in its original structure, and, then, wrapped in newspaper for transport. After air drying, the samples were then separated into clusters of size for each soil class, using a sieves system coupled to an orbital shaker (RETSCH K G/ 5657 Haan) with agitation for 10 min (dry aggregate stability - EMBRAPA, 1997). The machine's working speed was at range 10, when it provided options in the range from 0 to 10. The amount of sample (clods) used in the separation of aggregate classes was proportional to the receiving capacity of the upper sieve (which was of the same volume as each one of the rest). A sufficient quantity of clods was then sieved to harvest enough aggregate class for chemical and mineralogical analysis. And so, 4 classes (> 4mm; 2-4 mm; 0.5-2 mm; and < 0.5 mm) of aggregates were harvested for the Inceptisol and 5 classes (> 4mm; 2-4 mm; 0.5-2 mm; 0.21-0.5 mm; and <0.21 mm) of aggregates for the “Oxisol”.

2.2.3. EXPERIMENT WITH WHEAT (*triticum aestivum*)

The experiment was installed in June of 2016 in a greenhouse located on the campus of the Federal University of Paraná. An entirely randomized design with 9 treatments and 3 replicates was used. Each experimental unit consisted of the classes of aggregates placed in a defined volume tray (length 20 cm, width 14 cm and height 6.5 cm). Four aggregate (size) (> 4 mm, 2 – 4 mm, 0.5 – 2 mm and < 0.5 mm) from the B horizon of the Inceptisol and five aggregate classes from the B horizon of the Oxisol (> 4 mm, 2 – 4 mm, 0.5 – 2 mm, 0.21 – 0.5 mm and < 0.21 mm) were taken. The combination of soil class and aggregate size defined

the 9 treatments with triplicate: INC1, INC2, INC3, INC4 (for the Inceptisol) and OX1, OX2, OX3, OX4 and OX5 (for the Oxisol). Each experimental unit (27) contained about 1.1 kg of soil aggregates. For the Inceptisol the trays were filled up to a height of 3.3 cm and for the Oxisol up to 3.1 cm. The soil density was slightly higher in the Oxisol (1.3 g cm^{-3}) than in the Inceptisol (1.2 g cm^{-3}).

The winter wheat (*Triticum aestivum*) was used to carry on the experiment, and the “Sinuelo” variety was taken under account since at the time of implementation the average temperature were oscillating between 13°C and 20°C . The planting density was modified in relation to the field recommendation used by the rural growers in the state of Paraná (three time more the recommended density) for the sake of the experiment to allow a maximum organic acids secretion by the plants roots and to have a high K absorption pressure to induce the release of non-exchangeable and structural forms of the nutrient by the different classes of soil aggregates. After the germination of the seeds, a thinning was performed to have 27 plants in each pot (planting density of $964 \text{ plants m}^{-2}$). The irrigation was executed three times a week and was done at 80 % of field soil capacity and the level of soil humidity was maintained throughout the productive cycle.

A complete routine chemical analysis was conducted for each soil class to gauge the fertility level (Table 1a, Table 1b, Table 1c and Table 1d) (Embrapa, 1997): pH in $0.01 \text{ mol L}^{-1} \text{ CaCl}_2$ (soil/solution relation 1:2.5) and SMP solution; non-exchangeable potential acidity (H) extracted with pH 7 $0.5 \text{ mol L}^{-1} \text{ Ca}$ acetate; exchangeable Ca^{2+} , Mg^{2+} and Al^{3+} extracted with $1 \text{ mol L}^{-1} \text{ KCl}$; available P and exchangeable K^+ , Fe, Mn, Cu^{2+} and Zn^{2+} in $0.05 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ and $0.025 \text{ mol L}^{-1} \text{ HCl}$ (Mehlich-1). The total carbon content was determined by the K-dichromate method. For the fertilization of the different classes of aggregates, a concoction of nutritive solution containing all the essential nutrients (except Potassium (K)) necessary for a proper plant nutrition model was administered twice during the cycle to eliminate systematic errors regarding the soil fertility (Faquin, 2005). Limestone was also administered before planting to counteract the effect of acidity noted in the routine analysis results.

Eighty-five (85) days after the planting, at the end of the vegetative stage, the wheat was harvested from each tray. The plants were separated into roots and aerial part. Both roots and aerial parts were washed in deionized water and dried at 70°C until constant weight was reached. After determining the dry matter, both the shoot (aerial part) and the roots were grounded and made ready for the nitro-peroxide extraction (Gonçalves et al., 2006). After the extraction, the K was determined by flame emission photometry.

Table 1a. pH and nutrient availability index for an Inceptisol and an Oxisol

Soil type	Horizon	Clay content	pH		Nutrient availability index										
					Cmolc /dm ³				g / dm ³				mg / Kg		
		g kg ⁻¹	CaCl ₂	SMP	Ca	Mg	H ⁺	K	Al	C	P	Cu	Mn	Fe	Zn
Inceptisol	Bi	527.8	3.9	5.5	0.3	0.1	4.5	0.1	2.7	7.8	5.5	0.3	0.4	207.9	1
Oxisol	Bw	685.5	3.8	5.4	0.3	0	5.8	0.1	1.96	14.5	0.3	7.3	9.3	33	0.8

Table 1b. Percent base saturation, aluminum saturation, sum of bases, pH 7.0 CEC and Effective CEC for an Inceptisol and an Oxisol

Soil type	Horizon	Base Saturation	Aluminum saturation	Sum of bases	pH 7.0 Cation Exchange Capacity	Effective Cation exchange capacity
		%	%		Cmolc /dm ³	
Inceptisol	B	5.6	35.4	0.4	7.6	3.1
Oxisol	B	4.1	24.1	0.3	8.1	2.3

Table 1c. pH and nutrient availability index for the different aggregate classes of an Inceptisol and an Oxisol

Soil type	Soil Aggregates (mm)	pH		Nutrient Availability index											
				Cmolc dm ⁻³				g dm ⁻³				mg Kg ⁻¹			
		CaCl ₂	SMP	Ca	Mg	H ⁺	K	H ⁺ + Al	Al	C	P	Cu	Mn	Fe	Zn
Inceptisol	> 4 mm	4.00	4.70	0.10	0.00	9.76	0.03	13.10	3.34	5.60	14.00	0.10	0.10	152.15	0.90
Inceptisol	2 - 4 mm	4.01	4.73	0.20	0.00	9.72	0.03	13.10	3.38	16.70	6.00	0.20	0.10	158.00	0.60
Inceptisol	0.5 - 2 mm	4.00	4.69	0.20	0.00	9.73	0.03	13.10	3.37	7.80	10.00	0.40	0.20	166.83	0.80
Inceptisol	< 0.5 mm	4.06	4.82	0.40	0.20	8.95	0.04	12.10	3.15	4.60	24.00	0.60	0.50	152.99	5.68
Oxisol	> 4 mm	3.91	4.64	0.40	0.10	11.45	0.05	14.10	2.65	19.00	20.00	7.40	14.80	40.10	0.90
Oxisol	2 - 4 mm	3.88	4.63	0.30	0.00	11.53	0.05	14.10	2.57	21.30	6.00	7.35	15.00	40.42	0.89
Oxisol	0.5 - 2 mm	3.85	4.65	0.30	0.00	11.68	0.04	14.10	2.42	14.50	18.00	7.09	13.97	36.53	0.90
Oxisol	0.2 - 0.5 mm	3.86	4.63	0.30	0.00	11.47	0.04	14.10	2.63	17.90	10.00	7.84	15.28	40.97	0.99
Oxisol	< 0.2 mm	3.85	4.59	0.30	0.10	11.47	0.04	14.10	2.63	14.50	20.00	8.47	15.25	41.18	1.40

Table 1d. Percent base saturation, aluminum saturation, sum of bases, pH 7.0 CEC and Effective CEC for the different aggregate classes of an Inceptisol and an Oxisol

Soil type	Soil Aggregates (mm)	Base Saturation	Aluminum saturation	Sum of bases	pH 7.0 Cation Exchange Capacity	Effective Cation exchange capacity)
		%	%		Cmolc dm ⁻³	
Inceptisol	> 4 mm	0.97	25.25	0.13	13.23	3.47
Inceptisol	2 - 4 mm	1.69	25.36	0.23	13.33	3.61
Inceptisol	0.5 - 2 mm	1.71	25.28	0.23	13.33	3.60
Inceptisol	< 0.5 mm	5.05	24.72	0.64	12.74	3.79
Oxisol	> 4 mm	3.75	18.09	0.55	14.65	3.20
Oxisol	2 - 4 mm	2.40	17.79	0.35	14.45	2.92
Oxisol	0.5 - 2 mm	2.38	16.75	0.34	14.44	2.76
Oxisol	0.2 - 0.5 mm	2.36	18.21	0.34	14.44	2.97
Oxisol	< 0.2 mm	3.05	18.08	0.44	14.54	3.07

2.2.4. EXTRACTION OF SOLVABLE SILICON (Si)

This extraction was aimed at verifying the degree of confinement of the different clusters of aggregates. The method of acetic acid 0.5 mol L^{-1} was used for the extraction of solvable Si (Korndörfer et al., 1999). In order to give more similar Si extraction conditions, the two classes of greater aggregates ($> 4 \text{ mm}$ and $2\text{-}4 \text{ mm}$) were milled in a mortar and passed in a 2 mm sieve.

In Erlenmeyer flask (25 mL) of acid solution were added in 2.5 g of aggregate, and after 2 hours of stirring, the supernatant was filtered. The extracts were then prepared for Si reading, by using 10 mL of extract, together with 1 mL of mixed solution at 7.5% of ammonium molybdate (7.5 g of ammonium molybdate with 10 mL of sulfuric acid 9 mol L^{-1} , in 100 mL deionized water). The final solution was at rest for 10 min and then an addition of 2 mL of tartaric acid solution at 20% , was made. After 5 more minutes of rest, an addition of 1 mL of ascorbic acid solution at 0.3% took place. After 1 hour of rest, the Si content of each sample was then read in the spectrophotometer UV-visible with wavelength of 660 nm .

2.2.5. MINERAL FORMS OF POTASSIUM (K) WITHIN THE AGGREGATES OF THE SOILS

The two greater aggregate classes ($> 4 \text{ mm}$ and $2\text{-}4 \text{ mm}$) were milled in a mortar and passed in a 2 mm sieve. Except for the exchangeable contents, the other forms of K were estimated only before planting. In all extractions, the contents of K were determined by flame photometry.

2.2.5.1. Exchangeable K

To evaluate the exchangeable K contents in the different aggregate classes, two specific extractors were used: Mehlich-1 ($0.05 \text{ N HCl} + 0.025 \text{ N H}_2\text{SO}_4$), in samples obtained before and after planting; and 1 mol L^{-1} of ammonium oxalate (PAVAN et al., 1992), only in samples collected before planting.

2.2.5.2. Non-exchangeable and total K

For the extraction of non-exchangeable K, the boiling HNO_3 (partial) and HF (total) were used as extractors (Melo et al., 2016). 0.3 g of aggregate sample was placed before planting in a digestion vials in the presence of 9 mL of 1 mol L^{-1} HNO_3 solution. The tube was sealed and heated in a microwave oven (MARSS-XPRESS 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 . The extracts obtained were then filtered into a volumetric flask.

For Total K content, approximately 0.3 g of aggregate sample was placed in a digestion vial in the presence of a mixed solution (9 mL of HNO_3 and 3 mL of HF) (Batista et al., 2016). The vials were deposited on a circular tray and taken to a Digester (Digester MARSS-XPRESS 6). The vials remained for a 15 minutes' period, at a variable temperature reaching up to 200 °C. The extracts obtained were then filtered into a plastic flask. The extract volume was obtained based on the mass and density of the extract.

2.2.6. X RAY DIFFRACTION (XRD) OF THE SAND, SILT AND CLAY FRACTIONS IN THE DIFFERENT AGGREGATE CLASSES

After the separation of the soil fractions (Gee & Bauder, 1986) of the different classes of aggregates the fractions sand, silt and clay were studied by XRD. The samples were grounded and passed through a 0.2 mm sieve and were mounted onto a Koch plate (not oriented samples). The diffraction patterns were obtained in vertical goniometer Panalytical X'Pert3 Powder, with a speed of $0.42^\circ 2\theta \text{ s}^{-1}$ and range $5 - 70^\circ 2\theta$. The diffractometer, equipped with a Ni filter and using a $\text{CuK}\alpha$ radiation operated at 40 kV and 40 mA. The mineralogical data of the sand, silt and clay fractions for the lesser and greater aggregates in each soil type are presented in table 2.

Table 2. X ray diffraction analysis of sand, silt and clay fraction of the greater and lesser aggregate class for each soil type

Soil type	Aggregate size (mm)	Sand fraction		Silt fraction		Clay fraction	
		Much	Little	Much	Little	Much	Little
Inceptisol	> 4 - 2	Qtz	Dsp	Qtz	Chl, Fsp, Mca, Kln	Kln, Mca	Gbs, Ill, Chl, Rt
Inceptisol	< 0.5	Qtz	Dsp	Qtz	Chl, Fsp, Mca, Kln	Kln, Mca	Gbs, Ill, Chl, Rt
Oxisol	> 4 - 2	Qtz	Gbs, Hem	Qtz	Hem, Mca	Hem, Gbs, Kln	
Oxisol	0.5 - < 0.21	Qtz	Gbs, Hem	Qtz	Hem, Mca	Hem, Gbs, Kln	

Much = Reflection of higher intensity by XRD (more than 60 %). Little = Discrete reflections by XRD (less than 20%)

Qtz = Quartz; Dsp = Diaspore; Gbs = Gibbsite; Hem = Hematite; Chl = Chlorites; Fsp = K-Feldspar; Mca = Micas; Kln = Kaolinite; Ill = Illite; Rt = Rutile

2.2.7. DATA ANALYSIS

2.2.7.1. Nutritional balance of K

Before and after the wheat growing cycle in each experimental unit, the exchangeable K concentration extracted with Mehlich-1 was determined. The exchangeable K content was calculated, both before and after planting, through the product between the concentration and the total soil weight (1.1 kg) in the trays for the Inceptisol and for the Oxisol. By the difference between the K content in the soil, before and after planting, the amount of exchangeable K removed from the soil was found as a function of the wheat. Then, the total content of K absorbed by the plants was determined by considering the dry matter production and the nutrient content of each component (aerial part and roots). From the comparison between the amount of K absorbed by the plants and the amount of exchangeable K removed from the soil during the growing cycle, the contribution of the different forms of K (exchangeable and non-exchangeable) in wheat nutrition was estimated.

2.2.7.2. Statistical analysis and software

The data were submitted to the analysis of variance and comparison of means by Duncan test (5%) through the following programs: Statistica 10.0, Sigma Plot 12.0 and Microsoft office Excel 2016. The data related to the different forms of K and to the wheat production (yield) were subjected to the Principal Components Analysis (PCA). The K extracted by different methods was correlated with the nutrient contents in the plants.

2.3 RESULTS AND DISCUSSION

2.3.1. FORMS OF K IN DIFFERENT AGGREGATE CLASS

2.3.1.2. Exchangeable-K

The exchangeable-K was determined by both the Mehlich-1 and the NH_4Oac methods. The Mehlich-1 K content for the Inceptisol throughout the aggregates were similar with a mean value of 15.7 mg kg^{-1} , except for a significant variation occurring in the smallest aggregates ($< 0.5 \text{ mm}$) in which the concentration was interestingly higher (20.8 mg kg^{-1}). The Oxisol presented similar values with a mean value of 19.8 mg kg^{-1} (figure 1a) within the aggregates, indicating of a more homogeneous environment.

The NH_4Oac (Ammonium Oxalate) is a method that determine the exchangeable-K but also a little bit of the non-exchangeable-K (Sarkar, 2013). Due to the proximity of ionic radiuses (0.1 nm) between K^+ and NH_4^+ , there is the possibility of exchanging these ions at K^+ specific adsorption sites, making the nutrient available to the plants (Sarkar, 2013). However, in the samples from the present study, the behavior between the aggregate classes and the contents of K extracted by NH_4Oac were similar to the extraction with Mehlich-1 (Figure 1b). The only highlight was the intensification of the differences between the K- NH_4Oac content in the different aggregate classes of the Oxisol. Unlike the Inceptisol, the greater aggregate classes of the Oxisol had higher levels of K- NH_4Oac . Therefore, there was no consistent behavior between the two soils in terms of increase or reduction in exchangeable K contents towards the greater or lesser aggregates. Therefore, the hypothesis that the lesser aggregates represent a more confined environment and less solution exchange, maintaining higher concentrations of exchangeable forms of nutrients, was not confirmed. The distribution of K in the exchangeable form in the classes of aggregates was random, but with significant differences, it can be stated that the soil presents different side-by-side environments for the exploration of the root system.

It is important to notice that for both treatments (methods) the concentration of K was higher in the Oxisol, despite of the fact that the parental material of the Inceptisol is richer in this nutrient than that of the Oxisol. This is possibly a consequence of the climatic factors of both regions. The “serra do mar” (Inceptisol) in Parana is close to the coast and received in average per year almost twice as much precipitation as the Cascavel region were the Oxisol was sampled (IAPAR, 2013). K is one of the most mobile nutrients in the soil-water-plant system. It presents a high risk of being leached through the many horizons of the

soil, rendering it unavailable for plant uptake and practically undetectable in the soil chemical routine analysis (Marschner et al, 2012).

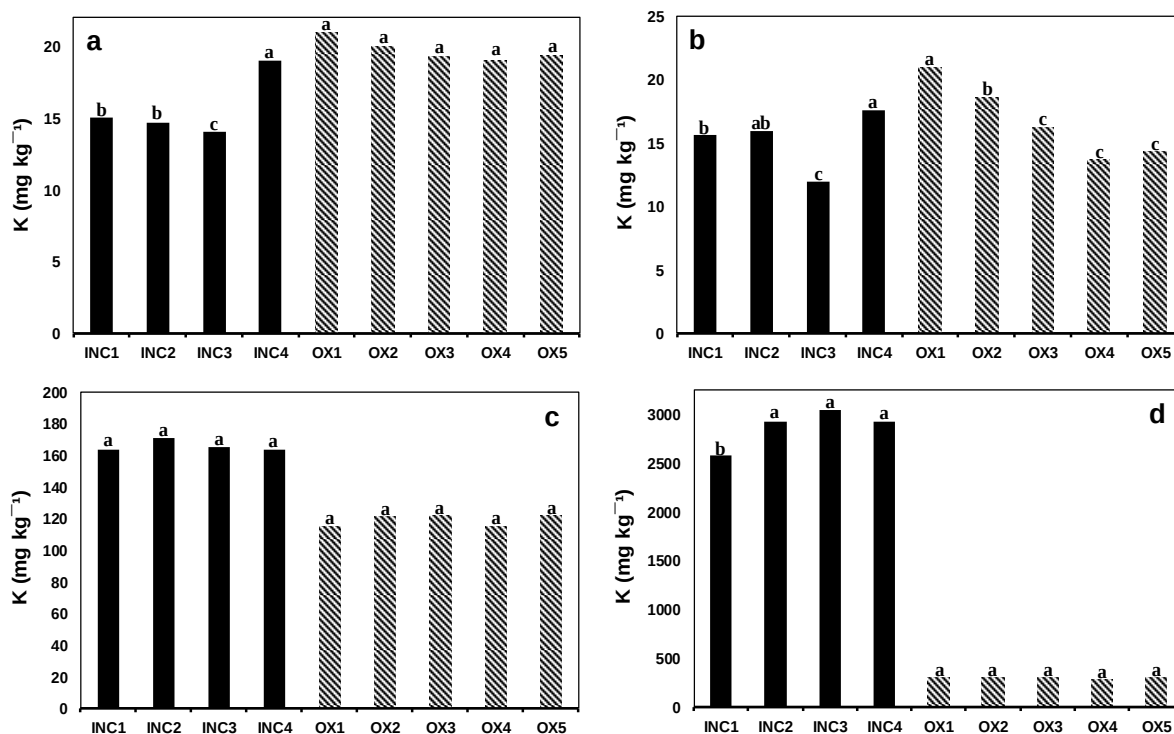


Figure 1. Concentration of K in different forms: (a) Mehlich-1 (b) NH₄OAc (c) HNO₃ (d) total HF. INC1 = > 4 mm; INC2 = 2 – 4 mm; INC3 = 0.5 – 2 mm; INC4 = < 0.5 mm; OX1 = > 4 mm; OX2 = 2 – 4 mm; OX3 = 0.5 – 2 mm; OX4 = 0.21 – 0.5 mm; OX5 = < 0.21 mm

2.3.1.3. Non-exchangeable and structural (total) K

The data shows values of non-exchangeable K which is the concentration of K soluble in 1 mol L⁻¹ HNO₃ ranging among the aggregates of the Inceptisol with a mean value of 167.1 mg kg⁻¹ for the greater aggregates and 164.3 mg kg⁻¹ for the lesser aggregates. As for the Oxisol, the values ranged with a mean value of 119.5 mg kg⁻¹ for the greater aggregates and 118.6 mg kg⁻¹ (figure 1c). In both, the Inceptisol and the Oxisol, the concentration of non-exchangeable K represented respectively 5.8 % and 40 % of the total K. This indicates that the weathering processes are far more advanced in the Oxisol than the Inceptisol. In table 2, a semi-quantitative mineralogy of the aggregates shows the presence of minerals such as micas, K-feldspar and illita for the Inceptisol in the clay and silt fractions and in the silt fraction for the Oxisol, micaceous minerals were found.

Following the non-exchangeable content, the concentration of structural K was significantly higher in the Inceptisol than in the Oxisol. In the Inceptisol, the total mean

concentration was $2869.2 \text{ mg kg}^{-1}$ with a tendency of being higher in the aggregates lesser than 2 mm (figure 1d). The Oxisol presented a more steadier concentration among the aggregates. With a mean concentration of 297.6 mg kg^{-1} (figure 1d).

2.3.2. SOLVABLE SILICON

The solvable silicon in both soils (Inceptisol and Oxisol) presented little variation between their respective aggregates. With mean concentration values of 29.2 mg kg^{-1} and 41.4 mg kg^{-1} for the Inceptisol and Oxisol respectively (figure 2). This is concurrent with the findings of Camargo et al (2005), in which a positive high correlation was found between the concentration of solvable silicon and clay content in soil. The Oxisol has higher clay content than the Inceptisol (Table 1).

The higher confinement of the lesser sizes of aggregates, maintaining higher concentrations of solvable forms of Si, was not observed. However, the positive relation between solvable Si and exchangeable K deserves attention. Inceptisol aggregate size 3 (INC3) had the lowest exchangeable K and solvable Si contents, which indicates either a higher leaching of these two elements in this class of aggregate or less release of them into the aggregates from the structural forms.

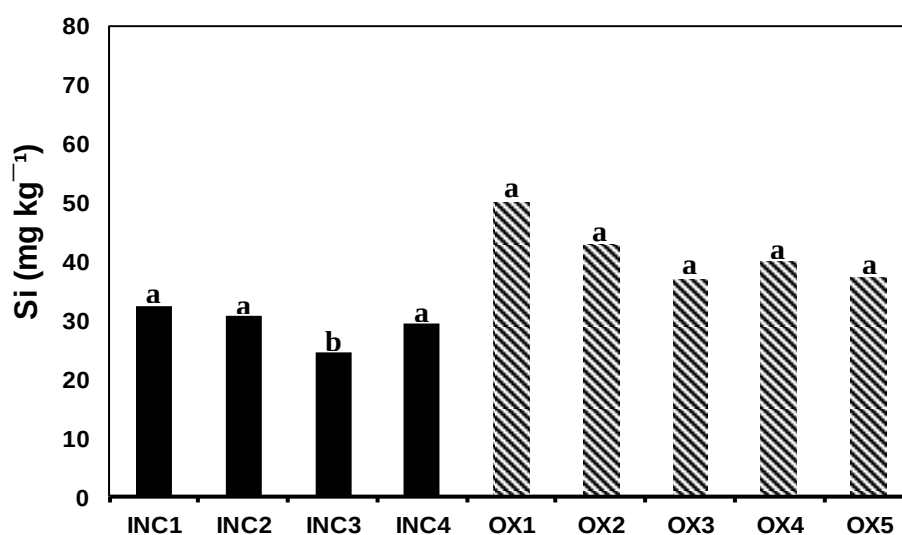


Figure 2. Solvable silicon (Si). INC1 = > 4 mm; INC2 = 2 – 4 mm; INC3 = 0.5 – 2 mm; INC4 = < 0.5 mm; OX1 = > 4 mm; OX2 = 2 – 4 mm; OX3 = 0.5 – 2 mm; OX4 = 0.21 – 0.5 mm; OX5 = < 0.21 mm

2.3.2. WHEAT TISSUE K CONCENTRATION AND CONTENT IN DIFFERENT AGREGATE CLASSES

The wheat roots tissue K concentration for the Inceptisol showed very little variation between the aggregates (Figure 3). The only significant difference for this soil was the highest concentration of K in the aerial part of the plants grown in the lesser classes of aggregate in relation to the greater ones. The highest exchangeable K contents extracted by Mehlich-1 were also observed for this Inceptisol aggregate class (Figure 3). For the Oxisol, the variations in K contents in the aerial part of the wheat was higher, but at random among the aggregate classes.

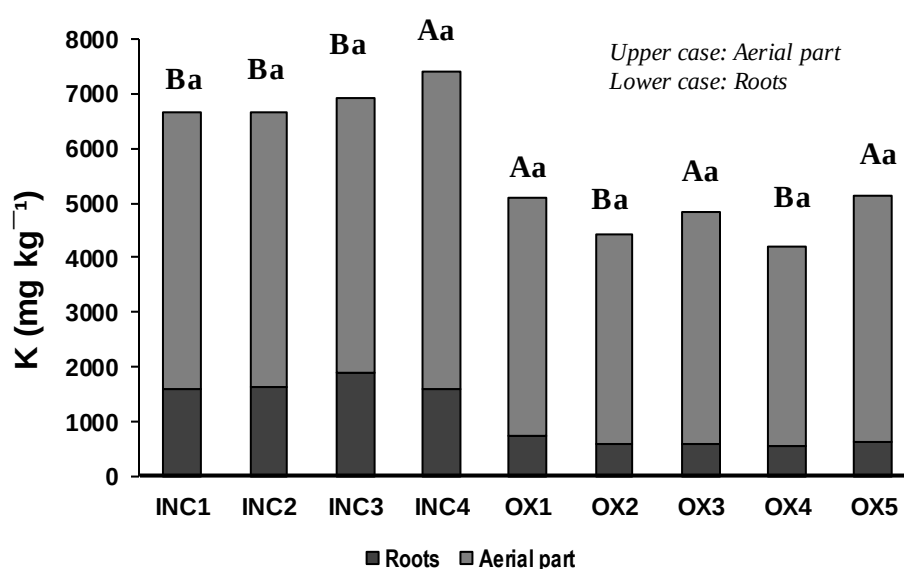


Figure 3. Tissue K concentration (roots and aerial part). INC1 = > 4 mm; INC2 = 2 – 4 mm; INC3 = 0.5 – 2 mm; INC4 = < 0.5 mm; OX1 = > 4 mm; OX2 = 2 – 4 mm; OX3 = 0.5 – 2 mm; OX4 = 0.21 – 0.5 mm; OX5 = < 0.21 mm

The total K mean concentration (0.71 % for the Inceptisol and 0.47 % for the Oxisol) (fig 3) in the plants, regardless of the soil type was within the critical value found by Leigh and Jones, (1984) (0.5 – 2 %). In counterpart Viana (2007) evaluated the optimum concentration level, necessary to an efficient productive cycle, and found it to be in the range of 2 to 5 %. The wheat plants for both the Inceptisol and the Oxisol, presented among all the aggregates symptoms of K deficiency

2.3.3. K UPTAKE BY WHEAT

2.3.3.1. Changes in exchangeable soil K with the planting of wheat

After cropping with wheat, the concentration of exchangeable K in the Inceptisol ranged from 9.9 mg kg⁻¹ to 10.9 mg kg⁻¹, with a mean of 10.5 mg kg⁻¹ (figure 4). A decrease in the original concentration (before planting) occurred in all the aggregate size after the harvest. However, the highest decrease rate (29.4 % and 44.2 %) were observed for the small aggregates (2 – 0.5 mm and < 0.5 mm respectively). This decrease shown in the small aggregates is coherent with the concentration found in figure 3 where, the plants of these aggregates presented higher concentration of K within their tissue (root and aerial part). For the Oxisol a more homogeneous pattern was observed for the decrease rate in exchangeable-K after cropping. Throughout the aggregates a mean decrease value of 52.2 % was detected (figure 4). In all aggregate sizes for the Oxisol the decrease rate was at least 50 %.

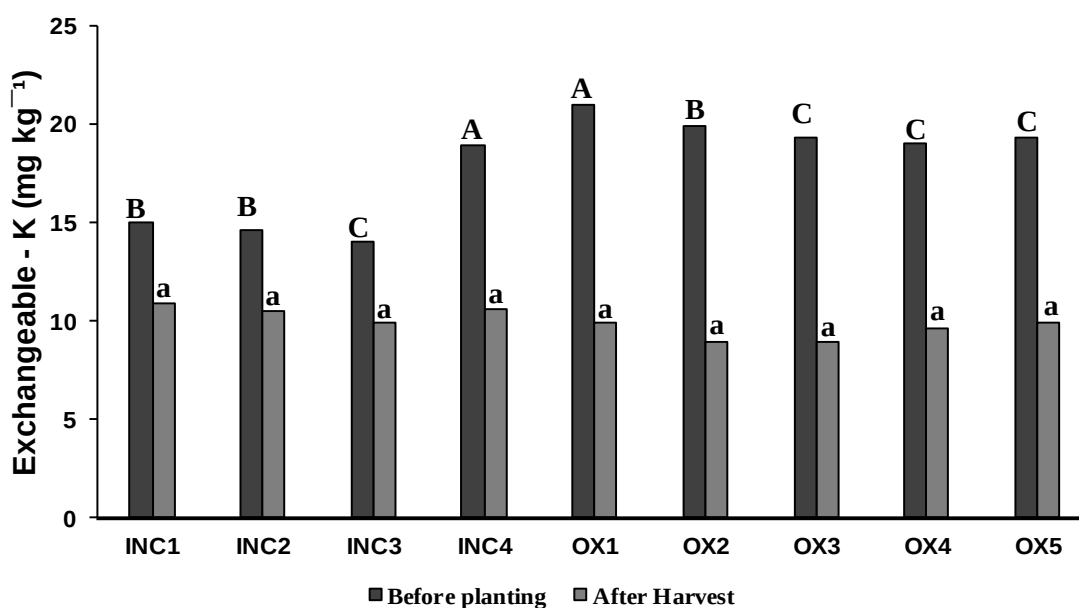


Figure 4. Changes in exchangeable-Extracted with Mehlich-1 in Inceptisol and Oxisol after planting. INC1 = > 4 mm; INC2 = 2 – 4 mm; INC3 = 0.5 – 2 mm; INC4 = < 0.5 mm; OX1 = > 4 mm; OX2 = 2 – 4 mm; OX3 = 0.5 – 2 mm; OX4 = 0.21 – 0.5 mm; OX5 = < 0.21 mm

2.3.3.2. Nutritional balance of K in plants

The Exchangeable K extracted with Mehlich-1 was positively correlated ($r = 0.82$, $p \leq 0.05$) to the K content (product of K content and dry matter production) in the plant (root and aerial part combined). However, there was no correlation ($p \geq 0.05$) between the NH₄Oac extraction and the plant accumulation. This indicates that the preferential extraction in

determining the available K to plant is the Mehlich-1. This extraction simulates at more than 80 % the soil-plant interface within the whole system (Pavan 1992).

The Principal Components Analysis could explain the variability of more than 88 % of the data (Figure 5). The horizontal axis, explained about 79 % of the data and separated the extraction methods into two groups (Non-exchangeable / structural, and exchangeable). Although it presented the NH_4Oac method as non-correlated not only with the plants but with the other extraction methods as well. The plant itself, presented higher correlation ($r > 0.8$, $p \leq 0.05$) than when considered by its parts (roots and aerial part).

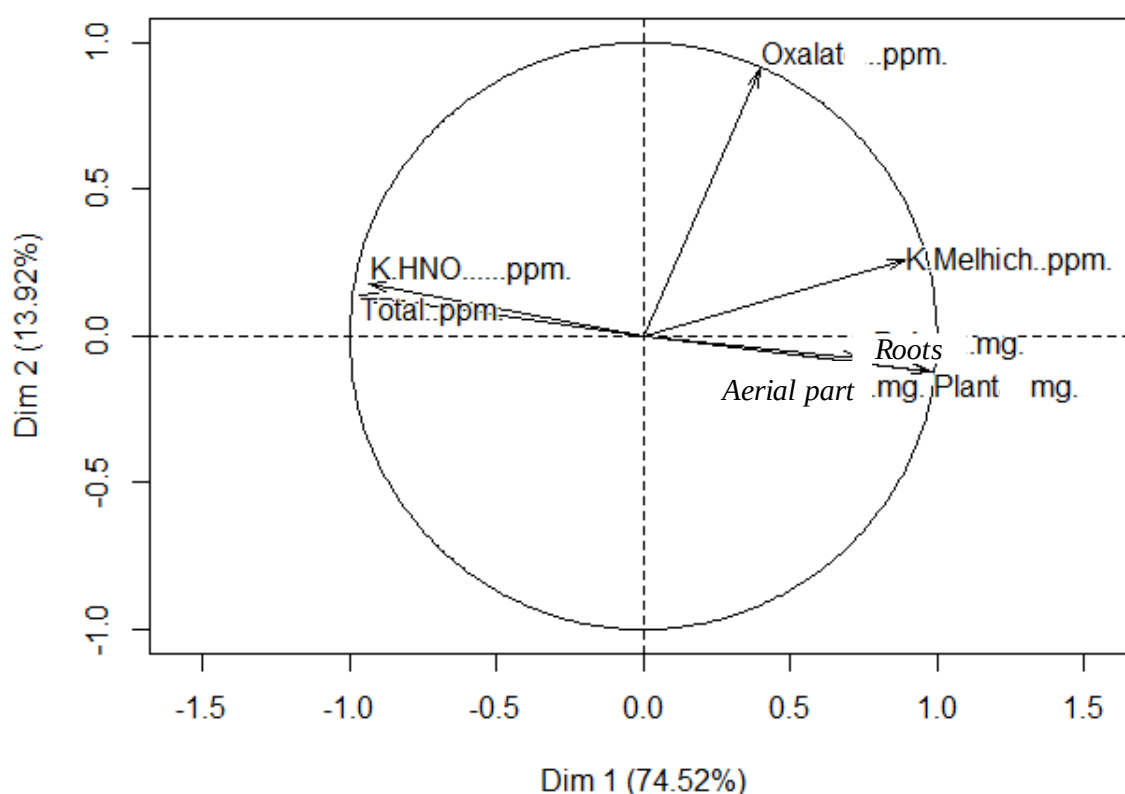


Figure 5. Principal Component Analysis for the variables

The mineral forms of K absorbed by the wheat had variations based upon the soil type and the aggregate size. In the Inceptisol, the greater aggregate ($> 4\text{mm}$) size had a different K-uptake pattern in which unlike the lesser aggregates ($2 - 0.5\text{ mm}$ and $< 0.5\text{ mm}$) The highest participation of non-exchangeable forms of K in wheat nutrition was in the aggregate sizes larger than 4 mm for the Inceptisol (7.90 %) (figure 6). The totality (100 %) of the K-uptake in the lesser aggregates came from the exchangeable K.

A more spatial distribution was observed in the K-uptake in the Oxisol. The K concentration in the plant came from both the exchangeable K and non-exchangeable K. Both greater and lesser aggregates had similar pattern regarding the K-uptake. Although most of the K came from the exchangeable form (84.2 %) (figure 6), it is very important to notice that even though the exchangeable K concentration after harvest was not depleted completely (figure 4), the non-exchangeable-K was favored up to a certain point. It is possible that the exhausting planting method contributed to k-uptake in the non-exchangeable form. The interlayer-K was taken and thrown to both the soil solution and to the CEC. Therefore, contributing to both the plant nutrition and the replenishment of K for the exchangeable form (Steiner, 2014; Egushi et al, 2015).

Tan et al (2012) assessing wheat grain producing soils in north China concluded that in the rhizosphere, the K-uptake in the plants are more correlated with the non-exchangeable-K. More than 40 % of K assessed in grains came from the reserve-K (non-exchangeable and possibly structural).

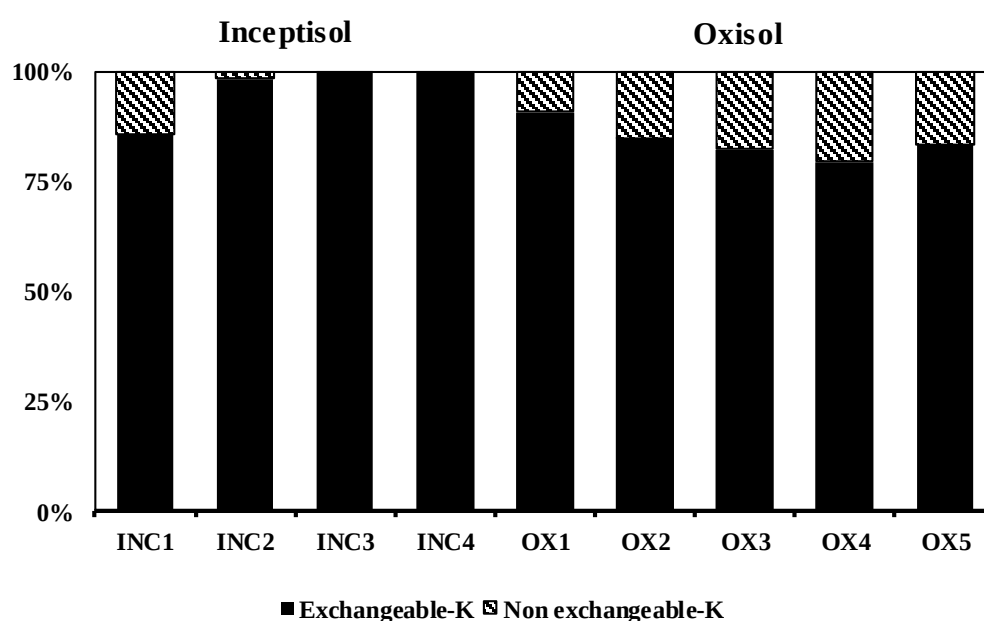


Figure 6. K mineral forms uptake by wheat. INC1 = > 4 mm; INC2 = 2 – 4 mm; INC3 = 0.5 – 2 mm; INC4 = < 0.5 mm; OX1 = > 4 mm; OX2 = 2 – 4 mm; OX3 = 0.5 – 2 mm; OX4 = 0.21 – 0.5 mm; OX5 = < 0.21 mm

2.4. CONCLUSIONS

The K uptake for both the Inceptisol and the Oxisol within the respective aggregate classes derived from the exchangeable and the non-exchangeable-K mineral forms. However, in the Inceptisol only the greater aggregate sizes (> 4 mm and $4 - 2$ mm) showed K content (7.91 %) deriving from the non-exchangeable K. The totality of K content in the lesser Aggregate sizes ($2 - 0.5$ mm and < 0.5 mm) for the Inceptisol derived entirely from the exchangeable-K forms. In the Oxisol all the aggregates (> 4 mm, $4 - 2$ mm, $2 - 0.5$ mm, $0.5 - 0.21$ mm, and < 0.21 mm) had K content from the non-exchangeable forms (15.81 %) with a tendency of being higher in the lesser aggregate size ($2 - 0.5$ mm, $0.5 - 0.21$ mm, and < 0.21 mm).

All the aggregates of the Oxisol showed higher content of solvable silicon, and more so in the greater aggregate size ($> 4 - 2$ mm), than those of the Inceptisol. The high content in clay of the Oxisol is a determinizing factor of the high solvable silicon within the aggregates. However, the acetic acid extraction tends to overestimate the content of solvable silicon in highly weathered soil due to the interaction that the silicon has with phosphorus. Therefore, the calcium chlorate extraction should be considered as a more precise method in the determination of this parameter.

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GENERAL CONCLUSIONS

The sand and silt fractions of both the Inceptisol and Oxisol throughout the respective aggregate classes is predominantly constituted by the mineral quartz with traces of minerals with lower intensity such as diaspore for the Inceptisol; gibbsite and Hematite for the Oxisol. These low intensity minerals reflect the parental material of each soil type, indicator of both nutrient availability and pedogenetic formation.

The clay fraction of Inceptisol presented the predominance of the mineral kaolinite (Kt) highly crystallized within the different aggregate classes. For the aggregate classes of the Oxisol, the predominant minerals were the gibbsite and hematite with moderate to high degree of crystallinity. Throughout all the aggregate sizes, no Hematite were found in the Inceptisol and the Oxisol only contained traces of the mineral goethite. The Inceptisol for its clay mineralogy within the aggregate size ($> 4 - < 0.5$ mm) revealed to be Kaolinitic, while the Oxisol ($> 4 - < 0.21$ mm) is more oxidic.

The exchangeable-K by the Mehlich-1 extraction, was found to be the most predictive K mineral form of the availability of this nutrient in wheat. The non-exchangeable forms of K both by the HNO_3 and HF, reflected the parental material for both the Inceptisol and the Oxisol and therefore can be indicators of soil fertility and management.

In the Inceptisol only the greater aggregate sizes (> 4 mm and $4 - 2$ mm) showed K content deriving from the non-exchangeable K. The totality of K content in the lesser Aggregate sizes ($2 - 0.5$ mm and < 0.5 mm) for the Inceptisol derived entirely from the exchangeable-K. In the Oxisol all the aggregates had K content from the non-exchangeable forms.

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